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Coulomb Systems at Low Density: A Review

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Results on the correlations of low-density classical and quantum Coulomb systems at equilibrium in three dimensions are reviewed. The exponential decay of particle correlations in the classical Coulomb system, Debye–Hückel screening, is compared and contrasted with the quantum case, where strong arguments are presented for the absence of exponential screening. Results and techniques for detailed calculations that determine the asymptotic decay of correlations for quantum systems are discussed. Theorems on the existence of molecules in the Saha regime are reviewed. Finally, new combinatoric formulas for the coefficients of Mayer expansions are presented and their role in proofs of results on Debye–Hückel screening is discussed.

KEY WORDS: Coulomb; plasma; Saha, screening; Debye–Hückel; virial; equation of state.

I. COULOMB SYSTEMS

A. Introduction

The emergence of thermodynamics and of various physical laws from the more fundamental levels of atomic theory and statistical mechanics were high points in our education in physics. But by the time we reached textbook treatments of the complex world of the Coulomb interaction, for example, formation of atoms and molecules and equilibria between them, we learned to demand less from theory and to be more content with reasoning by analogy consistent with thermodynamics. We know experimentally that atoms and molecules form, that they can behave like

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mixtures of ideal gases, so phenomenologically they have chemical potentials and we no longer insist that this emerge in some limit from *N*-body quantum Coulomb systems. We also know that Coulomb systems can have screening and dielectric phases. But when screening is expected to occur, it is quite a common practice to rather bluntly replace the Coulomb potential by a screened potential inherited from mean-field theories without inquiring too deeply into the legitimacy of this change. Likewise, there does not exist a first principle theory of the dielectric constant that does not presuppose the existence of atoms and molecules. At best, assuming that atoms form, one uses several laws, such as the Clausius–Mosotti formula, whose microscopic foundations have to be elucidated. In all these cases, this is a sensible attitude since most of non-relativistic physics is reputed to be hidden within the *N*-particle Coulomb Hamiltonian. There are however basic facts that can be cleanly formulated as limiting theories and shown to persist near the limit as well.

This review is devoted to these types of results on Coulomb systems at low density. At low density the most famous properties of Coulomb systems are related to screening. The classical Debye–Hückel theory and its quantum analogue the random phase approximation have been supplemented in recent years by additional information established both by rigorous proofs and by closer inspection of resummed perturbation theory consistent with aspects of the rigorous proofs. There is also a precise understanding how a dilute assembly of quantum nuclei and electrons can form gases of atoms and molecules in the Saha regime. These results are physically well understood but the challenge to derive them has shown that standard perturbation theories miss some effects; indeed it turns out that quantum Coulomb systems do not screen, in the strong sense that the classical system does. This is a principal focus of this review.

The first rigorous results were at the level of thermodynamics, the celebrated stability of matter theorem of Dyson and Lenard and the existence of thermodynamic behavior established by Lieb and Lebowitz. They hold for all states of nonrelativistic matter. The importance of the stability result is that it shows that quantum mechanics and electrostatics is a consistent simplified statistical mechanics of nature that needs no intervention from more fundamental levels of description.

The next level, which is the focus of this review, is to ask for information on correlations: here the variety of physical phenomena in question is so vast that we cannot hope for too much generality: thorough consideration of the low density behavior is the first and the most natural step in this direction.

There are three parts. The first is devoted to classical systems. Here a significant achievement is the proof that the Debye–Hückel theory is a limiting theory and Debye screening holds close to this limit, that is, at sufficiently low density (or high temperature). This is the subject of Section II.

Frequently proofs of such results are very long with tedious parts devoid of physical insight, but there are also components where a physical insight becomes a precise argument or where a useful new identity such as a resummation of perturbation theory appears. The philosophy here and throughout the review is to state the theorems and to give only those ideas in the proofs that conform to this specification. Many of these arguments are founded on the Sine–Gordon transformation, described in Section II. We hope that our applications will raise appreciation for this transformation. We hope to display enough arguments without overwhelming technicalities to satisfy the physicist curious to see the way between physical concepts and their full mathematical realization.

In the second part we consider quantum mechanics. In between there is a natural transition chapter (Section III) which revolves around the absence of screening in classical dipole systems. We present the simple proof of this lack of screening. This chapter prepares for the study of the quantum case because it turns out that the Feynman–Kac formula reduces quantum equilibrium statistical mechanics to a classical formalism in which both monopoles and higher order multipoles appear.

The proper quantum mechanical effects on screening are exhibited in Section IV in the simplified framework of the semi-classical approximation. The well known Feynman–Kac representation of quantum statistical mechanics is recalled and quantum statistics are neglected. Perturbing around the classical gas makes immediately clear why intrinsic quantum fluctuations always destroy Debye screening. This appears to have been first suggested by Federbush, see (Brydges & Federbush 1981, p. 428, Section 5). One also discovers that the remaining screening mechanisms are more subtle than in the classical case, as revealed by the different long distance behaviors of various types of correlations. This chapter is intended to be a gentle baptism before the confrontation with the full quantum mechanical setting in Section V.

Here the mathematics is much harder and less has been proved: in Sections V and VI the style is that of formal perturbation theory. In these chapters, following mainly the work of Alastuey, Cornu and collaborators, one exploits the full power of the Feynman–Kac representation including the quantum statistics. In this language, the quantum Coulomb gas is similar to a certain classical gas of fluctuating multipoles and all the efficient techniques of classical statistical mechanics are at hand. In particular, one can perform the usual partial resummations needed to cure the Coulomb divergences and end up with well defined Mayer-like diagrammatic rules. This offers a new perturbative scheme for the many-body problem which is particularly suited for low density expansions, in contrast to the standard Feynman perturbation theory with respect to the coupling constant.

The formalism is applied in Section VI to the determination of the long distance behavior of the correlations and to the equation of state at low density. The (formally) exact results presented here provide the most detailed information available now on these questions. Some of them are new, in particular the explicit formulae for the tails of the correlations at low density. Also one recovers and completes the equation of state already obtained by Ebeling and coworkers by different methods.

In Section VII we report on a nice development, initiated by Fefferman, on atomic and molecular phases at low density (the Saha regime). One considers a joint limit, the atomic or molecular limit, of vanishing density and vanishing temperature by fixing the chemical potentials (negatives) and letting the temperature tend to zero. Lowering the temperature enhances the probabilities for quantum mechanical binding whereas lowering the density favors ionization. It turns out that in this limit each value of the chemical potentials determines in principle certain chemical species and the system behaves as a mixture of these ideal substances. Ionization equilibrium phases are obtained in this way. In this asymptotic sense, it gives a precise meaning to the notion of atoms and molecules in the many-body problem.

The third part consists of a single Section VIII that is more technical: rigorous results at low density require control of the convergence of various types of cluster expansions. The proof of Debye screening has stimulated the development of resummation techniques which may be useful in other situations. For example there are new combinatoric formulae for Mayer coefficients. Without aiming at completeness, this last chapter provides the dedicated reader with some arguments left out in the main course of the text and gives an updated summary of some of the available tools in this field.

The considerations in this review are essentially concerned with our three dimensional world. There has of course been dramatic progress in the one and two dimensional solvable models of Coulomb systems, which we do not include in the review, apart from isolated comments included to demonstrate some contrast with three dimensions. Let us also mention that basic new results on the stability of Coulombic matter in presence of magnetic fields and quantized radiation field have been obtained recently (references in I.C).

The history of proofs of fundamental results, for example that statistical mechanics predicts phase transitions, suggests that difficult results can simplify over time and serve as consistency checks on what comes next.

Some but not all of the derivations in this review are far from this stage: nevertheless, the existence of the subtle tunneling corrections in the Debye asymptotic regime revealed by the Sine–Gordon representation is not seen by conventional Mayer graph summations. The suggestive view of the quantum gas as an assembly of random multipoles displayed by the Feynman–Kac representation and the related lack of screening are much easier to miss in the conventional many-body perturbation theory. The physically very natural molecular limit considered in the main theorem of Section VII should be introduced and discussed in any text book on quantum statistical mechanics.

We conclude this introduction with a list of some questions that seem to us of interest, to be pursued in the spirit of this review and perhaps by similar techniques.

CLASSICAL: *Debye regime*. A more detailed understanding of boundary conditions and charge expulsion. Results on correlations along walls, surface charges. Understanding the Improved Debye–Hückel theories of Fisher *et al.* as limiting theories.

Dipole systems. More definitive results on the dielectric constant and clarification of the literature in the light of such results.

QUANTUM: *Low density*. Prove absence of exponential screening or at least finiteness of each individual Mayer-like diagram of Section V. Correlations in non-uniform systems, e.g., along walls. Coherent treatment of para and diamagnetism, boundary currents.

Slightly imperfect molecular gases. Lowest order corrections to the molecular limit, atomic correlations and van der Waals forces. Possible existence of dielectric phases with true atomic dipoles.

Compatibility of Macroscopic electrostatics and statistical mechanics of quantum charges.

B. The Classical Coulomb Gas

We consider several species, $\alpha = 1,..., \mathscr{S}$, of charged particles with charges e_α of both signs, confined to a box Λ in $\mathbb{R}^3$. If there are N particles in total sitting in an external electrostatic potential ϕ then the potential energy is given by

$$U(\mathbf{r}_1, e_{\alpha_1},..., \mathbf{r}_N, e_{\alpha_N}) + \cdots + \sum_{i=1}^{N} e_{\alpha_i} \phi(\mathbf{r}_i) \tag{1.1}$$

where

$$U(\mathbf{r}_1, e_{\alpha_1},..., \mathbf{r}_N, e_{\alpha_N}) = \sum_{i<j=1}^{N} e_{\alpha_i} e_{\alpha_j} V(\mathbf{r}_i - \mathbf{r}_j) \tag{1.2}$$

V is the two body Coulomb potential energy

$$V(\mathbf{r}) = \frac{1}{|\mathbf{r}|} \tag{1.3}$$

and the ellipsis indicates potentials due to other forces, that are discussed below.

Suppose that N_α denotes the number of particles of species α. Then the equilibrium statistical mechanics is determined by the partition function

$$\begin{aligned} \Xi_\Lambda &= \Xi_\Lambda(\beta\phi) \\ &= \sum_{\{N_\alpha\}}^{\infty} \prod_{\alpha=1}^{\mathscr{S}} \frac{(z_\alpha)^{N_\alpha}}{N_\alpha!} \int_\Lambda d\mathbf{r}_1 \cdots \int_\Lambda d\mathbf{r}_N \exp\left(-\beta U - \beta \sum_{i=1}^{N} e_{\alpha_i} \phi(\mathbf{r}_i) \right) \end{aligned} \tag{1.4}$$

and z_α is called the activity of species α. In particular the pressure P is given by

$$\beta P = \lim_{|\Lambda| \to \infty} \frac{1}{|\Lambda|} \ln \Xi_\Lambda \tag{1.5}$$

The activities in the partition function are related to the chemical potential μ_α of species α by the standard formula

$$z_\alpha = \frac{e^{\beta\mu_\alpha}}{(2\pi\lambda_\alpha^2)^{3/2}} \tag{1.6}$$

where λ_α is the de Broglie length given below in (1.7). This formula results from the classical limit of quantum mechanics.

In three dimensions a purely Coulomb Boltzmann factor $\exp(-\beta U)$ is not integrable because of the Coulomb singularities at $\mathbf{r}_i = \mathbf{r}_j$: additional forces are necessary for stability. We suppose there is a length scale λ where the Coulomb potential gives way to these other forces. We used λ because it suggests a de Broglie length

$$\lambda_\alpha = \hbar(\beta/m_\alpha)^{1/2} \tag{1.7}$$

where m_α is the mass of species α. For example, for individual point particles, classical mechanics gives way to quantum mechanics when their wave functions overlap, which occurs at separation $O(\lambda_\alpha)$. For ions, λ would instead be the radius of an outer orbital. For Fermions, one attempts to model the Pauli principle together with electrostatic repulsion by classical effective short range forces. Various more or less elaborated forms of effective potentials that remain finite for $|\mathbf{r}| \leqslant \lambda$ have been derived from quantum mechanics[3] (see, e.g., (Deutsch, Furutani, and Gombert, 1981), Sec. 5, and (Kraeft, Kremp, Ebeling, and Röpke, 1986), Sec. 5.2). We will either represent these short range forces by a hard core of radius λ or we will smooth the Coulombic singularity by replacing $|\mathbf{r}|^{-1}$ by

$$V_{\infty,\lambda}(\mathbf{r}) = |\mathbf{r}|^{-1}\,(1-\exp(-|\mathbf{r}|/\lambda)) \tag{1.8}$$

Neither choice is likely to be a realistic description of the physics at this length scale, so these are only claimed to be useful when one can show that there are predictions which are not very dependent on how the short range force is chosen.

The notation $V_{\infty,\lambda}$ conveys the equation

$$V_{\infty,\lambda} = V_{\infty} - V_{\lambda} \tag{1.9}$$

where we set

$$V_{\lambda}(\mathbf{r}) = |\mathbf{r}|^{-1}\exp(-|\mathbf{r}|/\lambda); \qquad V_{\infty}(\mathbf{r}) = 1/|\mathbf{r}| \tag{1.10}$$

The potential $V_{\infty,\lambda}$ is the Green's function for $(-\Delta + \lambda^2\,\Delta^2)/(4\pi)$ with the boundary condition appropriate for a system confined to a box Λ with insulating walls. We shall also consider systems confined in a box with conducting grounded walls. In these cases $V_{\lambda}(\mathbf{r}-\mathbf{r}')$ is replaced by $V_{\lambda}(\mathbf{r},\mathbf{r}')$ which then denotes the Greens' function with zero boundary conditions.

Consider the case where the ellipsis in (1.1) represent a hard core of radius λ. By Newton's theorem each point charge can then be spread out into an equivalent charge on a sphere of radius λ without changing the Coulomb interaction energy. If self-energies of the spheres are added into the Coulomb energy then it is positive because it can be written as the integral of the square of the electric field. Since the self-energy of N spheres is $\frac{1}{2}\sum_{\alpha} e_{\alpha}^2/\lambda$ this argument shows that

$$\text{Stability: } U \geqslant -BN; \qquad B = O\left(\frac{e_{\alpha}^2}{2\lambda}\right) \tag{1.11}$$

Thus the introduction of the hard cores has made Ξ_{Λ} finite (Onsager, 1939).

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[3] For instance by identifying the two particle quantum mechanical matrix element $\langle \mathbf{r}_1, \mathbf{r}_2|\times \exp(-\beta H_2)\,|\mathbf{r}_1, \mathbf{r}_2\rangle$ with a classical Boltzmann weight.

The same stability bound holds in the other case where the additional terms in the ellipsis in (1.1) smooth out the Coulombic singularity. The total potential energy with self-energies added is

$$\frac{1}{2}\sum_{i,j} e_{\alpha_i} e_{\alpha_j} \frac{1-e^{-|\mathbf{r}_i-\mathbf{r}_j|/\lambda}}{|\mathbf{r}_i-\mathbf{r}_j|} \tag{1.12}$$

which is positive because it equals, in Fourier space,

$$\frac{1}{2}\frac{4\pi}{(2\pi)^3}\int d\mathbf{k}\left(\frac{1}{|\mathbf{k}|^2}-\frac{1}{\lambda^{-2}+|\mathbf{k}|^2}\right)\left|\sum_i e_{\alpha_i} e^{i\mathbf{k}\cdot\mathbf{r}_i}\right|^2 \geqslant 0 \tag{1.13}$$

The self energies are again $\frac{1}{2}\sum_\alpha e_\alpha^2/\lambda$ so we obtain (1.11). Analogous arguments using the appropriate eigenfunctions in place of $\exp(i\mathbf{k}\cdot\mathbf{r})$ show that stability bounds hold also for particles in a grounded container.

We use the summation identity

$$\sum_{\{N_\alpha\}}^{\infty}\prod_\alpha \frac{1}{N_\alpha!}\cdots = \sum_{N=0}^{\infty}\frac{1}{N!}\sum_{\alpha_1,\dots,\alpha_N}^{\mathscr{S}}\cdots \tag{1.14}$$

to write the partition function (1.4) in the form

$$\Xi_\Lambda = \sum_{N=0}^{\infty}\frac{1}{N!}\int\prod_{k=1}^{N} d\mathscr{E}_k\, z(\mathscr{E}_k)\exp\left(-\beta U(\mathscr{E}_1,\dots,\mathscr{E}_k)-\beta\sum_{i=1}^{N}\phi(\mathscr{E}_i)\right) \tag{1.15}$$

where $\mathscr{E}=(\mathbf{r},\alpha)$ unites the spatial and species coordinate so that $\phi(\mathscr{E})=e_\alpha\phi(\mathbf{r})$ and the $d\mathscr{E}$ integration means

$$\int d\mathscr{E}\cdots = \sum_{\alpha=1}^{\mathscr{S}}\int_\Lambda d\mathbf{r}\cdots \tag{1.16}$$

and $z(\mathscr{E})=z_\alpha$.

We denote by $\omega=(\mathscr{E}_1,\dots,\mathscr{E}_N)$ a configuration of the particles, $U(\omega)=U(\mathscr{E}_1,\dots,\mathscr{E}_N)$ and $z(\omega)=z(\mathscr{E}_1)\cdots z(\mathscr{E}_N)$. The grand canonical summation over these configurations is

$$\int_\Lambda d\omega\cdots = \sum_{N=0}^{\infty}\frac{1}{N!}\int\prod_{k=1}^{N} d\mathscr{E}_k\cdots \tag{1.17}$$

and the grand canonical average is, for zero external potential,

$$\langle\cdots\rangle = \frac{1}{\Xi_\Lambda}\int_\Lambda d\omega\, z(\omega)\, e^{-\beta U(\omega)}\dots \tag{1.18}$$

A system in which the species occur in pairs of equal but opposite charge with equal activities is said to be charge-symmetric.

The observable that measures density of particles of species α at $\mathbf{r}$ is given by

$$\hat{\rho}(\mathscr{E}, \omega) = \sum_{j=1}^{N} \delta(\mathscr{E}, \mathscr{E}_j) = \sum_{j=1}^{N} \delta_{\alpha, \alpha_j} \delta(\mathbf{r} - \mathbf{r}_j) \tag{1.19}$$

and n-particle distributions for points $\mathbf{r}_a$, $a = 1,..., n$ are defined by

$$\rho(\mathscr{E}_1,..., \mathscr{E}_n) = \left\langle \prod_{a=1}^{n} \hat{\rho}(\mathscr{E}_a) \right\rangle \tag{1.20}$$

These definitions coincide with the standard definitions of distribution functions in statistical mechanics when $\mathscr{E}_1,..., \mathscr{E}_n$ are distinct. If they are not all distinct (coincident points) then our definition includes squares or higher powers of delta functions. At various points in the text we will use the phrase "does not include contributions from coincident points" to indicate that such powers of delta functions are omitted. To illustrate what "including contributions from coincident points" means, consider $\int d\mathscr{E}\, f(\mathscr{E})\, \rho(\mathscr{E}, \mathscr{E}_1)$. The integral smooths the delta function in (1.19) so that the diagonal terms $\sum_j \delta(\mathscr{E}, \mathscr{E}_j)\, \delta(\mathscr{E}_1, \mathscr{E}_j)$ in $\hat{\rho}(\mathscr{E}, \omega)\, \hat{\rho}(\mathscr{E}_1, \omega)$ give the "coincident contribution" $\sum_j f(\mathscr{E}_j)\, \delta(\mathscr{E}_1, \mathscr{E}_j)$.

We also introduce the charge density observable

$$\hat{c}(\mathbf{r}, \omega) = \sum_{\alpha} e_\alpha \hat{\rho}_\alpha(\mathbf{r}, \alpha, \omega) = \sum_{j=1}^{N} e_{\alpha_j} \delta(\mathbf{r} - \mathbf{r}_j) \tag{1.21}$$

and the charge distributions

$$c(\mathbf{r}_1,..., \mathbf{r}_n) = \left\langle \prod_{a} \hat{c}(\mathbf{r}_\mathbf{a}) \right\rangle \tag{1.22}$$

More generally one obtains mixed charge–particle distributions by taking the average of products of density observables and charge observables (1.19) and (1.21).

We shall also consider the corresponding truncated distributions (correlations) ρ_T and c_T defined in the usual way

$$\rho_T(\mathscr{E}_1, \mathscr{E}_2) = \rho(\mathscr{E}_1, \mathscr{E}_2) - \rho(\mathscr{E}_1)\, \rho(\mathscr{E}_2) \tag{1.23}$$

and so on.

Correlation functions of charge densities can also be obtained as the response to an infinitesimal external potential by variational differentiation of the logarithm of the partition function $\Xi_\Lambda(\beta\phi)$ with respect to $-\beta\phi$. In particular, the charge density induced in the system by a potential perturbation at $\mathbf{r}_1$ is

$$c(\mathbf{r}_1)=\frac{\delta}{\delta(-\beta\phi(\mathbf{r}_1))}\ln \Xi_\Lambda(\beta\phi) \tag{1.24}$$

and the truncated distribution of two charge densities is

$$c_T(\mathbf{r}_1,\mathbf{r}_2)=\frac{\delta}{\delta(-\beta\phi(\mathbf{r}_1))}\frac{\delta}{\delta(-\beta\phi(\mathbf{r}_2))}\ln \Xi_\Lambda(\beta\phi) \tag{1.25}$$

By this definition, we find that

$$c_T(\mathbf{r}_1,\mathbf{r}_2)=\langle \hat{c}(\mathbf{r}_1)\,\hat{c}(\mathbf{r}_2)\rangle-\langle \hat{c}(\mathbf{r}_1)\rangle\langle \hat{c}(\mathbf{r}_2)\rangle \tag{1.26}$$

The physical properties of an homogeneous infinitely extended charged fluid are conveniently described by its linear response to an external classical charge density $c^{\mathrm{ext}}(\mathbf{r})$. One defines the static susceptibility $\chi(\mathbf{r}_2-\mathbf{r}_1)$ as the linear response at $\mathbf{r}_2$ of the charge density of the fluid to the external density at $\mathbf{r}_1$

$$\chi(\mathbf{r}_2-\mathbf{r}_1)=\left[\frac{\delta}{\delta c^{\mathrm{ext}}(\mathbf{r}_1)}\,c(\mathbf{r}_2)\right]_{c^{\mathrm{ext}}=0} \tag{1.27}$$

The function $\chi(\mathbf{r})$ describes the shape of the screening cloud around an infinitesimal point test charge at the origin. In Fourier space,

$$\tilde{\chi}(\mathbf{k})=\int \chi(\mathbf{r})\,e^{-ik\cdot\mathbf{r}}\,d\mathbf{r} \tag{1.28}$$

is related to the Fourier transform $S(\mathbf{k})$ of the charge-charge correlations $c_T(\mathbf{r},\mathbf{0})$ (1.26) at zero potential (the structure factor of the fluid) by

$$\tilde{\chi}(\mathbf{k})=-\frac{4\pi\beta}{|\mathbf{k}|^2}\,S(\mathbf{k}) \tag{1.29}$$

Finally, the total effective potential due to the test charge plus its screening cloud is

$$\tilde{V}^{\mathrm{eff}}(\mathbf{k})=(1+\tilde{\chi}(\mathbf{k}))\,\tilde{V}(\mathbf{k})=\varepsilon^{-1}(\mathbf{k})\,\tilde{V}(\mathbf{k}) \tag{1.30}$$

where we have defined the static dielectric function $\varepsilon(\mathbf{k})$ by $\varepsilon^{-1}(\mathbf{k}) = \tilde{\chi}(\mathbf{k}) + 1$. Equivalently we immerse two test charges $(\mathbf{r}_a, e_a)_{a=1,2}$ in the ensemble. Their (nonlinear) effective potential energy is the excess free energy due to the external charge distribution given by

$$\exp(-\beta V^{\text{eff}}((\mathbf{r}_a, e_a)_{a=1,2}) \\ = \frac{\langle \exp(-\beta e_1 V * \hat{c}(\mathbf{r}_1) - \beta e_2 V * \hat{c}(\mathbf{r}_2) - \beta e_1 e_2 V(\mathbf{r}_1 - \mathbf{r}_2)) \rangle}{\langle \exp(-\beta e_1 V * \hat{c}(\mathbf{r}_1)) \rangle \langle \exp(-\beta e_2 V * \hat{c}(\mathbf{r}_2)) \rangle} \tag{1.31}$$

But then we take the test charges infinitesimal and find the leading term

$$\begin{aligned} V^{\text{eff}}((\mathbf{r}_a, e_a)_{a=1,2}) &\sim e_1 e_2 V^{\text{eff}}(\mathbf{r}_1 - \mathbf{r}_2) \\ V^{\text{eff}}(\mathbf{r}_1 - \mathbf{r}_2) &= V(\mathbf{r}_1 - \mathbf{r}_2) - \beta V * c_T * V(\mathbf{r}_1 - \mathbf{r}_2) \end{aligned} \tag{1.32}$$

which is equivalent to our previous formula (1.30).

A well known criterion for the plasma phase of the Coulomb system is the vanishing of $\varepsilon^{-1}(\mathbf{k})$ as $\mathbf{k} \to 0$. This implies with (1.29) that $S(\mathbf{k}) \simeq (4\pi\beta)^{-1} |\mathbf{k}|^2$, $\mathbf{k} \to 0$, which is equivalent with the second moment rule (Stillinger–Lovett rule) for the charge-charge correlation

$$\int d\mathbf{r}\, |\mathbf{r}|^2\, c_T(\mathbf{r}, \mathbf{0}) = -\frac{3}{2\pi\beta} \tag{1.33}$$

If the Coulomb interaction U is set to zero the partition function is

$$\begin{aligned} \Xi_{\text{ideal}, \Lambda}(\beta\phi) &= \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{k=1}^{N} d\mathscr{E}_k\, z(\mathscr{E}_k) \exp\left(-\beta \sum_{j=1}^{N} e_{\alpha_j} \phi(\mathbf{r}_j) \right) \\ &= \exp\left(\int d\mathscr{E}\, z(\mathscr{E})\, e^{-\beta e_\alpha \phi(\mathbf{r})} \right) \end{aligned} \tag{1.34}$$

We will call the resulting system an ideal gas, because the external potential is just a multiplication of the activities by $\exp(-\beta e_\alpha \phi(\mathbf{r}))$. In this case all distributions are computable, e.g.,

$$\langle \hat{c}(\mathbf{r}_1) \rangle_{\text{ideal}, \beta\phi} = \frac{\delta}{\delta(-\beta\phi(\mathbf{r}_1))} \ln \Xi_{\text{ideal}, \Lambda}(\beta\phi) = \sum_{e_{\alpha_1}} e_{\alpha_1} z_{\alpha_1}\, e^{-\beta e_{\alpha_1} \phi(\mathbf{r}_1)} \tag{1.35}$$

where we used (1.24).

C. The Quantum Coulomb Gas

We consider $\mathscr{S}$ species of quantum point charges (electrons and nuclei) in a box Λ in $\mathbb{R}^3$, with masses m_α, charges e_a and spins s_α, $\alpha = 1,..., \mathscr{S}$. Each species obeys Fermi or Bose statistics and at least one species is Fermionic. The system is governed by the non-relativistic N-particle Hamiltonian

$$H_{\Lambda, N} = -\sum_{i=1}^{N} \frac{\hbar^2}{2m_{\alpha_i}} \Delta_i + \sum_{i<j} e_{\alpha_i} e_{\alpha_j} V(\mathbf{r}_i - \mathbf{r}_j) + \sum_{i=1}^{N} e_{\alpha_i} \phi(\mathbf{r}_i) \tag{1.36}$$

acting on the N-particle Hilbert space appropriately symmetrized according to the statistics of each species. The Laplacians Δ_i in (1.36) have Dirichlet boundary conditions on the boundary of Λ. The external electrostatic potential is set to zero unless we warn the reader otherwise.

We denote by H_N the Hamiltonian for particles in infinite space. The stability of the Hamiltonian is the statement that if at least one of the particle species obeys Fermi statistics, then

$$H_N \geqslant -BN \tag{1.37}$$

with B a positive constant independent of N (Dyson and Lenard, 1967; Dyson and Lenard, 1968). The proof has been greatly simplified by Lieb and Thirring with the use of the Thomas-Fermi theory. This is reviewed in (Lieb, 1976). A new proof (Graf, 1997) is based on a remarkable electrostatic inequality for the classical Coulomb interaction (1.1). For a review on recent developments on these questions, see (Lieb, 1990). We mention here that the problem of the stability of matter in presence of magnetic fields (Lieb, Loss, and Solovej, 1995; Fefferman, 1995) and the quantized radiation field[4] (Bugliaro, Fröhlich, and Graf, 1996; Fefferman, Fröhlich, and Graf, 1998) has received much attention lately.

Let

$$P_\alpha = \frac{1}{N_\alpha!} \sum_{p_\alpha} (\eta_\alpha)^{p_\alpha} p_\alpha, \qquad \eta_\alpha = \pm 1 \tag{1.38}$$

be the projection onto the symmetric ($\eta_\alpha = +1$) or antisymmetric ($\eta_\alpha = -1$) states of particles of species α. The sum runs on all permutations p_α of the N_α particles and $(\eta_\alpha)^{p_\alpha}$ is the signature of p_α; p_α acts both on the position $\mathbf{r}$ and the spin variable σ of the particle. The projection onto the subspace of states of a many-body system with $N = \sum_\alpha N_\alpha$ particles having the appropriate statistics is given by

$$P = \prod_\alpha P_\alpha = \sum_p \left(\prod_\alpha \frac{(\eta_\alpha)^{p_\alpha}}{N_\alpha!} \right) p \tag{1.39}$$

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[4] The matter is non-relativistic and an ultraviolet cutoff is imposed.

where the sum runs now on all permutations of the N particles that are compositions $p = p_{\alpha_1} \cdots p_{\alpha_{\mathscr{S}}}$ of permutations of particles of each species.

Associating to each species a chemical potential μ_a, the grand canonical partition function of the quantum gas is given by the sum

$$\begin{aligned}\Xi_\Lambda &= \sum_{\{N_\alpha\}} \operatorname{Tr} P \exp\left(-\beta \left(H_{\Lambda, N} - \sum_\alpha \mu_\alpha N_\alpha \right)\right) \\ &= \sum_{\{N_\alpha\}} \sum_p \prod_\alpha \frac{(\eta_\alpha)^{p_\alpha} \exp(\beta \mu_\alpha N_\alpha)}{N_\alpha!} \int_\Lambda d\mathbf{r}_1 \cdots \mathbf{r}_N \\ &\quad \times \sum_{\{\sigma_{\alpha_i}\}} \langle \{\mathbf{r}_{p(i)}, \sigma_{\alpha_{p(i)}}\} |\exp(-\beta H_{\Lambda, N})| \{\mathbf{r}_i, \sigma_{\alpha_i}\} \rangle \end{aligned} \tag{1.40}$$

In (1.40), $|\{\mathbf{r}_i, \sigma_i\}\rangle = \prod |\mathbf{r}_i, \sigma_i\rangle$ is a product of states of individual particles that also diagonalize the spin component along a fixed direction with quantum numbers σ_α taking the values $-s_\alpha$, $-s_\alpha + 1, ..., s_\alpha$.

The pressure is defined as in (1.5). Particle and charge distributions are defined as in the classical case, replacing the average (1.18) by

$$\langle \cdots \rangle = \frac{1}{\Xi_\Lambda} \operatorname{Tr} P(e^{-\beta H_{\Lambda, N}} \cdots) \tag{1.41}$$

Here the particle and charge distributions and correlations are defined as in (1.20) and (1.22) where now the particle coordinates $\mathbf{r}_j$ in (1.19) are the quantum mechanical position operators.[5]

In contrast to the classical situation, the response to an external electrostatic potential yields a new type of correlation functions, the imaginary time Green's functions. They are obtained by variational differentiation with respect to the external potential. Of special interest is the charge distribution at $\mathbf{r}_2$ induced by an external potential perturbation at $\mathbf{r}_1$ in the linear response regime

$$\begin{aligned} c^{\text{ind}}(\mathbf{r}_1 \mid \mathbf{r}_2) &= \left[\frac{\delta}{\delta(-\beta \phi(\mathbf{r}_1))} \langle \hat{c}(\mathbf{r}_2) \rangle \right]_{\phi = 0} \\ &= \left[\frac{\delta}{\delta(-\beta \phi(\mathbf{r}_1))} (\Xi_\Lambda^{-1} \operatorname{Tr} P \exp(-\beta H_{\Lambda, N})\, \hat{c}(\mathbf{r}_2)) \right]_{\phi = 0} \\ &= \frac{1}{\beta} \int_0^\beta d\tau\, c_T(\mathbf{r}_1, \tau, \mathbf{r}_2) \end{aligned} \tag{1.42}$$

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[5] We use the same symbol **r** for the quantum mechanical position operator and for the argument of a correlation function. We do not consider spin correlations. All the quantum correlations in the review are purely positional with spin variables averaged out.

In (1.42)

$$c_T(\mathbf{r}_1, \tau, \mathbf{r}_2) = \langle e^{\tau H_{\Lambda, N}}\, \hat{c}(\mathbf{r}_1)\, e^{-\tau H_{\Lambda, N}}\, \hat{c}(\mathbf{r}_2) \rangle - \langle \hat{c}(\mathbf{r}_1) \rangle \langle \hat{c}(\mathbf{r}_2) \rangle \tag{1.43}$$

is the imaginary time displaced charge-charge correlation (or Duhamel function): it reduces to the static charge-charge truncated distribution at $\tau = 0$.

For an infinitely extended quantum charged fluid, we introduce the spatial Fourier transform $S(\mathbf{k}, \tau)$ of $c_T(\mathbf{r}, \tau, \mathbf{0})$. The static structure factor of the fluid is then

$$S(\mathbf{k}) = S(\mathbf{k}, \tau = 0) \tag{1.44}$$

and the generalization of the classical relations (1.29) and (1.30) to the quantum mechanical situation is

$$\tilde{\chi}(\mathbf{k}) = \varepsilon^{-1}(\mathbf{k}) - 1 = -\frac{4\pi}{|\mathbf{k}|^2} \int_0^\beta d\tau\, S(\mathbf{k}, \tau) \tag{1.45}$$

Notice that in the latter case, the susceptibility $\tilde{\chi}(\mathbf{k})$ (defined as in (1.27)) is no longer proportional to the static structure factor.

Equivalence of ensembles and existence of thermodynamic functions was established in (Griffith, 1968; Lebowitz and Lieb, 1969; Lieb and Lebowitz, 1972; Lieb and Narnhofer, 1975). The analogous results for classical systems are corollaries.

There are no results on existence of the infinite volume limit of distribution functions except for charge symmetric Bose systems with positive-definite interactions.[6] In this case at any density and temperature for which the system is stable[7] all particle distribution functions have unique infinite volume limits (Fröhlich and Park, 1978; Fröhlich and Park, 1980; Kiessling, 1992).[8] These results include charge-symmetric classical systems with positive-definite potentials. They rely on the Sine–Gordon transformation described later.

The physical content of these results on the existence of the infinite volume limit is that the limit exists independently of the way the container is enlarged. For example, we could consider two sequences of increasingly large containers related by a fixed translation. Both sequences would have

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[6] The assumption of positive definiteness means here that the Fourier transform of the potential is positive and integrable. In particular the potential is continuous at the origin. Note that (1.8) is a positive-definite interaction but hard cores plus Coulomb are not.

[7] For sufficiently large activity the grand canonical ensemble diverges. For the ideal gas this happens at the Bose–Enstein condensation.

[8] Their proof only works for some choices of boundary conditions but his is probably not a physical limitation.

the same infinite volume limit, so the limit must be translation invariant. In particular the limiting distributions could not describe a crystal with a low density of defects. On the other hand one would expect to be able to select such a state by choosing a sequence of containers whose boundaries match the natural planes of the crystal, unless the system never forms crystals. Therefore these results are evidence that stable charge symmetric systems with positive-definite potentials are always in a fluid phase.

Further results on existence of the infinite volume limit of classical distribution functions at low density are included in the work on Debye screening (Brydges and Federbush, 1978; Imbrie 1983a) reviewed in the next chapter, but these are low density results.

D. Neutrality

In systems with short range interactions the densities of different species can be varied independently, but Coulomb systems maintain charge neutrality

$$\sum_{\alpha} \rho_{\alpha} e_{\alpha} = 0 \tag{1.46}$$

by expelling excess charge to the boundary (Lieb and Lebowitz, 1972; Graf and Schenker, 1995a). We introduce a vector notation

$$\underline{\mathbf{e}} = (e_1, ..., e_{\mathscr{S}}), \qquad \underline{\boldsymbol{\mu}} = (\mu_1, ..., \mu_{\mathscr{S}}) \tag{1.47}$$

for the set of charges and chemical potentials, and decompose $\underline{\boldsymbol{\mu}}$

$$\underline{\boldsymbol{\mu}} = \boldsymbol{\mu} + \nu \underline{\mathbf{e}}, \qquad \boldsymbol{\mu} \cdot \underline{\mathbf{e}} = 0, \qquad \nu = \frac{\underline{\boldsymbol{\mu}} \cdot \underline{\mathbf{e}}}{|\underline{\mathbf{e}}|^2} \tag{1.48}$$

into its components perpendicular and parallel to the charge vector. Then, the charge neutrality is equivalent with the fact that the infinite volume limit of grand canonical pressure does not depend on the component ν of $\underline{\boldsymbol{\mu}}$ along the charge vector

$$P(\beta, \underline{\boldsymbol{\mu}}) = P(\beta, \boldsymbol{\mu} + \nu \underline{\mathbf{e}}) = P(\beta, \boldsymbol{\mu}) \tag{1.49}$$

This means that different choices of chemical potentials μ_{α} or activities z_{α}, do not necessarily lead to different densities. It is common to break this redundancy by imposing

$$\text{pseudo-neutrality:} \quad \sum_{\alpha} e_{\alpha} z_{\alpha} = 0 \tag{1.50}$$

The system will be neutral regardless of whether pseudo-neutrality is imposed or not, but in Section II.F we will argue that charges that are expelled to the boundary create a constant external electrostatic potential ψ which renormalizes the activities $z_\alpha \to z_\alpha \exp[-\beta e_\alpha \psi]$ in such a way as to restore the condition for the renormalized activities. Thus imposing the condition amounts to working with the renormalized activities.

II. DEBYE SCREENING

This chapter is devoted to screening in classical Coulomb systems. We begin with a review of the original theory of Debye and Hückel followed by an account of some rigorous theorems. Then there follow several sections that illustrate the main ideas used in the proofs with discussions concerning open problems.

A. Debye–Hückel Theory

The mean field theory approximation for the dilute plasma phase (Debye and Hückel, 1923) is at the center of our discussion. We will briefly review their argument to prepare the way for further developments. For further background see (McQuarrie, 1976; Hansen and McDonald, 1976).

The activity z_α has dimension length^{-3} and βe_α^2 and λ have dimensions length. Thus if l_D is defined by

$$l_D = \left(4\pi \sum_\alpha e_\alpha^2 z_\alpha \beta\right)^{-1/2} \tag{2.1}$$

then l_D is a length, called the Debye length. The activities in this definition of l_D are required to satisfy the pseudo-neutrality condition (1.50). It is standard to define the Debye length in terms of densities by the formula

$$\kappa^{-1} = \left(4\pi \sum_\alpha e_\alpha^2 \rho_\alpha \beta\right)^{-1/2} \tag{2.2}$$

and we have used the notation l_D instead of the standard κ^{-1} because the two definitions are not equal, although their ratio tends to one in the Debye–Hückel limit described below.

The conclusions of Debye–Hückel theory include that the pressure P and charge-charge correlation obey

$$\beta(P-P_{\text{ideal}}) \sim \frac{1}{12\pi l_D^3}$$

$$c_T(\mathbf{r}_1,\mathbf{r}_2) \sim -((4\pi)^2\,\beta l_D^4\,|\mathbf{r}_1-\mathbf{r}_2|)^{-1}\exp\left(-\frac{|\mathbf{r}_1-\mathbf{r}_2|}{l_D}\right) + (4\pi\beta l_D^2)^{-1}\,\delta(\mathbf{r}_1-\mathbf{r}_2) \tag{2.3}$$

The Debye–Hückel argument suggests that these are really limiting laws, holding in a limit in which the number of particles in a volume l_D^3 tends to infinity, while the number in a volume λ^3 tends to zero. Perturbation expansions (Mayer, 1950; Meeron, 1961; Lebowitz and Stell, 1968; Hansen and McDonald, 1976; Mayer and Mayer, 1977) are also likely to be asymptotic as opposed to convergent, but it is still natural to believe that the second result holds in a stronger sense: that without taking the limit there can be exponential decay of correlations, particularly if one is reasonably close to the limit. We shall refer to this stronger statement as Debye screening.

The first law in (2.3) can be expressed in terms of densities by using $\rho_\alpha = z_\alpha\,\partial\beta P/\partial z_\alpha$ and $\beta P_{\text{ideal}} = \sum z_\alpha$. One finds that

$$\beta P - \sum_\alpha \rho_\alpha \sim -\frac{\kappa^3}{24\pi} \tag{2.4}$$

The second result (2.3) was based on an argument that can be paraphrased as follows. Consider a grand canonical ensemble of particles interacting with each other and also with a charge e_0 held fixed at the origin. This is the same as adding to βU the external potential term $\beta\int e_0\hat{c}(\mathbf{r},\omega)\,V(\mathbf{r})\,d\mathbf{r}$. Then the potential at another point $\mathbf{r}$ will be the sum of $V(\mathbf{r})$ and another potential ϕ created by the charges in the gas. Debye and Hückel approximate this ϕ by assuming that the gas reacts to the combined potential $f = e_0V+\phi$ as an ideal gas, which leads to the self-consistent scheme

$$\frac{1}{4\pi}\Delta f(\mathbf{r},\omega) = -\hat{c}(\mathbf{r},\omega) - e_0\,\delta(\mathbf{r}) \approx -\langle\hat{c}(\mathbf{r})\rangle_{\text{ideal},\,\beta f} - e_0\,\delta(\mathbf{r}) \tag{2.5}$$

We wrote $f(\mathbf{r},\omega)$ to emphasize that the exact field is configuration dependent but having made this approximation we write $f(\mathbf{r})$ from now on. From (1.35),

$$\frac{1}{4\pi}\Delta f(\mathbf{r}) = -\sum_\alpha z_\alpha\,e_\alpha\exp[-\beta e_\alpha f(\mathbf{r})] - e_0\,\delta(\mathbf{r}) \tag{2.6}$$

If $\beta f(\mathbf{r})$ is a weak potential then $\exp(x) \approx 1 + x$ and pseudo-neutrality (1.50) leads to

$$[\Delta - l_D^{-2}]\, f(\mathbf{r}) = -4\pi e_0\, \delta(\mathbf{r}) \tag{2.7}$$

which has the solution

$$f(\mathbf{r}) = e_0\, |\mathbf{r}|^{-1} \exp(-|\mathbf{r}|/l_D) \tag{2.8}$$

The exponential decay of f is the origin of exponential decay of charge density correlations within this mean field approximation. Indeed noting that f is related to the effective potential introduced in Section I.B by $f = e_0 V^{\text{eff}}$ we can obtain the second Debye–Hückel law from (1.32) using the Fourier transform.

In (2.5) the $\langle \hat{c}(\mathbf{r}) \rangle_{\text{ideal}, \beta f}$ is the mean density of a spherically symmetric opposite charge "screening" cloud that forms around the positive charge at the origin. Note that within the linear approximation $\exp(x) = 1 + x$ our calculations imply

$$\int d\mathbf{r} \langle \hat{c}(\mathbf{r}) \rangle_{\text{ideal}, \beta f} \sim -e_0 \tag{2.9}$$

By Newton's theorem, such a cloud is equivalent to an additional negative charge at the origin that neutralizes the fixed charge up to a remainder exponentially small in the radius to the point $\mathbf{r}$. Of course no single charge configuration of point particles can be spherically symmetric. The cloud is an ensemble average over configurations. This cancellation of charge is captured in "sum rules" which will be discussed in Section II.B. Related to this point is the fact that the integral over $\mathbf{r}_2$ of the right hand side of (2.3) vanishes.

B. Theorems on Debye Screening

In this section we will survey the rigorous results on Debye screening and the Debye–Hückel approximation concentrating on three dimensional systems but with some remarks about other dimensions.

The one dimensional Coulomb system without hard core has been solved exactly (Lenard, 1961; Edwards and Lenard, 1962). Lenard's solution has Debye screening for charge density observables, but one dimensional systems have exceptional screening properties, because the linear potential $-|x-y|$ has no multipoles. For example, the electric field is piecewise-constant with jumps at the positions of particles so that outside an interval containing any neutral configuration, one can achieve a zero electric field. On the other hand if a single fractional charge is placed in a system of integer charges then the resulting potential can never be screened because the ensemble of integer charges can do no more than cancel integer parts of the corresponding electric field. One dimensional Coulomb systems have been reviewed in (Choquard, Kunz, Martin, and Navet, 1981). Since then, highly non-trivial results have been obtained on the correlations of classical charges confined to a circle and interacting with a logarithmic potential (Forrester, 1992; Forrester, 1993b; Forrester, 1993a). Some comments on two dimensional systems are given at the end of this section.

For three dimensions the results are complicated to state completely and the complications are probably artifacts of the proofs. Therefore let us restrict ourselves to a simple case of a hard core plasma with two species, whose charges e_α have rational ratio. Recall that the combination βe_α^2 has dimensions of length. By absorbing a fundamental unit of charge into β we assume that β carries the dimension of length while e_α is dimensionless. To put it another way, we state results regarding β, z_α, λ as parameters, and keeping e_α fixed. The results below are valid in a thermodynamic limit in which there are boundary conditions on the Coulomb potential. Details may be found on page 199 of (Brydges and Federbush, 1980); the boundary conditions are a little artificial but their essence is that the walls of the container are grounded, so that all electrostatic potentials vanish at the boundary $\partial\Lambda$.

Theorem II.1. Suppose that

$$\text{Pseudo-Neutrality:} \quad \sum_\alpha z_\alpha e_\alpha = 0 \tag{2.10}$$

$$\text{Debeye Sphere Assumptions:} \quad \begin{cases} z_\alpha l_D^3 e^{-\beta/2\lambda} \gg 1 \\ z_\alpha \lambda^3 \ll 1 \end{cases} \tag{2.11}$$

then all (truncated) n-point particle and charge density correlations decay exponentially on length scale $l \approx l_D$. Furthermore, if $\Xi_\Lambda(\mathbf{r}_1, \mathbf{r}_2)$ is the grand canonical charge symmetric ensemble of integer charges with two fractional charges held fixed at $\mathbf{r}_1, \mathbf{r}_2$, then the two fractional charges are screened in the sense that

$$\frac{\Xi_\Lambda(\mathbf{r}_1, \mathbf{r}_2)}{\Xi_\Lambda} = \frac{\Xi_\Lambda(\mathbf{r}_1)}{\Xi_\Lambda} \frac{\Xi_\Lambda(\mathbf{r}_2)}{\Xi_\Lambda} + O(\exp(-|\mathbf{r}_1 - \mathbf{r}_2|/l)) \tag{2.12}$$

The Debye sphere assumptions say that the number of particles in a volume of size λ^3 is small, so that the hard core is out of play, and the number of particles inside a sphere of size l_D is large. For comparing these statements with the ones in the references it is useful to realize that

$$4\pi \sum_\alpha e_\alpha^2 z_\alpha l_D^3 = \frac{l_D}{\beta} \tag{2.13}$$

so the first Debye sphere condition is equivalent to β/l_D being small. Theorem II.1 is a combination of results from (Brydges, 1978; Brydges and Federbush, 1980; Imbrie, 1983b; Brydges and Kennedy, 1987).

It is shown in (Imbrie, 1983a) that there is Debye screening in Jellium and in systems with irrational charges. Jellium is a limit in which all species with positive charges are smeared out into a background charge density by letting their charge tend to zero as their density increases. The results of Brydges and Federbush were not proved with enough uniformity to persist as this limit is taken.

The Debye–Hückel limiting laws should hold in the

$$\text{Debeye–Hückel Limit:}\quad z_\alpha \lambda^3 \to 0; \qquad z_\alpha l_D^3 e^{-\beta/2\lambda} \to \infty \tag{2.14}$$

but published proofs (Kennedy, 1983; Kennedy, 1984) have the much more stringent conditions that β/λ is kept bounded and the system be charge symmetric. Similar results for quantum systems have been established by (Fontaine, 1986). The original Debye–Hückel results included correction terms containing a hard core[9] of radius a. More systematically, hard core corrections have been obtained by resummations of Mayer expansions (Meeron, 1958; Meeron, 1961)[10] and by the Kac limit developed in (Lebowitz and Stell, 1968) which develop corrections in κa. There is also a long history of intuitive extensions of the Debye–Hückel theory to include corrections from hard cores and dipolar effects. These are reviewed and advanced in (Fisher and Levin, 1993; Fisher, 1994; Levin and Fisher, 1995; Fisher, 1996, Lee and Fisher, 1996; Lee and Fisher, 1997; Zuckerman, Fisher, and Lee, 1997).[11] However consistency of these approximations is guesswork: is there an asymptotic expansion in κa? What physical effects provide the next largest corrections to Debye–Hückel theory?

In the proofs of screening complications at the boundary have been avoided by artificial boundary conditions, but only laziness stands in the way of proofs for the case where the particles are in a conducting grounded

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[9] $\beta P - \sum_\alpha \rho_\alpha \sim -(\kappa^3/24\pi)\,\sigma(\kappa a)$ where $\sigma(\kappa a) = (3/(\kappa a)^3)(1 + \kappa a - 1/(1+\kappa a) - 2\ln(1+\kappa a))$.

[10] This is compared with extended Debeye–Hückel theories in (Bekiranov and Fisher, 1998; Bekiranov and Fisher, 1999).

[11] There is a competing program (Stell, 1995; Yeh, Zhou, and Stell, 1996) based in part on the mean spherical approximation instead of Debeye–Hückel theory.

container so that the Coulomb potential vanishes at the boundary. Particles with $1/r$ forces, i.e., particles in an insulating container, have not been completely analyzed, but Debye screening for a simplified model is established (Federbush and Kennedy, 1985). This case is discussed some more in Section II.G. It is difficult because screening fails at the boundary; there are power law forces between charges on the boundary.

It should be possible to omit the pseudo-neutrality condition (2.10), but to do it rigorously may require insight into the boundary condition problem. In Section II.F we will discuss these issues along with charge expulsion.

We return to (2.9). The $\sim$ involves approximations but the theorems known as sum rules say that if truncated distributions decay integrably or better then the screening cloud around a fixed infinitesimal charge neutralizes it. More generally any fixed set of charges surrounds itself with a screening cloud in such a way that all multipoles are canceled. In particular, the function of $\mathbf{r}$ defined by

$$\begin{aligned} &c_T(\mathbf{r} \mid \mathbf{r}_1, e_{\alpha_1},..., \mathbf{r}_n, e_{\alpha_n}) \\ &\quad = \langle \hat{c}(\mathbf{r})\, \hat{\rho}(\mathbf{r}_1, e_{\alpha_1}) \cdots \hat{\rho}(\mathbf{r}_n, e_{\alpha_n})\rangle - \langle \hat{c}(\mathbf{r})\rangle \langle \hat{\rho}(\mathbf{r}_1, e_{\alpha_1}) \cdots \hat{\rho}(\mathbf{r}_n, e_{\alpha_n})\rangle \end{aligned} \tag{2.15}$$

which represents the excess charge density at $\mathbf{r}$ when particles in the system are fixed at $\mathbf{r}_1,..., \mathbf{r}_n$ has no multipole moments in the Debye regime

$$\int d\mathbf{r}\; g_l(\mathbf{r})\, c_T(\mathbf{r} \mid \mathbf{r}_1, e_{\alpha_1},..., \mathbf{r}_n, e_{\alpha_n}) = 0 \tag{2.16}$$

for all harmonic polynomials $g_l(\mathbf{r})$ of order $l = 0, 1,...$. In (2.16) the contribution of coincident points $\mathbf{r} = \mathbf{r}_i$ is included. The case $l = 0$, $g_0(\mathbf{r}) = 1$, called the charge sum rule, is expected to hold very generally in homogeneous phases of Coulomb systems (classical and quantum). These results are reviewed in (Martin 1988). Results on the effect of slow decay at boundaries are also covered in this review. In the next section, we present a derivation of the sum rules with the help of the Sine–Gordon formalism, extending the arguments of (Fontaine and Martin, 1984) to charges with hard cores.

There are also results (Alastuey and Martin, 1985) that say that if truncated distributions are integrable and decay monotonically at infinity then they must decay faster than any inverse power. A different result of the same genre was obtained by (Federbush, 1979).

Two dimensions, no short range forces: in units where the Coulomb interaction between two unit charges is $-\ln r$ let $\beta_1 = 2$, $\beta_\infty = 4$ and define the sequence of intermediate thresholds $\beta_n = \beta_\infty(2n-1)/(2n)$ with $n = 1, 2,...$. The Coulomb potential is not stable in the sense of (1.11) but the instability is weak enough to permit thermodynamic behavior anyway (Hauge and Hemmer, 1971; Deutsch and Lavaud, 1974; Fröhlich, 1976), at least for $\beta<\beta_1$. At β_1 the Gibbs factor $\exp -\beta_1 V_2$ for two oppositely charge particles is no longer integrable and the partition function diverges. The partition function for the Yukawa gas also diverges and, in the Yukawa gas Mayer expansion, the diagram with two vertices becomes infinite at $\beta=\beta_1=2$. However, all diagrams with more vertices remain finite. Similarly, at β_2, neutral diagrams with 2, 4 vertices diverge, all diagrams with more vertices remain finite, and so on. It has been proved (Brydges and Kennedy, 1987) that for $\beta<4/3\beta_1$ the Mayer expansion without the infinite two vertex term is convergent for small activity. The natural extension of this result to the higher thresholds almost certainly holds for $\beta<\beta_\infty$.[12] These results imply that there are natural infinite renormalizations of the partition function. Presumably, this enables some version of the Yukawa and Coulomb gases to be defined in the range $\beta\in[\beta_1,\beta_\infty)$ as a renormalized limit of systems with regularized interaction, because dropping a divergent term in the Mayer expansion is the same as multiplying the partition function by an infinite factor. This has not been discussed clearly in the literature, but see (Gallavotti and Nicolo, 1985b; Speer, 1986).

It has been proven (Yang, 1987) that the two species charge symmetric Coulomb gas of point particles in a grounded container has exponential screening if $\beta\ll\beta_1$ and the activity is small. The grand canonical ensemble with insulating boundary conditions is harder to analyze because it has to be restricted to neutral configurations, whereas image charges provide neutrality for free in the grounded container case.

As the last paragraph suggests, boundary conditions are more important in two dimensions than in three. For example it is known (Fröhlich and Spencer, 1981b, Theorem 4.1) that a pair of oppositely charged fractional charges immersed in a two dimensional Coulomb gas are not screened from each other when the thermodynamic limit is taken with insulating container boundary conditions. On the other hand, although the details are not published anywhere, it ought to follow from the results of Yang that they are screened when the thermodynamic limit is taken with grounded containers. This influence of boundary conditions does not happen in three dimensions. We will discuss this further in Section II.G.

Two dimensions, with stabilizing short range forces: The significance of β_∞ is that the Kosterlitz–Thouless transition takes place at a critical

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[12] An almost equivalent result appeared in (Dimock and Hurd, 1993), but the authors have reported a serious error invalidating their proof (Dimock, 1998). They are preparing a manuscript in which the error is fixed.

$\beta_c \approx \beta_\infty$.[13] By stabilizing the interaction with short range forces such as hard cores one can reach β_c without infinite renormalizations and see the $\beta > \beta_c$ dipole phase. The original argument (Kosterlitz and Thouless, 1973) was given a complete proof (Fröhlich and Spencer, 1981a) for the Coulomb system on a lattice. A more detailed analysis of the Kosterlitz–Thouless phase, based on term by term analysis of the Mayer expansion, is given in (Alastuey and Cornu, 1992; Alastuey and Cornu, 1997c; Alastuey and Cornu, 1997a). There is confusion over whether the thresholds β_n should be interpreted as the successive collapse into neutral clusters of 2, 4,... particles. (Gallavotti and Nicolo, 1985b; Speer, 1986) proposed such an interpretation based on successive divergences in the Mayer expansion. This is analogous to the Yukawa gas alluded to above, except that now infra-red divergences cause the thresholds. To complete their argument one must show that there are bulk observables whose correlations have associated singularities. On the other hand (Fisher, Li, and Levin, 1995) argue that no singularities show up in thermodynamic functions and consequently the thresholds are not physical.

The heuristic renormalization group argument (Kosterlitz and Thouless, 1973) predicts that exponential screening of particle distributions holds for all $\beta < \beta_c$ if the density is sufficiently small. A complete proof of screening at low activity for β in this range would be a wonderful achievement.

Exact formulas in two dimensions for the excess free energy of a single charge fixed at the origin are conjectured in (Lukyanov and Zamolodchikov, 1997). See also (Smirnov, 1992) for other interesting formulas. These formulas in principle could be used to express the excess free energy of a fractional charge in terms of the density (or the activity) and temperature. The authors study the Sine–Gordon functional integral with boundary conditions that correspond to a grounded conducting container so that violating neutrality by fixing a fractional charge makes sense. Their conjecture translates, via the Sine–Gordon transformation, to the two component charge symmetric gas with a purely Coulomb potential, at least for $\beta < \beta_1$. With limitations on the size of the fractional charge their formulas apply for $\beta \in [\beta_1, \beta_\infty)$.

In two dimensions, there are a number of exactly solvable models for the special value of the temperature that corresponds to β_1, starting with the two dimensional one component plasma (Jancovici, 1981). These models (Alastuey, 1987; Jancovici, 1990; Jancovici, 1992) exhibit "super-Debye screening", namely Gaussian decay of the correlations. They have

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[13] $\beta_c \to \beta_\infty$ as the density tends to zero.

played an important role in testing various refined screening properties in presence of walls and of different types of inhomogeneities.

Although a characteristic of Debye phases is the rapid decay of the particle correlations, one should be aware that it is never the case for potential and electric field fluctuations (Lebowitz and Martin, 1984; Martin, 1988). For instance, correlations of the components of the electric field E_μ always have an asymptotic dipolar behavior

$$\langle E_\mu(\mathbf{r})\, E_\nu(\mathbf{0})\rangle \simeq -\frac{1}{\beta}\nabla_\mu\nabla_\nu\left(\frac{1}{|\mathbf{r}|}\right) \tag{2.17}$$

This observation has recently led to the development of the interesting view point that there are some universal properties of Debye phases that closely resemble those of a system with short range forces at its critical temperature (Jancovici, Manificat, and Pisani, 1994; Jancovici, 1996; Forrester, Jancovici, and Téllez, 1996). Actually, potential and field fluctuations are critical in Debye phases, and this leads to universal finite size corrections to the free energy as in critical systems.

C. The Sine–Gordon Transformation

1. The Fourier Transform of a Gaussian is a Gaussian. In Section I we have defined a potential

$$V_{\infty,\lambda}(\mathbf{r}) = |\mathbf{r}|^{-1}\,(1-\exp(-|\mathbf{r}|/\lambda))$$

which is a Coulomb potential smoothed at the origin. We saw that $V_{\infty,\lambda}$ has a positive Fourier transform. For such potentials there is an identity that expresses the interaction in terms of external potentials–an exact version of the mean field idea of Debye–Hückel. This is the Sine–Gordon transformation (Kac, 1959; Siegert, 1960). Kac and Siegert noticed that if self-energies are included, then the Gibbs factor

$$e^{-(\beta/2)\sum_{i,j=1}^{N} e_{\alpha_i} e_{\alpha_j} V_{\infty,\lambda}(\mathbf{r}_i,\mathbf{r}_j)} = e^{-(\beta/2)\int d\mathbf{r}\int d\mathbf{r}'\,\hat{c}(\mathbf{r})\,V_{\infty,\lambda}(\mathbf{r},\mathbf{r}')\,\hat{c}(\mathbf{r}')} \tag{2.18}$$

is Gaussian in $\hat{c}(\mathbf{r})$. By a functional integral generalization (Simon, 1979) of "the Fourier transform of a Gaussian is a Gaussian" there exists a Gaussian probability measure, intuitively described by

$$d\mu_\lambda(\phi) = \mathscr{D}\phi\; e^{-(1/2)\int \phi(\mathbf{r})\, V_{\infty,\lambda}^{-1}\phi(\mathbf{r})\, d\mathbf{r}} \tag{2.19}$$

such that

$$e^{-(\beta/2)\sum_{i,j=1}^{N} e_{\alpha_i} e_{\alpha_j} V_{\infty,\lambda}(\mathbf{r}_i,\mathbf{r}_j)} = \int d\mu_\lambda(\phi)\, e^{-(i\beta^{1/2})\int d\mathbf{r}\, \hat{c}(\mathbf{r})\, \phi(\mathbf{r})} \tag{2.20}$$

$V_{\infty,\lambda}^{-1}$ is the operator inverse of the operator whose kernel is $V_{\infty,\lambda}$. In our case we find from (1.10) that it is the partial differential operator

$$V_{\infty,\lambda}^{-1} = \frac{1}{4\pi}(-\Delta + \lambda^2 \Delta^2) \tag{2.21}$$

possibly with boundary conditions on Δ. Equation (2.20) says that the Gibbs factor is a superposition of Gibbs factors for external potentials $i\phi$. It follows that if an ideal gas of particles in an external potential is integrated over the external potentials then the result is a partition function for a gas with two-body interaction $V_{\infty,\lambda}$, including self-energies. Self-energies are equivalent to a shift in the activities. We define

$$z^{(\lambda)}(\mathscr{E}) = z(\mathscr{E})\, e^{(\beta/2)\, e_\alpha^2 V_{\infty,\lambda}(\mathbf{r},\mathbf{r})} \tag{2.22}$$

Then the partition function with potential energy $U(\omega)$ built out of $V_{\infty,\lambda}$ and an external potential ψ,

$$\Xi_\Lambda(\beta^{1/2}\psi) = \int_\Lambda d\omega\, z(\omega)\, e^{-\beta U(\omega) - \beta^{1/2}\int \psi \hat{c}(\omega)\, d\mathbf{r}} \tag{2.23}$$

is given by

$$\Xi_\Lambda(\beta^{1/2}\psi) = \int d\mu_\lambda(\phi)\, \Xi_{\mathrm{ideal},\,\Lambda,\, z^{(\lambda)}}(\beta^{1/2}[i\phi + \psi]) \tag{2.24}$$

where

$$\Xi_{\mathrm{ideal},\,\Lambda,\, z^{(\lambda)}}(f) = \int_\Lambda d\omega\, z^{(\lambda)}(\omega)\, e^{-\int f \hat{c}\, d\mathbf{r}} \tag{2.25}$$

is the ideal gas partition function (1.34) with the renormalized activities (2.22). (2.24) is the Sine–Gordon representation. It says that the partition function for the interacting system exactly equals a (functional) integral over *imaginary* external fields of the ideal gas partition function.

Gaussian measures have been studied in the mathematical literature and it is known that for this one the typical potential ϕ is a continuous function (Glimm and Jaffe, 1987, Theorem A.4.4). This result holds provided $\lambda \neq 0$; when $\lambda = 0$ the instability of the Coulomb potential returns to haunt us in the shape of the typical ϕ becoming a distribution instead of a function.

The right hand side of formula (2.19) is best understood as a mnemonic for the translation formula, also known as the Cameron–Martin formula,

$$d\mu_\lambda(\phi + g) = d\mu_\lambda(\phi)\, e^{-(1/2)\int gV^{-1}_{\infty,\lambda} g\, d\mathbf{r} - \int \phi V^{-1}_{\infty,\lambda} g\, d\mathbf{r}} \tag{2.26}$$

which is valid for any function g for which $\int gV^{-1}_{\infty,\lambda} g$ exists.[14] Translations $\phi \to -ig$ are legitimate as well whenever the integrand permits analytic continuation to $\alpha = i$ after the change of variable $\phi \to \phi + \alpha g$. The translation formula is the reason why computations with the intuitive formula (2.19) are usually correct.

It is not physically very reasonable to try to capture the very local fluctuations on length scales much smaller than l_D in a mean field picture. For example, the activity $z^{(\lambda)}$ is very different from z when λ is small, but we shall see in Section II.E that z is the correct effective activity, in the sense that an ideal gas with this activity is the best approximation in the Debye–Hückel limit. Also hard cores do not have positive Fourier transforms and cannot be represented by a Sine–Gordon potential. For these reasons we now consider a better class of representations in which the particle picture is retained on scales less than $O(l_D)$ and the mean field or Sine–Gordon is used to represent interactions on larger scales. Define the Yukawa interaction with a decay length $L \geqslant \lambda$,

$$V_L(\mathbf{r}) = |\mathbf{r}|^{-1} e^{-|\mathbf{r}|/L}; \qquad V_{L,\lambda}(\mathbf{r}) = |\mathbf{r}|^{-1} (e^{-|\mathbf{r}|/L} - e^{-|\mathbf{r}|/\lambda}) \tag{2.27}$$

We split the interaction $V_{\infty,\lambda}$ according to

$$V_{\infty,\lambda} = V_{\infty,L} + V_{L,\lambda} \tag{2.28}$$

and use the Sine–Gordon transformation to represent just the part $V_{\infty,L}$. The result is

$$\Xi_\Lambda(\beta^{1/2}\psi) = \int d\mu_L(\phi)\, \Xi_{L,\Lambda,z^{(L)}}(\beta^{1/2}[i\phi + \psi]) \tag{2.29}$$

where

$$\Xi_{L,\Lambda,z^{(L)}} = \int_\Lambda d\omega\, z^{(L)}(\omega)\, e^{-\beta U_L(\omega) - \int f\hat{c}(\omega)\, d\mathbf{r}} \tag{2.30}$$

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[14] In the sense $\int (|\nabla g|^2 + |\lambda \Delta g|^2)\, d\mathbf{r} < \infty$.

is no longer ideal; U_L is built out of two-body interactions $V_{L,\lambda}$. If hard cores are used in place of the cutoff λ in $V_{L,\lambda}$ then U_L is built out of V_L and hard cores.

The replacement of V by $V_{\infty,L}$ is the same as smoothing the Coulomb interaction by introducing form factors for the charges so they are smeared out into spherical distributions of characteristic radius L. Note that

$$\tilde{V}_{\infty,L}(\mathbf{k}) = \tilde{F}(L^2k^2)\,\frac{4\pi}{k^2}\,\tilde{F}(L^2k^2), \qquad \tilde{F}(L^2k^2) = \left(\frac{1}{1+L^2k^2}\right)^{1/2} \tag{2.31}$$

which shows that $\tilde{F}$ is the Fourier transform of the form factor.

2. Sum Rules. Sum rules provide a good illustration of aspects of the Sine–Gordon transformation that will reappear in the sequel. Here we sketch how the argument in (Fontaine and Martin, 1984)[15] applies to a Coulomb system with hard cores. We will show that sum rules result from an invariance of the Sine–Gordon measure under infinitesimal translation by harmonic functions. Formulas arising from infinitesimal symmetries are called Ward identities in quantum field theory. While it is interesting that sum rules are Ward identities, it is also easy to derive them without the Sine–Gordon transformation (Martin, 1988; Brydges and Martin, 1999).

We consider charged particles with hard core interactions of radius λ in a box Λ whose boundary is grounded and impenetrable to the hard cores. We spread each charge in the ensemble uniformly onto the surface of its hard core sphere. By Newton's theorem the interaction energy U is unchanged by the spreading out. However the self-energy of each particle becomes finite and of the order of $1/\lambda$. It can be added into U and the change in U is compensated by replacing z_α by $z_\alpha^{(\lambda)} = z_\alpha \exp(\beta e_\alpha^2/(2\lambda))$. By the Sine–Gordon transformation

$$\begin{aligned} \Xi_\Lambda &= \int \Xi_\Lambda(i\beta^{1/2}\bar{\phi}_\lambda)\, d\mu(\phi) \\ d\mu(\phi) &= e^{-1/(8\pi)\int_\Lambda (\partial\phi)^2}\, \mathscr{D}\phi \end{aligned} \tag{2.32}$$

where $\bar{\phi}_\lambda(\mathbf{r})$ is the average of ϕ over a sphere of radius λ and center $\mathbf{r}$ and $\Xi_\Lambda(\phi)$ is the hard core gas in external field ϕ:

$$\Xi_\Lambda(\phi) = \sum_{\{N_\alpha\}}^{\infty} \prod_{\alpha=1}^{\mathscr{S}} \frac{(z_\alpha^{(\lambda)})^{N_\alpha}}{N_\alpha!} \int_\Lambda d\mathbf{r}_1 \cdots \int_\Lambda d\mathbf{r}_N \exp\left(-\sum_j e_{\alpha_j}\phi(\mathbf{r}_j) - \text{hard core}\right) \tag{2.33}$$

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[15] This paper uses the smooth short range regularization (1.8).

$d\mu(\phi)$ is characterized by

$$d\mu(\phi+g)=d\mu(\phi)\, e^{1/(4\pi)\int_\Lambda \phi\Delta g-1/(8\pi)\int_\Lambda (\partial g)^2} \tag{2.34}$$

where g is any function which vanishes on the boundary with $\int_\Lambda (\partial g)^2<\infty$.

The complete expectation

$$\langle F\rangle=\frac{1}{\Xi_\Lambda}\sum_{\{N_\alpha\}}^{\infty}\prod_{\alpha=1}^{\mathscr{S}}\frac{(z_\alpha^{(\lambda)})^{N_\alpha}}{N_\alpha!}\int_\Lambda d\mathbf{r}_1\cdots\int_\Lambda d\mathbf{r}_N \exp(-\beta U-\text{hard core})\, F \tag{2.35}$$

can be taken in two stages; the first stage is an expectation conditioned on ϕ

$$\langle F\mid\phi\rangle=\frac{1}{\Xi_\Lambda(\phi)}\sum_{\{N_\alpha\}}^{\infty}\prod_{\alpha=1}^{\mathscr{S}}\frac{(z_\alpha^{(\lambda)})^{N_\alpha}}{N_\alpha!}\int_\Lambda d\mathbf{r}_1\cdots\int_\Lambda d\mathbf{r}_N$$
$$\times\exp\left(-\sum_j e_{\alpha_j}\phi(\mathbf{r}_j)-\text{hard core}\right)F$$

and the second is the remaining integration over ϕ

$$\mathbb{E}[F]=\int e^{\ln \Xi_\Lambda(i\beta^{1/2}\bar\phi)}F\,d\mu(\phi)\Big/\int e^{\ln \Xi_\Lambda(i\beta^{1/2}\bar\phi)}\,d\mu(\phi) \tag{2.36}$$

and these fit together by

$$\langle F\rangle=\mathbb{E}[\langle F\mid\psi\rangle]\qquad\text{where}\quad \psi=i\beta^{1/2}\bar\phi_\lambda \tag{2.37}$$

To obtain a sum rule we make the change of variables $\phi\to\phi+tg$ in the $d\mu(\phi)$ integral on the right hand side and differentiate with respect to t at $t=0$. The derivative must vanish since the left hand side is independent of t. The derivative of $\ln\Xi_\Lambda(\phi)$ with respect to $\phi(\mathbf{r})$ is $-\langle\hat c(\mathbf{r})\mid\phi\rangle$, which accounts for the first line in the next equation. The second line arises because the derivative of $\langle F\mid\phi\rangle$ with respect to $\phi(\mathbf{r})$ is the truncated expectation $-\langle F\hat c(\mathbf{r})\mid\phi\rangle+\langle F\mid\phi\rangle\langle\hat c(\mathbf{r})\mid\phi\rangle$.

$$\begin{aligned}0={}&\mathbb{E}[\langle F\mid\psi\rangle\langle\hat c(\bar g_\lambda)\mid\psi\rangle]-\mathbb{E}[\langle F\mid\psi\rangle\ \mathbb{E}[\langle\hat c(\bar g_\lambda)\mid\psi\rangle]\\&+\mathbb{E}[\langle F\hat c(\bar g_\lambda)\mid\psi\rangle-\langle F\mid\psi\rangle\langle\hat c(\bar g_\lambda)\mid\psi\rangle]\\&+\text{contributions from (2.34)}\end{aligned} \tag{2.38}$$

The contributions from (2.34) are proportional to

$$\mathbb{E}\left[\langle F\mid\psi\rangle\int\phi\Delta g\right]-\mathbb{E}[\langle F\mid\psi\rangle]\,\mathbb{E}\left[\int\phi\Delta g\right] \tag{2.39}$$

We would like to choose g to be a harmonic polynomial because then these contributions vanish. However this is not a legal choice of g because no harmonic polynomial can vanish on the boundary of Λ. Instead choose g to be a harmonic polynomial multiplied by another function h that is one in the interior of Λ and which goes to zero near the boundary. Now there are non-vanishing contributions from $\int \phi g \, \Delta h$ and $\int \phi \, \partial g \, \partial h$ localized near the boundary. Suppose that the container Λ is enlarged: there is competition between the growth of the harmonic polynomial $g(\mathbf{r})$ for $\mathbf{r}$ near the boundary and the decay of the truncated expectation (2.39). If the system is in a screening phase where truncated expectations of local functions of ϕ decay exponentially then the polynomial growth of g is crushed as the container is enlarged and the contributions in (2.39) vanish in the thermodynamic limit. It is true that the conditional expectations $\langle \hat{c}(\mathbf{r}) \mid \psi \rangle$ are not exactly local in ϕ but if the Mayer expansion of $\langle \hat{c}(\mathbf{r}) \mid \psi \rangle$ is convergent then $\langle \hat{c}(\mathbf{r}) \mid \phi \rangle$ is almost (exponentially) local in ϕ. This captures a physically natural condition that the system should not be so dense that there are long range correlations caused by the hard core. If the Mayer expansion converges at $\psi = 0$ then it converges uniformly for all ψ because $\psi \neq 0$ just means that activities are multiplied by modulus one phase factors.

Thus in the infinite volume limit (2.38) simplifies to $0 = \mathbb{E}[\langle F\hat{c}(\bar{g}_\lambda) \mid \psi \rangle] - \mathbb{E}[\langle F \mid \psi \rangle] \, \mathbb{E}[\langle \hat{c}(\bar{g}_\lambda) \mid \psi \rangle]$ where g is a harmonic polynomial. Now we simplify further using (2.37) and Newton's theorem (spherical average of harmonic = value at center) $\bar{g}_\lambda(\mathbf{r}) = g(\mathbf{r})$ to reach

$$0 = \langle F\hat{c}(g) \rangle - \langle F \rangle \langle \hat{c}(g) \rangle \qquad g \text{ any harmonic polynomial} \tag{2.40}$$

For example by choosing $F = \hat{\rho}(\mathbf{r}_1, \alpha_1) \cdots \hat{\rho}(\mathbf{r}_n, \alpha_n)$ (2.40) becomes the same as (2.16). In conclusion, the sum rules (2.16) for a system of classical charges with hard cores hold if the Mayer expansion for the hard core system without Coulomb interaction is convergent and if the system is in a screening phase.

D. Debye Spheres

In the previous section we divided the interaction into the Yukawa part $V_{L,\lambda}$ whose decay length is L and a remaining part, the slow part $V_{\infty,L}$, which carries the slowly varying long range piece of the Coulomb interaction. In this section, and in detail in Section VIII.B, the Yukawa part is shown to leave the gas essentially ideal, provided its range L is of order the Debye length l_D and the Debye sphere assumptions (2.11) are imposed. The underlying idea is that the effect of the $V_{L,\lambda}$ part of the interaction is to associate some of the monopoles into aggregates which can be regarded as new species so that the resulting multi-species gas is ideal. The Mayer expansion is used to express this. Instead of leaving out the long range part of the interaction, one can instead say that the gas inside a sphere of radius less than the Debye length is close to ideal. This illuminates the Debye–Hückel argument in which the charge density was computed by an ideal gas formula: the mean field captures the part of the interaction with range larger than L and the interactions of shorter range are small enough to use an ideal gas calculation.

Consider the partition function for a Yukawa gas in an external potential ϕ,

$$\Xi_{L,\Lambda}(\beta^{1/2}\phi)=\int d\omega\, z(\omega)\, e^{-\beta U_L(\omega)-\beta^{1/2}\int \phi\hat{c}(\omega)\,d\mathbf{r}} \tag{2.41}$$

The Mayer expansion is an expansion for the logarithm of the partition function or the pressure P in powers of the activities z_α whose first term $\beta PV=\sum z_\alpha+\cdots$ gives the ideal gas law when $\phi=0$: it has the form

$$\Xi_{L,\Lambda}(\beta^{1/2}\phi)=\exp\left(\sum_{m\geqslant 1}\frac{1}{m!}\int\prod_k d\mathscr{E}_k\, z(\mathscr{E}_k)\, e^{-\beta^{1/2}e_{\alpha_k}\phi(\mathbf{r}_k)}u_m(\mathscr{E}_1,\dots,\mathscr{E}_m)\right) \tag{2.42}$$

where u_m are given (Ruelle, 1969; Hansen and McDonald, 1976) as sums of contributions from connected "Mayer" graphs. In particular $u_1(\mathscr{E})=1$ so that the $m=1$ contribution to the product is

$$\exp\left[\sum_\alpha\int d\mathbf{r}\, z_\alpha e^{-\beta^{1/2}e_\alpha\phi}\right]$$

which equals the ideal gas partition function $\Xi_{\text{ideal},\Lambda}(\beta^{1/2}\phi)$ that appeared above in (1.34).

The higher m terms in (2.42) have the form of additional ideal gas species, e.g., the $m=2$ term is an ideal gas partition function for a gas whose particles are the possible aggregates of two of original particles, with a cluster activity $(1/2!)\, z(\mathscr{E}_1)\, z(\mathscr{E}_2)\, u_2(\mathscr{E}_1, \mathscr{E}_2)$. Such a cluster describes two particles bound together because the functions u_m decay exponentially in the separation of any pair of arguments, because the graphs that contribute to them are connected. Although these "Mayer" aggregates do capture effects of aggregates of particles they are not directly physical because their activities need not be positive.

This decomposition of the interacting gas into species of ideal gases is only useful if the activities of large aggregates are small. In fact we need them to be summable which is the same as demanding that the Mayer expansion is convergent. The standard condition (Ruelle, 1969) for convergence of the Mayer expansion for a gas with activity $z(\mathscr{E})$ and two-body potential $v(\mathscr{E}, \mathscr{E}')$ is

$$\sup_{\mathscr{E}} \int |e^{-\beta v(\mathscr{E}, \mathscr{E}')} - 1| \, |z(\mathscr{E}) \, e^{-\beta^{1/2} \phi(\mathscr{E})}| \, d\mathscr{E}' \, e^{2B\beta} < e^{-1}$$

where B is the stability constant, i.e., the best constant such that

$$\sum_{1 \leqslant i < j \leqslant N} v(\mathscr{E}_i, \mathscr{E}_j) \geqslant -BN$$

Suppose for simplicity that there are two species with equal but opposite charges $e_\alpha = \pm 1$ and equal activities

$$z(\mathscr{E}) = z_\alpha = z$$

Using the stability estimate (1.11) we find the Mayer expansion converges if

$$|z| \, \beta L^2 \exp(\beta/\lambda) \ll 1 \tag{2.43}$$

which we calculated using $\exp(\pm V_{L,\lambda}) - 1 \approx \pm V_{L,\lambda}$. This condition is sufficient for convergence of the Mayer expansion, but it is not a very accurate condition when $\lambda < \beta < L$. In Section VIII.B we will show that there is a better condition, namely

$$z\beta^3 e^{\beta/\lambda} \ll 1; \qquad z\beta L^2 e^{\beta/\beta} \ll 1 \tag{2.44}$$

The β/β emphasizes why the estimate is an improvement. For the Yukawa potential and hard core, one needs

$$z_\alpha \lambda^3 \ll 1 \tag{2.45}$$

as well. Now observe that when $L = \gamma l_D$ the second condition in (2.44) drops out, provided γ is small, but independent of z, β, λ. The other two conditions are implied by our Debye sphere hypotheses (2.11), when combined with the definition of l_D. Thus the Debye sphere hypotheses say that the gas inside a sphere of radius $L = \gamma l_D$ is a multi-species ideal gas whose activities are small according to

$$\frac{1}{m!} \int \prod_k d\mathscr{E}_k \, |z(\mathscr{E}_k)| \, |u_m(\mathscr{E}_1, ..., \mathscr{E}_m)| \leqslant O\left(\frac{L}{l_D}\right)^{2(m-1)} |z| \, |\Lambda| \tag{2.46}$$

where z is the largest of the z_α. For details on the derivation of this estimate see Section VIII.B.

The conditions for convergence of the Mayer expansion when there is an external potential are the same except that the exponential of the potential is absorbed into the activity. Thus an imaginary potential has no effect in (2.46) because of the absolute value in $|z(\mathscr{E}_k)|$.

E. The Debye–Hückel Limit

The standard derivation (Mayer, 1950) of the thermodynamics, the first part of the Debye–Hückel law (2.3), proceeded by resumming a class of ring diagrams in the Mayer expansion or low density expansion. A more systematic basis for this resummation is based on the Kac limit, see (Lebowitz and Stell, 1968). In this section, following (Kennedy, 1982; Kennedy, 1983; Kennedy, 1984), we sketch a proof of the Debye–Hückel law based on the fact that the representation (2.29) becomes an explicitly integrable Gaussian integral in the Debye–Hückel limit (2.14). The Debye–Hückel mean field emerges as the stationary point for the Sine–Gordon action. This line of argument has the advantage of not using any expansion which might be divergent.

Our definition of the Debye–Hückel limit is low density in the extreme sense that the hard core becomes irrelevant and the effects of association into dipoles and other aggregates are out of play. The original Debye–Hückel theory (footnote 7) has terms in κa that would disappear in this limit. a is the hard core radius. Debye–Hückel theories (see the discussion below (2.14)) have been advocated as a good description for some transitions in ionic fluids at higher densities in which phase separation occurs. These are extensions of Debye–Hückel theory in which hard core corrections remain and effective dielectric constants, which represent the effect of charges pairing to form dipoles, are used. For consistency considerations it is desirable to show that these theories are also limiting cases of the Coulomb system or obtainable in some systematic approximation.

Let us work in units where $l_D = 1$. This means that in the right hand side of the representation (2.29) we rescale lengths by $\mathbf{r} = l_D \mathbf{r}'$ so that the Debye length becomes $l'_D = 1$ and $\mathbf{r}'$ becomes dimensionless. Then we have exactly the same formulas but the parameters are replaced by dimensionless parameters:

$$\beta' = \beta / l_D, \qquad \lambda' = \lambda / l_D, \qquad z'_\alpha = z_\alpha l_D^3, \qquad L' = L / l_D, \qquad \Lambda' = l_D^{-3} \Lambda \tag{2.47}$$

In terms of the primed parameters the Debye–Hückel limit becomes

$$z'_\alpha \to \infty, \qquad \beta' \to 0 \qquad \text{with} \quad \begin{cases} 4\pi \sum_\alpha e_\alpha^2 z'_\alpha \beta' = 1 \\ z'_\alpha \lambda'^3 \to 0 \\ z'_\alpha l'^3_D e^{-\beta'/2\lambda'} \to \infty \end{cases} \tag{2.48}$$

From now on in this section all formulas involve the primed quantities, so we will save on notation by dropping the primes.

We write (2.29) in the form

$$\Xi_\Lambda(\beta^{1/2}\psi) = \int d\mu_L(\phi) \exp(F(i\phi + \psi)) \tag{2.49}$$

where

$$F(i\phi + \psi) = \ln \Xi_{L, \Lambda, z^{(L)}}(i\beta^{1/2}\phi + \beta^{1/2}\psi) \tag{2.50}$$

We define the action functional $S(\psi, g)$ by

$$-S(\psi, g) = \tfrac{1}{2} \int g V_{\infty, L}^{-1} g \, d\mathbf{r} + F(g + \psi) \tag{2.51}$$

The partition function $\Xi_\Lambda(\beta^{1/2}\psi)$ does not depend on L in the left hand side of (2.49) so we may take the infinite volume and Debye–Hückel limits at fixed L and then afterwards let $L \to 0$. The correct order of limits is infinite volume limit followed by Debye–Hückel limit, but we do it in the opposite order. A serious technical point in the papers we cited is to show that these limits can be interchanged.

In the Debye–Hückel limit the action $S(\psi, i\phi)$ becomes a quadratic polynomial in ϕ. We forestall the appearance of some terms linear in ϕ by using the translation formula (2.26) with $\phi \to \phi - ig$ applied to (2.49)

$$\Xi_\Lambda(\beta^{1/2}\psi) = e^{(1/2)\int g V_{\infty, L}^{-1} g \, d\mathbf{r}} \int d\mu_L(\phi) \times \exp\left[\int i\phi V_{\infty, L}^{-1} g \, d\mathbf{r} + F(i\phi + \psi + g)\right] \tag{2.52}$$

g will be chosen later. By (2.46) the Mayer expansion for $F(i\phi + g + \psi)$ is convergent uniformly in the Debye–Hückel limit, provided $L \ll 1$: indeed the $O(z^{N+1})$ term in the Mayer expansion is $O(L^N)\, z|\Lambda|$ uniformly in the Debye–Hückel limit. The $z|\Lambda|$ is a common volume factor. Divide it out and fix $L \ll 1$. Then the first term in the Mayer expansion dominates the sum of all the others uniformly in the Debye–Hückel limit. Therefore the Debye–Hückel limit can be taken term by term under the sum in the Mayer expansion and under the $d\mu$ integral by standard theorems of analysis (dominated convergence). Every term becomes a quadratic polynomial in ϕ and only the first term in the Mayer expansion contributes in the limit $L \to 0$. To see this in more detail, note that the first term is

$$\sum_{\alpha} \int_{\Lambda} d\mathbf{r}\, z_{\alpha}^{(L)} e^{-e_{\alpha}\beta^{1/2}(i\phi + g + \psi)} \tag{2.53}$$

By (2.48) terms of order $O(z_{\alpha}^{(L)} \beta^{3/2})$ vanish in the Debye–Hückel limit. The $O(z_{\alpha}^{(L)} \beta^{1/2})$ term vanishes by pseudo-neutrality (2.10). Therefore, in the Debye–Hückel limit, the non-vanishing part of $F(i\phi + g + \psi)$ is

$$\begin{aligned} F_{\mathrm{DH}}(i\phi + g + \psi) = {} & \int_{\Lambda} d\mathbf{r} \left(\sum_{\alpha} z_{\alpha} + \frac{1}{8\pi} (i\phi + g + \psi)^2 + \frac{1}{8\pi} V_{\infty, L}(0) \right) \\ & + R_2(i\phi + g + \psi) + R_0 \end{aligned} \tag{2.54}$$

where $V_{\infty, L}(0)$ arose from the difference between z_{α} and $z_{\alpha}^{(L)}$; see (2.22). R_2 is a quadratic remainder term

$$R_2(f) = \iint f(\mathbf{r}_1)\, r(\mathbf{r}_1, \mathbf{r}_2)\, f(\mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2 \tag{2.55}$$

R_0 is independent of $f = i\phi + g + \psi$. R_0 and R_2 account for all the remaining terms in the Mayer expansion. There is no term linear in f: inspection of $O(f)$ contributions from the Mayer expansion is required to verify that the pseudo-neutrality condition makes them all vanish in the Debye–Hückel limit. Furthermore R_0 and R_2 are independent of z, β and vanishing as $L \to 0$. If we substitute F_{DH} back into (2.52) and regroup into terms independent of ϕ, terms linear in ϕ and terms quadratic in ϕ, the result is

$$\Xi_{\Lambda} / \Xi_{\mathrm{ideal}, \Lambda} \sim e^{-S_{\mathrm{DH}}(\psi, g)} \int d\mu_L(\phi)\, e^{-(1/8\pi) \int_{\Lambda} (\phi^2 - V_{\infty, L}(0))\, d\mathbf{r}} e^{-S'_{\mathrm{DH}}(\psi, g; i\phi) + R_2(i\phi)} \tag{2.56}$$

Note that the activity in the ideal gas $\Xi_{\mathrm{ideal}, \Lambda}$ is z, whereas a naive calculation based on (2.24) might draw us into using $z^{(\lambda)}$. The $\sim$ means that we keep only the terms that are non-vanishing in the Debye–Hückel limit. We have defined the quadratic functional

$$-S_{\mathrm{DH}}(\psi, g) = \frac{1}{2} \int g V_{\infty, L}^{-1} g\, d\mathbf{r} + \frac{1}{8\pi} \int (g + \psi)^2\, d\mathbf{r} + R_2(\psi + g) + R_0 \tag{2.57}$$

whose first variation in direction ϕ is

$$-S'_{\mathrm{DH}}(\psi, g; \phi)=\int \phi V_{\infty, L}^{-1} g \, d\mathbf{r}+\frac{1}{4\pi} \int \phi(g+\psi) \, d\mathbf{r}+R_2'(\psi+g; \phi) \tag{2.58}$$

$R_2'(\psi+g; \phi)$ is the first variation of $R_2(\psi+g)$ in direction ϕ. It is natural to choose g to make S'_{DH} vanish, but instead we settle for making it almost vanish by choosing g to solve

$$-\Delta g+g+\psi=0 \tag{2.59}$$

because then by (2.21)

$$-S'_{\mathrm{DH}}(\psi, g; \phi)=\frac{1}{4\pi} L^2 \int \phi \Delta^2 g \, d\mathbf{r}+R_2'(\psi+g; \phi) \tag{2.60}$$

which means that $S'_{\mathrm{DH}}(\psi, g; \phi)$ disappears at the end when we take $L \to 0$. However we will keep these terms around for a few more lines because we want to derive some formulas that will be used in later sections.

Define

$$\Xi_{\mathrm{DH}, \Lambda}=\int d\mu_L(\phi) \, e^{-(1/8\pi) \int_\Lambda (\phi^2-V_{\infty, L}(0)) \, d\mathbf{r}+R_2(i\phi)} \tag{2.61}$$

which is the normalization for a new Gaussian probability measure

$$d\mu_{\mathrm{DH}}(\phi)=\Xi_{\mathrm{DH}, \Lambda}^{-1} \, d\mu_L(\phi) \, e^{-(1/8\pi) \int_\Lambda (\phi^2-V_{\infty, L}(0)) \, d\mathbf{r}+R_2(i\phi)} \tag{2.62}$$

Then (2.56) is the same as

$$\Xi_\Lambda/\Xi_{\mathrm{ideal}, \Lambda} \sim e^{-S_{\mathrm{DH}}(\psi, g)} \Xi_{\mathrm{DH}, \Lambda} \int d\mu_{\mathrm{DH}}(\phi) \, e^{-S'_{\mathrm{DH}}(\psi, g; i\phi)} \tag{2.63}$$

As we have explained above, when $L \to 0$, we can drop the S'_{DH} so that the normalized $d\mu_{\mathrm{DH}}$ also disappears and we are down to the evaluation of $\Xi_{\mathrm{DH}, \Lambda}$.

The normalization $\Xi_{\mathrm{DH}, \Lambda}$ can be expressed as a determinant using

$$\int d\mu_L(\phi) \, e^{-(\alpha/8\pi) \int_\Lambda \phi^2 \, d\mathbf{r}}=\det\left(I+\frac{\alpha}{4\pi} V_{\infty, L}\right)^{-1/2} \tag{2.64}$$

We have dropped the R_2 term because (2.46) implies that

$$|R_2(i\phi)| \leqslant O(L^2) \int_{\Lambda} \phi^2 \, d\mathbf{r} \tag{2.65}$$

and so it gives no contribution in the limit $L \to 0$. To obtain this estimate from (2.46) note that R_2 involves two variational derivatives with respect to ϕ. Each derivative brings a factor $\beta^{1/2}$. These factors combine with z in (2.46) and become a Debye length $l_D = 1$. We want $\alpha = 1$, but we put it there because taking $\alpha = 0$ shows that both sides are correctly normalized. $V_{\infty, L}$ is the operator whose kernel is the potential $V_{\infty, L}(\mathbf{r}_1 - \mathbf{r}_2)$. The arguments $\mathbf{r}_1, \mathbf{r}_2$ are confined to the finite volume Λ either by boundary conditions on the Coulomb potential, if the particles are in a grounded conducting container, or by restriction on the range of integration, if the particles are in an insulating container. It can be shown that the thermodynamic limit washes out the difference, but the easier case is the first; then there are zero boundary conditions on the Laplacian in $V_{\infty, L}$ so that the eigenfunctions are trigonometric functions when Λ is a box. Using $\det(I + X) = \exp[\sum_{\xi} \ln(1 + \xi)]$, where ξ runs over the eigenvalues of the operator X, one can show that the leading term in the infinite volume limit is

$$\Xi_{\mathrm{DH}, \Lambda} \approx \exp\left[-\frac{1}{2} (2\pi)^{-3} |\Lambda| \int d\mathbf{k} \left(\ln\left(1 + \frac{1}{4\pi} \tilde{V}_{\infty, L} \right) - \frac{1}{4\pi} \tilde{V}_{\infty, L} \right) \right] \tag{2.66}$$

where the Fourier transform $\tilde{V}_{\infty, L}$ is given in (1.13). The limit as $L \to 0$ of this expression is

$$\exp\left[-\frac{1}{2} (2\pi)^{-3} |\Lambda| \int d\mathbf{k} \left(\ln\left(1 + \frac{1}{\mathbf{k}^2} \right) - \frac{1}{\mathbf{k}^2} \right) \right] = \exp[|\Lambda|/(12\pi)] \tag{2.67}$$

Returning to (2.63) we have shown that the leading terms in the Debye–Hückel limit followed by infinite volume limit followed by $L \to 0$ are

$$\ln(\Xi_{\Lambda}/\Xi_{\mathrm{ideal}, \Lambda}) \sim \frac{|\Lambda|}{12\pi} + \frac{1}{8\pi} \int g(-\Delta) \, g \, d\mathbf{r} + \frac{1}{8\pi} \int (g + \psi)^2 \, d\mathbf{r} \tag{2.68}$$

where g satisfies the stationarity condition (2.59). When $\psi = 0$ we recover the thermodynamic part of the Debye–Hückel law, (2.3). Furthermore the stationarity condition coincides with the linearized Debye–Hückel equation (2.7) in units where $l_D = 1$ when

$$f = \beta^{-1/2}(g + \psi), \qquad \psi(\mathbf{r}) = e_0 \beta^{1/2} V(\mathbf{r}) \tag{2.69}$$

The strange factors of $\beta^{1/2}$ appear because of the way we normalized the Sine–Gordon transformation. The Debye–Hückel result (2.3) on correlations, in units where $l_D = 1$, is obtained by taking two functional derivatives of the approximation (2.68) for $\ln(\Xi_\Lambda / \Xi_{\text{ideal}, \Lambda})$ with respect to $-\beta^{1/2}\psi$. This interchange of functional derivatives with Debye–Hückel limit might be hard to justify, but convexity helps in the case of the single charge density expectation (Kennedy, 1983).

There may be inequalities comparing the Debye–Hückel limit with the exact system. Some results follow from Jensen's inequality, but they are limited to the unrealistic case of charge-symmetric systems (Kennedy, 1982). See also Theorem III.2 in the next section.

Questions: Are extended Debye–Hückel theories such as the ones considered by Fisher *et al.* limiting theories? One should no longer let $L \to 0$ and should choose g to be the exact stationary configuration for $S_{\text{DH}}(\psi, g)$, which contains quadratic remainder terms R_2 giving corrections to the dielectric constant. Also the activity may be renormalized, whereas in our case $L \to 0$ causes $z^{(L)}$ to coincide with z. Is the expansion (Lebowitz and Stell, 1968) asymptotic in κa?

F. Charge Expulsion

We continue to use units in which $l_D = 1$ introduced in Section II.E. In our preliminary discussion of the Debye–Hückel theory in Section II.A we claimed that the activities should be constrained by the pseudo-neutrality condition (2.10). If we start with a system that does not satisfy this condition, then even when $\psi = 0$, the action $S(0, i\phi)$ defined in (2.51) is not stationary in ϕ at $\phi = 0$. However, a translation $\phi \to \phi - ig$ such that $S(0, g + i\phi)$ is stationary in ϕ at $\phi = 0$ reveals the physical effect of charge expulsion and an attendant renormalization of activities. This is a nonlinear effect, not small enough to fit within the approximation of the last section. The physical interpretation is that excess charge is expelled to the boundary where it forms a boundary layer of total charge proportional to the surface area. This layer modifies the electrostatic potential in the interior in such a way that the activities are renormalized to satisfy pseudo-neutrality, which is why the excess charge is of order surface area and not volume in this grand canonical ensemble.

For simplicity we omit the complications that arose in the last section due to the length scale λ by considering a system with interaction $V_{\infty, L}$ with insulating boundary conditions and no other forces. In this case we can use the Sine–Gordon representation (2.24) to represent the entire interaction. We can also apply the translation formula (2.26) for $\phi \to \phi - ig$. The result is

$$\Xi_L(\beta^{1/2}\psi) = \int d\mu_L(\phi)\, e^{(1/2)\int gV_{\infty,L}^{-1} g\, d\mathbf{r} + \int i\phi V_{\infty,L}^{-1} g\, d\mathbf{r}}\, \Xi_{\text{ideal},\, z^{(L)}}(\beta^{1/2}[i\phi + g + \psi]) \tag{2.70}$$

The translation g is chosen so that the linear term $\int \phi V_{\infty,L}^{-1} g\, d\mathbf{r}$ is canceled by a corresponding term from $\Xi_{\text{ideal},\, z^{(L)}}$. This is the same as choosing g to be the minimizer g of

$$-S_{\infty,L}(\psi, g) = \tfrac{1}{2} \int gV_{\infty,L}^{-1} g\, d\mathbf{r} + \ln \Xi_{\text{ideal},\, z^{(L)}}(\beta^{1/2}[g + \psi]) \tag{2.71}$$

Insulating boundary conditions mean that $V_{\infty,L}^{-1}$ is given by (2.21). The $\int d\mathbf{r}$ integral extends over infinite volume but the $\Xi_{\text{ideal},\, z^{(L)}}$ is an ideal gas in the finite volume Λ. There exists (Kennedy 1984) a unique g that minimizes this functional. Uniqueness is an easy consequence of it being convex. Let $\psi = 0$. Then, in the deep interior of Λ, g is close to the constant g_0 that minimizes

$$\ln \Xi_{\text{ideal},\, z^{(L)}}(\beta^{1/2} g_0) = \int_\Lambda d\mathscr{E}\, z^{(L)}(\mathscr{E})\, e^{-\beta^{1/2} e_\alpha g_0} \tag{2.72}$$

Outside Λ, g solves $V_{\infty,L}^{-1} g = 0$ and $g \to 0$ at infinity. Define renormalized activities $z^{(L,R)}$ by

$$z_\alpha^{(L,R)} = \exp(-e_\alpha \beta^{1/2} g_0)\, z_\alpha^{(L)} \tag{2.73}$$

and note that

$$\Xi_{\text{ideal},\, z^{(L)}}(\beta^{1/2} f) = \Xi_{\text{ideal},\, z^{(L,R)}}(\beta^{1/2}[f - g_0]) \tag{2.74}$$

Since $g \approx g_0$ inside Λ the bulk contribution to $S_{\infty,L}(g)$ comes from the ideal gas term which has the renormalized activities $z^{(L,R)}$. But since Δg is non-zero near the boundary there is a boundary contribution to the pressure in $\frac{1}{2}\int gV_{\infty,L}^{-1} g\, d\mathbf{r}$ and also in the ideal gas term because $g \neq g_0$ at the boundary. These arise from the surface charge expelled from the interior and account for the capacity term in the free energy, discussed in the analysis of systems with net charge (Lieb and Lebowitz, 1972, page 55), (Graf and Schenker, 1995a).[16]

From (2.70)

$$\Xi_L(0) = e^{-S_{\infty,L}(g)} \int d\mu_L(\phi)\, e^{\int i\phi V^{-1}_{\infty,L}\, g\, d\mathbf{r}}\, \frac{\Xi_{\text{ideal},\, z^{(L,R)}}(\beta^{1/2}[i\phi + g - g_0])}{\Xi_{\text{ideal},\, z^{(L,R)}}(\beta^{1/2}[g - g_0])}$$

By our choice of translation g we have arranged that the $i\phi$ fluctuates around zero so that $\exp(-S_{\infty,L}(g))$ should be the leading term in the Debye–Hückel limit. The next term in the approximation would be a Debye–Hückel term that comes from integrating over the ϕ fluctuations using a quadratic approximation as in Section II.E.

G. Symmetries and Tunneling

We continue to work in units in which $l_D = 1$. There is a loss of intuition entailed by the Sine–Gordon transformation because the integration extends over imaginary potentials, but there are also aspects one can see more easily in the Sine–Gordon language. In particular if all charges e_α are integral multiples of a fundamental unit of charge, which for simplicity we assume to be one, then the action $S(\psi, g)$ in (2.51) is invariant under the discrete symmetry

$$S(\psi, g) = S(\psi, g + i\delta h), \qquad \delta h = 2\pi\beta^{-1/2} \tag{2.75}$$

This section is concerned with the breaking of this symmetry, which plays a role in the proofs of screening. We will see also that there are tunneling corrections associated with the symmetry.

Let us first note that the Coulomb system in an insulating container in three or more dimensions cannot enjoy this symmetry because the Gaussian measure $d\mu_L(\phi)$ satisfies

$$\int d\mu_L(\phi)\, \phi^2(0) = V_{\infty,L}(0) < \infty \tag{2.76}$$

precluding any symmetry of the form $\phi \to \phi + c$.

We have seen in Section II.E that the Debye–Hückel approximation is a quadratic approximation around the stationary configuration $\phi = 0$. The

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[16] If $L = 0$ and g is chosen to be constant in the interior of Λ and harmonic in the exterior, then the boundary contribution in (2.71) exactly equals the electrostatic energy stored in a perfect conductor with shape Λ.

symmetry (2.75) tells us that there are infinitely many stationary configurations related by the symmetry to $\phi = 0$. We claim that even though (2.76) implies that the stationary configuration $\phi = 0$ is favored, in the thermodynamic limit there are arbitrarily large regions where ϕ is trapped in the other stationary configurations. This is analogous to the Ising model at low temperature in which there occur arbitrarily large islands of $-$ spins even though the boundary is set at $+$ and the majority of spins are $+$. In the zero temperature limit in the Ising model, the islands of $-$ spins disappear, but if one wants to understand low temperature as opposed to zero temperature, then they are important. In the same way, to obtain screening near, as opposed to in the Debye–Hückel limit, the presence of large islands where the $\phi = 0$ approximation breaks down has to be taken into account.

To take into account the presence of many stationary configurations related by the symmetry we use a functional version of the Villain approximation

$$e^{\cos(x)} \approx \sum_n e^{-(1/2)(x - 2\pi n)^2 + 1} \tag{2.77}$$

on the term $\exp(F)$ in (2.49). In (8.80) in Section VIII.E we explain in terms of this one dimensional analogue why taking into account the extra wells in this way improves the convergence of perturbation theory.

$\exp(F)$ is invariant under a translation $\phi \to \phi + h$ where $h = h(\mathbf{r})$ is any function of $\mathbf{r}$ that takes values in the set $\{n\delta h\}$ of periods, because $\Xi_{L, \Lambda, z^{(L)}}$ clearly has this property. Also from (2.54) it has the quadratic approximation

$$F_{\mathrm{DH}}(\psi + i\phi) = \int_\Lambda d\mathbf{r} \left(\sum_\alpha z_\alpha + \frac{1}{8\pi} (i\phi + \psi)^2 + \frac{1}{8\pi} V_{\infty, L}(0) \right) + R_2(i\phi + \psi) + R_0 \tag{2.78}$$

Thus an analogue of (2.77) is

$$e^{F(\psi + i\phi)} = e^{R_3(\psi + i\phi)} \sum_h e^{F_{\mathrm{DH}}(\psi - ih + i\phi)} \tag{2.79}$$

where R_3 is an $O(\beta^{1/2})$ error term representing cubic corrections to each well and put there to obtain exact equality. $h = h(\mathbf{r})$ is summed over all functions that vanish outside Λ, take values in the set $\{n\delta h\}$ of periods and are piecewise constant on a lattice of unit cubes filling Λ.

If we think of a typical piecewise constant function $h(\mathbf{r})$ as a height, then the resulting landscape splits into plateaus where $h(\mathbf{r})$ is constant but more important are the jumps from one plateau to another. In analogy with the Ising model we call the connected surfaces in Λ where h jumps "contours." Our objective is to argue that near the Debye–Hückel limit the sum over h is dominated by terms in which these contours are small and very dilute. The value of h in a given plateau fixes the well in which ϕ is trapped and the contour is where ϕ tunnels from one well to another.

We substitute (2.79) into the Sine–Gordon transformation (2.49) and retrace the analysis of Section II.E leading up to the Debye–Hückel approximation (2.63) with ψ replaced by $\psi - ih$ and g replaced by ig

$$\Xi_\Lambda / \Xi_{\text{ideal}, \Lambda} = \Xi_{\text{DH}, \Lambda} \sum_h e^{-S_{\text{DH}}(\psi - ih,\, ig)} \times \int d\mu_{\text{DH}}(\phi)\, e^{-S'_{\text{DH}}(\psi - ih,\, ig;\, i\phi) + R_3(\psi + ig + i\phi)} \tag{2.80}$$

For each h in the sum $g(\mathbf{r})$ can be any function. We choose it to make $S_{\text{DH}}(\psi - ih, ig)$ stationary so that S'_{DH} vanishes.

For the moment we drop the term R_3, then the $d\mu_{\text{DH}}$ integral drops out because it is normalized and we are left with an approximation

$$\Xi_\Lambda / \Xi_{\text{ideal}, \Lambda} \approx \Xi_{\text{DH}, \Lambda} \sum_h e^{-S_{\text{DH}}(\psi - ih,\, ig)} \tag{2.81}$$

where

$$S_{\text{DH}}(\psi - ih, ig) = \frac{1}{2} \int g V_{\infty, L}^{-1} g \, d\mathbf{r} + \frac{1}{8\pi} \int (g - h - i\psi)^2 \, d\mathbf{r} + R_2 + R_0 \tag{2.82}$$

When $\psi = 0$ g minimizes $S_{\text{DH}}(-ih, ig)$ by trying to make $(g-h)^2$ vanish but cannot quite succeed because $\int g V_{\infty, L}^{-1} g \, d\mathbf{r}$ forces g to be smooth whereas h has jumps. Suppose $h(\mathbf{r}) = h_\Gamma(\mathbf{r})$ has only one contour Γ and h vanishes at the boundary of Λ. Then Γ has an exterior "sea-level" plateau where $h = 0$ and an interior plateau where $h \neq 0$. In the interiors of both plateaus $g(\mathbf{r}) \approx h(\mathbf{r})$. The error in the $\approx$ is $O(\exp(-\text{dist}(\mathbf{r}, \Gamma))$.

Any h with $h = 0$ at the boundary can be decomposed in a unique way

$$h = \sum_j h_j \tag{2.83}$$

where each h_j has only one contour Γ_j and h_j vanishes at the boundary. Thus h_j is defined on the whole box Λ but it assumes just two values: zero outside the contour Γ_j and $h_j(\text{int})$ at all points in the interior of the contour. Across the contour Γ_j h_j jumps by $h_j(\text{int})$ which is the same as the jump of h across Γ_j.

The minimizers are linear functions of h so $g=\sum g_j$ where g_j is the minimizer for the single contour h_j. If the contours are well separated then by $g(\mathbf{r})=h(\mathbf{r})+O(\exp(\mathrm{dist}(\mathbf{r}, \Gamma))$.

$$S_{\mathrm{DH}}(\psi-ih, ig)\approx\sum_j S_{\mathrm{DH}}(\psi-ih_j, ig_j) \tag{2.84}$$

Thus

$$\Xi_\Lambda/\Xi_{\mathrm{ideal}, \Lambda}\approx\Xi_{\mathrm{DH}, \Lambda}\sum_h\prod_j e^{-S_{\mathrm{DH}}(\psi-ih_j, ig_j)} \tag{2.85}$$

The approximation in these two equations was to leave out exponentially small cross terms in S_{DH} involving $(g_i-h_i)(g_j-h_j)$ and derivatives of g_i times derivatives of g_j.

The sum over h is equivalent to summing over the number N of contours, the shapes Γ_j of the contours and the jumps $h_j(\mathrm{int})$ at each contour so that

$$\Xi_\Lambda/\Xi_{\mathrm{ideal}, \Lambda}\approx\Xi_{\mathrm{DH}, \Lambda}\sum_N\frac{1}{N!}\sum_{\Gamma_1,\ldots,\Gamma_N}\prod_j\sum_{h_j(\mathrm{int})}e^{-S_{\mathrm{DH}}(\psi-ih_j, ig_j)} \tag{2.86}$$

The exponential of $S_{\mathrm{DH}}(\psi-ih_j, ig_j)$ suppresses the jump $h_j(\mathrm{int})$ at Γ_j by a factor

$$\exp[-O(|\Gamma_j|)\, h_j(\mathrm{int})^2] \tag{2.87}$$

where $|\Gamma_j|$ is the area of the contour. The $h_j(\mathrm{int})^2$ dependence is because S_{DH} is quadratic in g, h when $\psi=0$, g_j is linear in h_j and h_j is just $h_j(\mathrm{int})\times$ a unit jump configuration.

In (2.86) the term with no contours, $N=0$, is our original Debye–Hückel approximation (2.68). From (2.86), (2.87) we see that the contours should behave like an ideal gas with an exponentially tiny density near the Debye–Hückel limit. Nevertheless they represent a phenomenon that probably makes the standard perturbation series asymptotic but not convergent and incapable of proving that there is screening near as opposed to at the limit. In contrast (2.86) is the basis for a convergent expansion which does imply screening near the Debye–Hückel limit. The terms we left out in arriving at this representation are exponentially small interactions between the dilute contours. There are also constraints (hard core interactions) in the sum that forbid intersections of contours. Such interactions are within the purview of conventional convergent Mayer expansions, which is why it is possible to develop a convergent expansion. However this expansion is clumsy in comparison with standard perturbation theory. One has to show for example that the R_3 error term does not destroy the picture we have just developed. One of the principal accomplishments (Glimm and Jaffe, 1987) of the constructive quantum field theory program was to develop a calculus for the analysis of "almost Gaussian" integrals and this is what is used at this point. The reader who suffers from residual curiosity can turn to Section VIII for a compressed and updated account of this calculus and its applications, or to (Brydges and Federbush, 1981) for an older review.

Note the role of grounded container boundary conditions is to anchor g and therefore h at zero on the boundary. The $1/r$ potential with no boundary conditions, i.e., particles in an insulating container, is more difficult than the case of grounded boundary because the anchoring is weaker, since it comes from (2.76). This has been partially investigated (Federbush and Kennedy, 1985). Their argument is hard because there are long range forces at the boundary which make it difficult to control the size of boundary effects.

In the case of two dimensions with insulating boundary conditions, there is no anchoring at the boundary because the Gaussian measure[17] $d\mu_L$ does not break the symmetry (2.75). We mentioned in Section II.B a result of Fröhlich and Spencer (Fröhlich and Spencer, 1981b, Theorem 4.1) that fractional charges are not screened when insulating boundary conditions are imposed. This is because of this symmetry. Intuitively there is no preference for which potential well $\phi(\mathbf{r}_1)$ is trapped in, but once it has made up its mind, $\phi(\mathbf{r}_2)$ wants to choose the same well, which is a long range correlation. This argument predicts that the correlation decays to a constant. On the other hand, if the boundary is grounded, then the 0 well is selected essentially everywhere, except for a very dilute gas of contours that enclose regions where ϕ is in other wells. In this case all local observables are expected to have exponential decay, but this is only proved for integer charge observables (Yang, 1987). Recall in analogy that the Ising model at low temperature with plus boundary conditions has exponential decay but this decay is lost if the boundary spins are not tied down because the state is no longer pure. It is an open problem to prove that two dimensional systems with insulating boundary conditions have screening of integer charge observables.

Returning to three dimensions, when there are irrational charges the symmetry is replaced by a quasi-periodicity, nevertheless there is screening

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[17] Defined by taking a limit outside the integral as a small mass tends to zero.

in these systems without exact symmetry (Imbrie, 1983a). The argument requires Pirogov–Sinai theory.

There is an intriguing difference between fractional charge observables and integer charge observables. Suppose the gas consists of unit positive and negative charges but there is an additional half-integer charge fixed at the origin $\mathbf{r}=0$, represented by a factor $\exp(-\beta^{1/2} i\phi(0)/2)$. The $\phi(0)$ fluctuates around $g(0) \approx h(0)$, so there is a factor $\exp(-\beta^{1/2} ih(0)/2)$ which is ± 1 in a way that depends on all contours surrounding the origin, which is a more non-local (topological) effect than when an integer charge is placed at the origin. To put it another way: a phase factor $\exp(-\beta^{1/2} ih_j(0)/2)$ must be included in the sum over $h_j(\text{int})$ in (2.86) whenever Γ_j encloses the origin. This does not destroy screening in three dimensions, but it might be worth further study.

We will show, in Appendix VIII.E, that the tunneling corrections are of size $\exp(-O(l_D/\beta))$ so they are not of any consequence in the Debye–Hückel asymptotic regime. However, they should be important if β/l_D is not particularly small because then the period is small and the potential wells that trap ϕ are close together and shallow. There could be a phase transition in which the imaginary potential $i\phi$ ceases to be well localized in wells. If as a consequence there are more fluctuations in the typical ϕ, then the gas will be organized into more tightly bound neutral aggregates because when the position $\mathbf{r}$ of a cluster or particle with charge e_α is integrated, the rapidly varying phase factor $\exp(-ie_\alpha \beta^{1/2} \phi(\mathbf{r}))$ will give cancellations.[18] Note that the Kosterlitz–Thouless phase transition fits this description.

Tunneling represents a phenomenon which arises because the system consists of discrete charges as opposed to infinitely divisible charge distributions, which would give a single well as in the Debye–Hückel approximation.

III. DIPOLES

The Coulomb plasma is the main focus of this review. However in Sections IV and V we will find that a system of point quantum charges has a close analogy to a certain system of dipoles and higher order multipoles. The resulting multipole forces are al the origin of a breakdown of exponential screening in quantum mechanics. It is therefore of interest to give here a short review concerning the lack of screening in classical dipole systems and estimates on the dielectric constant.

Concerning the analogy an important caveat should be kept in mind. In a classical system exponential screening is restored as soon as free

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[18] We tank James Glimm for conversations on this point.

charges are added to classical dipoles. At any non-zero temperature, the quantum gas always has a proportion of free charges due to ionization processes, but these free *quantum* charges are not able to restore exponential screening. The analogies and differences between the behavior of quantum point charges and classical dipoles are made more precise in Section IV.F.

A. The Dipole Ensemble

A dipole is specified by the coordinate $\mathscr{E} = (\mathbf{r}, \mathbf{d})$ that unites the position $\mathbf{r}$ and the dipole moment $\mathbf{d}$. We suppose that in the absence of interaction a single dipole experiences no preferred directions so that

$$\int d\mathscr{E} \cdots = \int_{\Lambda} d\mathbf{r} \int d\Omega \cdots \qquad \text{with} \quad \int d\Omega = 1 \tag{3.1}$$

where $d\Omega$ is surface measure on the sphere of unit vectors $\hat{\mathbf{d}}$ and $\mathbf{d} = d\hat{\mathbf{d}}$ with d a fixed dipole moment.

The interaction between a pair of dipoles is

$$V(\mathscr{E}_1, \mathscr{E}_2) = (\mathbf{d}_1 \cdot \nabla_1)(\mathbf{d}_2 \cdot \nabla_2)\, V(\mathbf{r}_1 - \mathbf{r}_2) \tag{3.2}$$

where ∇_i is the gradient operator that acts on $\mathbf{r}_i$. $V(\mathbf{r}_1 - \mathbf{r}_2)$ should be the Coulomb potential between two unit charges at $\mathbf{r}_1, \mathbf{r}_2$, but the singularity of the Coulomb potential at short distance will lead to instability for the dipole system. We choose a length scale L and a form factor F and set

$$\tilde{V}(\mathbf{k}) = (4\pi)\, |\mathbf{k}|^{-2}\, \tilde{F}^2(L^2 k^2) \tag{3.3}$$

The form factor satisfies $\int F(\mathbf{r})\, d\mathbf{r} = 1$ and means that point charges are replaced by "charge clouds." This should be regarded as an effective interaction which arises by integrating out forces on length scales less than L in a more realistic description of the short range physics. An effective action of this form is not appropriate unless the gas is dilute so that interactions such as hard cores are not playing a strong role. See for example the use of a Mayer expansion as in Section II.D which led to such an effective interaction.

The partition function is

$$\Xi_{\Lambda} = \sum_{N} \frac{z^N}{N!} \int d\mathscr{E}_1 \cdots \int d\mathscr{E}_N\, e^{-\beta U(\mathscr{E}_1, \ldots, \mathscr{E}_N)} \tag{3.4}$$

where the interaction *includes* self-energies,

$$U(\mathscr{E}_1,\dots,\mathscr{E}_N)=\tfrac{1}{2}\sum_{i,\,j=1}^{N}V(\mathscr{E}_i,\mathscr{E}_j)\tag{3.5}$$

If instead the interaction is $\sum f(\mathscr{E}_j)$ where f is an external field, then we obtain an ideal gas partition function

$$\begin{aligned}\Xi_{\text{ideal},\,\Lambda}(f)&=\sum_N\frac{z^N}{N!}\int d\mathscr{E}_1\cdots\int d\mathscr{E}_N\exp\left(-\sum_{j=1}^{N}f(\mathscr{E}_j)\right)\\&=\exp\left(z\int d\mathscr{E}\,e^{-f(\mathscr{E})}\right)\end{aligned}$$

As in Section II.C we can reconstruct the interaction between the dipoles by integrating over an imaginary external field, $f(\mathscr{E})=\beta^{1/2}\,\mathbf{d}\cdot\nabla i\phi(\mathbf{r})$, with respect to the measure $d\mu_L$ discussed in (2.19):

$$\Xi_\Lambda=\int d\mu_L(\phi)\,\Xi_{\text{ideal},\,\Lambda}(\beta^{1/2}\mathbf{d}\cdot\nabla i\phi)\tag{3.6}$$

Formally this is $\int\mathscr{D}\phi\exp(-S(i\phi))$ where we define the action S by

$$\begin{aligned}-S(g)&=\tfrac{1}{2}\int gV^{-1}g+z\int d\mathscr{E}\exp(-\beta^{1/2}\mathbf{d}\cdot\nabla g)\\&=\tfrac{1}{2}\int gV^{-1}g+z\int d\mathscr{E}\cosh(\beta^{1/2}\mathbf{d}\cdot\nabla g)\end{aligned}\tag{3.7}$$

where the inverse operator V^{-1} has a kernel whose Fourier transform is $\tilde{V}^{-1}(\mathbf{k})$.

We shall consider the observable that measures the density of dipoles with coordinate $\mathscr{E}$ in a configuration $\omega=(\mathscr{E}_1,\dots,\mathscr{E}_N)$, namely

$$\hat{\rho}(\mathscr{E},\omega)=\sum_{i=1}^{N}\delta(\mathscr{E},\mathscr{E}_j)\tag{3.8}$$

Distribution functions such as the two point function $\langle\hat{\rho}(\mathscr{E}_a)\,\hat{\rho}(\mathscr{E}_b)\rangle$ are defined in analogy to Section I.B. Distributions at non-coincident points of $\hat{\rho}(\mathscr{E},\omega)$, where $\mathscr{E}=(\mathbf{r},\mathbf{d})$, become expectations of $z\exp(-i\beta^{1/2}\mathbf{d}\cdot\nabla\phi(\mathbf{r}))$ in the Sine–Gordon language.

Another useful quantity is

$$\langle e^{-\beta^{1/2}\int i\phi f}\rangle = \Xi_{\Lambda}^{-1} \int d\mu_L(\phi)\, \Xi_{\text{ideal},\,\Lambda}(i\beta^{1/2}\mathbf{d}\cdot\nabla\phi(\mathbf{r}))\, e^{-i\beta^{1/2}\int \phi f} \tag{3.9}$$

which measures ($\beta\times$)energy of a charge distribution f in the sea of dipoles. By unraveling the Sine–Gordon transformation one finds that the charge distribution f has self-energy determined by the potential $V(\mathbf{r}_1-\mathbf{r}_2)$ corresponding to (3.3) and it interacts with system dipoles according to potential energy $(\mathbf{d}_2\cdot\nabla_2)\, V(\mathbf{r}_1-\mathbf{r}_2)$.

We are using the expected value $\langle\ \rangle$ to indicate either the finite volume or infinite volume limit(s). This infinite volume limit is known to exist for several choices of boundary conditions (Fröhlich and Park, 1980; Fröhlich and Spencer, 1981b; Funaki and Spohn, 1997).

We shall also consider expectations of ϕ. The two-point function measures the effective potential between two infinitesimal charges: as in (1.31), but in the Sine–Gordon language, $\beta\times$ the effective potential between two infinitesimal test charges $(\mathbf{r}_a, e_a)_{a=1,2}$ is given by

$$e^{-\beta e_1 e_2 V^{\text{eff}}(\mathbf{r}_1-\mathbf{r}_2)} = \frac{\langle e^{-ie_1\beta^{1/2}\phi(\mathbf{r}_1)}\, e^{-ie_2\beta^{1/2}\phi(\mathbf{r}_2)}\rangle}{\langle e^{-ie_1\beta^{1/2}\phi(\mathbf{r}_1)}\rangle\langle e^{-ie_2\beta^{1/2}\phi(\mathbf{r}_2)}\rangle} \tag{3.10}$$

The numerator removes the self-energies of the test charges. Since $e_1, e_2\to 0$ we have

$$V^{\text{eff}}(\mathbf{r}_1-\mathbf{r}_2) = \langle\phi(\mathbf{r}_1)\,\phi(\mathbf{r}_2)\rangle \tag{3.11}$$

Furthermore the dielectric constant ε is obtained from the large $\mathbf{r}$ asymptotics

$$V^{\text{eff}}(\mathbf{r}) \sim \frac{1}{\varepsilon\,|\mathbf{r}|} \tag{3.12}$$

B. A No-Screening Theorem for Dipoles

The action $S(g)$ in (3.7) is invariant under $g\to g+c$, where c is any constant. This is a continuous symmetry and the action is local. Locality and continuous symmetry generally lead to power law correlations because fluctuations, $\phi\to\phi+f$, where $f(\mathbf{r})$ is slowly varying as a function of $\mathbf{r}$, are very weakly suppressed.[19]

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[19] The Coulomb system possessed a similar symmetry, but with the essential difference that c could only have discrete values.

No-screening theorems for dipoles have been obtained (Park, 1979). Subsequently (Fröhlich and Spencer, 1981b) gave the proof we present. This no-screening theorem is a little remarkable because it is valid for all activities and all temperatures, but its validity at high density is dependent on the way the short distance singularity in the dipole force is stabilized. If there are hard cores, then crystalline phases are likely. This is proven (Fröhlich and Spencer, 1981b) for dipoles on a lattice. For models where the Coulomb potential is smoothed out such as our $V_{\infty, L}$ potential Fröhlich and Spencer proved further results to the effect that the two point function has no oscillations, suggesting that this system is always in a fluid phase.

Theorem III.1. For all activities $z \geqslant 0$ and all inverse temperatures $\beta \geqslant 0$ there is no screening in the sense that the two point function has a singularity at $\mathbf{k} = 0$ in its Fourier transform and

$$\tilde{V}^{\text{eff}}(\mathbf{k}) \geqslant \tilde{\mathscr{V}}(\mathbf{k}) \tag{3.13}$$

where

$$\tilde{\mathscr{V}}(\mathbf{k}) = \left(\tilde{V}^{-1}(k) + \frac{z\beta d^2}{3} \mathbf{k}^2 \right)^{-1} \tag{3.14}$$

is the Fourier transform of the dipole potential with a dielectric correction.

$\tilde{\mathscr{V}}(\mathbf{k})$ is the Fourier transform of the kernel $\mathscr{V}(\mathbf{r} - \mathbf{r}')$ which is the inverse of the Hessian of S at $\phi = 0$. A version of this theorem holds in any dimension and also for a large class of positive-definite interactions in place of dipole-dipole. The factor 3 is the dimension of space. We will remark in the proof the main property of the interaction being used. The reader will see that the argument is a very general mean field theory bound.

From this theorem and discussion of the dielectric constant in Section I.B we immediately obtain a mean field theory bound for the dielectric constant, assuming there is a dielectric constant:

$$\varepsilon \leqslant 1 + \frac{z\beta d^2}{3} 4\pi \tag{3.15}$$

There is a large literature on the molecular theory of the dielectric constant, with atoms and molecules modeled by preformed classical permanent dipoles, using various short range regularizations. See, for example, (Stell, Patey, and Høye, 1981) and references therein. In particular, the

Clausius–Mosotti law $(\varepsilon-1)(\varepsilon+2)^{-1}=4\pi\rho\beta d^2/9$ was derived in (Høye and Stell, 1974; Høye and Stell, 1976) by taking the Kac limit, in which $V(\mathbf{r})$ is replaced by $\gamma^3 V(\gamma\mathbf{r})$ and $\gamma\to\infty$. However, this law is contradicted by the bound (3.15) if one just sets $z=\rho$ at low density. The reason is that the result of the Kac limit depends on the treatment of dipoles in the vicinity of the test charge and the scaling of test charges. The literature would benefit from clarification of this point. See the further comment at the end of this section.

Theorem III.1 is a consequence of

Theorem III.2 (*The mean field upper bound*):

$$\langle e^{-\int i\phi f}\rangle \leqslant \exp(\inf_g - S(g,f)) \tag{3.16}$$

where

$$-S(g,f)=\tfrac{1}{2}\int gV^{-1}g-\int gf+z\int d\mathscr{E}(\cosh(\beta^{1/2}\,\mathbf{d}\cdot\nabla g)-1) \tag{3.17}$$

Proof. We make a complex translation $\phi\to\phi-ig$. This is done using the translation formula (2.26), but we arrive at the same place if we do it in the intuitive formula $\int\mathscr{D}\phi\exp(-S(i\phi)-\int i\phi f)$, which is the numerator of $\langle e^{-\int i\phi f}\rangle$. On expanding out the exponent we obtain an upper bound on $|\exp(\cdots)|$ by dropping all the imaginary terms. Thus

$$\begin{aligned}
&-\operatorname{Re} S(i\phi+g)-\operatorname{Re}\int(i\phi+g)\,f\\
&\quad=\operatorname{Re}\tfrac{1}{2}\int(i\phi+g)\,V^{-1}(i\phi+g)-\int gf+z\operatorname{Re}\int d\mathscr{E}\cosh(\beta^{1/2}\,\mathbf{d}\cdot\nabla(i\phi+g))\\
&\quad=-\tfrac{1}{2}\int\phi V^{-1}\phi+\tfrac{1}{2}\int gV^{-1}g-\int gf\\
&\qquad+z\int d\mathscr{E}\cos(\beta^{1/2}\,\mathbf{d}\cdot\nabla\phi)\cosh(\beta^{1/2}\,\mathbf{d}\cdot\nabla g)\\
&\quad\leqslant -S(i\phi)-S(g,f)
\end{aligned} \tag{3.18}$$

so that in the resulting bound on $\langle\exp(-\int i\phi f)\rangle$ the $\int\mathscr{D}\phi\exp(-S(i\phi))$ cancels in numerator and denominator and we obtain the mean field upper bound, since g is arbitrary. ▮

Proof of Theorem III.1. We rewrite the mean field upper bound as

$$1 - \langle e^{-i\alpha \int \phi f} \rangle \geqslant 1 - \exp(-S(\alpha g, \alpha f)) \tag{3.19}$$

which holds for any function g. Let $\alpha \to 0$ to obtain

$$\tfrac{1}{2} \left\langle \left(\int \phi f \right)^2 \right\rangle \geqslant -\tfrac{1}{2} \int g V^{-1} g + \int g f - \tfrac{1}{2} z \int d\mathscr{E} (\beta^{1/2} \mathbf{d} \cdot \nabla g)^2 \tag{3.20}$$

This is valid provided g has enough decay so that the terms of higher order than α^2 are convergent integrals. *This and positive-definiteness are the only properties of the dipole interaction used in the proof of* (3.13).

Now choose $g = \mathscr{V} f$. The result is

$$\left\langle \left(\int \phi f \right)^2 \right\rangle \geqslant \int f \mathscr{V} f \tag{3.21}$$

This is the same as

$$\int f V^{\mathrm{eff}} f \geqslant \int f \mathscr{V} f \tag{3.22}$$

so that

$$\int \tilde{V}^{\mathrm{eff}}(\mathbf{k}) \, |\tilde{f}(\mathbf{k})|^2 \, d\mathbf{k} \geqslant \int \tilde{\mathscr{V}}(\mathbf{k}) \, |\tilde{f}(\mathbf{k})|^2 \, d\mathbf{k} \tag{3.23}$$

which, being true for a large class of f, is the result we claimed. ▮

A Kac limit can be defined by replacing $V(\mathbf{r})$ by $\gamma^{-1} V(\gamma \mathbf{r})$ and letting $\gamma \to 0$, which is the same as taking $L \to \infty$. By scaling one can show that it is equivalent to replacing $S(i\phi)$ by $\gamma^{-3} S(i\phi)$ in the Sine–Gordon transformation (3.6), (3.7). This selects the stationary point of the action so that bounds such as Theorem III.1 are saturated in this limit, *provided* the external charge density f is also scaled suitably.

C. The Scaling Limit of the Lattice Dipole Gas

The results of the last section show absence of screening but one would like to know that the system is in a phase characterized by correlations that are asymptotic to canonical power laws prefaced by a dielectric constant or tensor. In this section we will describe preliminary attempts to delineate when the system is actually in a dielectric phase in this more detailed sense.

Unfortunately the most appealing result is established only for lattice systems, but the removal of the restriction to lattice models is a feasible mathematical problem.

In a lattice model each site $\mathbf{r}$ in a simple cubic lattice $\mathscr{Z}^\nu$ in a $\nu \geqslant 1$ dimensional box Λ can be occupied by zero, one or more dipoles, each of which can only point in a lattice direction. The Sine–Gordon transformation of such systems leads to a partition function of the form

$$\Xi_\Lambda = \int \mathscr{D}\phi \, e^{-S(\phi)} \tag{3.24}$$

where $\mathscr{D}\phi = \prod_{\mathbf{r} \in (\mathscr{Z})^\nu \cap \Lambda} d\phi(\mathbf{r})$ is a finite dimensional integration and the action S has the general form

$$S(\phi) = \sum_{\langle \mathbf{r}\mathbf{r}' \rangle} W(\phi(\mathbf{r}) - \phi(\mathbf{r}')) \tag{3.25}$$

where $\langle \mathbf{r}\mathbf{r}' \rangle = \langle \mathbf{r}'\mathbf{r} \rangle$ is a nearest neighbor pair of sites. For example, a dipole gas with no interactions other than the dipole interaction with lattice regularization is given by

$$W(\phi(\mathbf{r}) - \phi(\mathbf{r}')) = \frac{1}{8\pi} (\phi(\mathbf{r}) - \phi(\mathbf{r}'))^2 - \frac{z}{\nu} \cos(d\beta^{1/2}(\phi(\mathbf{r}') - \phi(\mathbf{r})) \tag{3.26}$$

The first term is the finite difference version of $(\nabla\phi)^2$ and the second term corresponds to the $\cosh(i\beta^{1/2} \, \mathbf{d} \cdot \nabla\phi)$ we have seen before. If there is a hard core interaction preventing more than one dipole per lattice site then $(z/\nu)\cos$ is replaced by $\ln(1 + (z/\nu)\cos)$. Some of the results we are about to state were derived assuming periodic boundary conditions on the lattice.

This partition function is also called the *anharmonic bedspring*, in which case the variables ϕ are considered to be displacements of the nodes of a bedspring (in a distinguished direction).

General results (Naddaf and Spencer, 1997) have been obtained under the assumption that S is convex and is a local (or nearly local) function of the gradient of ϕ, namely assume there is a positive number $\delta > 0$ independent of ϕ such that the matrix

$$S''(\phi; \mathbf{r}, \mathbf{r}') = \frac{\partial^2 S}{\partial\phi(\mathbf{r}) \, \partial\phi(\mathbf{r}')} \tag{3.27}$$

of second derivatives obeys

$$\sum_{\langle \mathbf{r}\mathbf{r}' \rangle} \zeta(\mathbf{r}) \, S''(\phi; \mathbf{r}, \mathbf{r}') \, \zeta(\mathbf{r}') \geqslant \delta \sum_{\langle \mathbf{r}\mathbf{r}' \rangle} (\zeta(\mathbf{r}) - \zeta(\mathbf{r}'))^2 \tag{3.28}$$

for all ζ. The finite difference Laplacian Δ associated to the lattice is a matrix defined by

$$\sum_{\langle \mathbf{r}\mathbf{r}'\rangle} (\zeta(\mathbf{r})-\zeta(\mathbf{r}'))^2 = \sum_{\langle \mathbf{r}\mathbf{r}'\rangle} \zeta(\mathbf{r})(-\Delta)(\mathbf{r},\mathbf{r}')\,\zeta(\mathbf{r}') \tag{3.29}$$

Thus this convexity assumption is, by definition, the matrix inequality

$$\text{Convexity:}\quad S''(\phi)\geqslant \delta(-\Delta) \tag{3.30}$$

This type of assumption has a natural continuum analogue: a lower bound on the second variation of S by $\delta\int(\nabla\phi)^2$ or perhaps a quadratic form in $-\Delta+L^2\Delta^2$, but the next assumption brings in the lattice in a strong way.

The assumption is that there is a constant C such that

$$\sum_{\langle \mathbf{r}\mathbf{r}'\rangle} \zeta(\mathbf{r})\,S''(\phi;\mathbf{r},\mathbf{r}')\,\zeta(\mathbf{r}')\leqslant C\sum_{\langle \mathbf{r}\mathbf{r}'\rangle}\zeta(\mathbf{r})^2 \tag{3.31}$$

This is not as natural as the convexity assumption and is false for a continuum model whose action contains $\delta\int(\nabla\phi)^2$ or higher order derivatives.

Now we come to the *scaling limit* which concerns expectations of functions of fields averaged over a length scale ℓ that is taken to infinity. For any smooth compactly supported function f with $\sum f(\mathbf{r})=0$ define

$$\phi(f_\ell)=\sum_{\mathbf{r}}\phi(\mathbf{r})\,\ell^{-\nu/2+1}f\left(\frac{\mathbf{r}}{\ell}\right) \tag{3.32}$$

The $\sum f(\mathbf{r})=0$ means that $\phi(f_\ell)$ is really an integral of $\nabla\phi$ against a function of compact support.

The theorem will say that when ℓ is large $\phi(f_\ell)$ becomes Gaussian. Gaussian random variables are characterized by their covariance, which, in the theorem, will be the continuum Green's function $C(\mathbf{r},\mathbf{r}')$ solving

$$-\sum_{i,j=1,\ldots,d}\varepsilon_{ij}\,\partial_i\partial_j C(\mathbf{r},\mathbf{r}')=\delta(\mathbf{r}-\mathbf{r}') \tag{3.33}$$

where $\partial_i=\partial/\partial r_i$ and ε_{ij} will be the dielectric tensor.

For the theorem we need to define the Gaussian measure

$$d\mu_C(\phi)=\frac{1}{Z}\,\mathscr{D}\phi\,\exp\left(-\frac{1}{2}\int\sum_{i,j}\varepsilon_{ij}\,\partial_i\phi(\mathbf{r})\,\partial_j\phi(\mathbf{r})\,d\mathbf{r}\right) \tag{3.34}$$

Such a Gaussian measure exists (essentially the massless free field) and is characterized by Wick's theorem which says

Theorem III.3. Define the functional Laplacian

$$\mathbb{\Delta} = \int d\mathbf{r} \int d\mathbf{r}' \, \frac{\delta}{\delta\phi(\mathbf{r})} \, C(\mathbf{r}, \mathbf{r}') \, \frac{\delta}{\delta\phi(\mathbf{r}')} \tag{3.35}$$

Let P be a polynomial in fields $\phi(\mathbf{r}_1),..., \phi(\mathbf{r}_n)$, then

$$\int d\mu_C(\phi) \, P(\phi) = \exp(\tfrac{1}{2} \mathbb{\Delta}) \, P(\phi)|_{\phi=0} \tag{3.36}$$

where $\exp(\frac{1}{2}\mathbb{\Delta})$ is a power series $I + \frac{1}{2}\mathbb{\Delta} + \cdots$ which terminates after a finite number of terms when applied to a polynomial P.

An immediate consequence is $\int d\mu_C(\phi) \, \phi(\mathbf{r}) \, \phi(\mathbf{r}') = C(\mathbf{r}, \mathbf{r}')$ which is why C is called a covariance. The theorem (Naddaf and Spencer, 1997) is

Theorem III.4. Under the convexity assumption (3.30) and the uniform upper bound (3.31) the continuum scaling limit of the anharmonic bedspring is a continuum massless free field. In other words there exists a constant positive-definite dielectric tensor ε_{ij} such that, for any $f^1,..., f^n$ as $\ell \to \infty$,

$$\left\langle \prod_i \phi(f^i_\ell) \right\rangle \to \int d\mu_C \prod_i \phi(f^i) \tag{3.37}$$

Thus, in dimension $\nu = 3$, the lattice dipole gas (3.26) is in a dipolar phase characterized by a dielectric constant at least when $\frac{1}{3} z\beta d^2 4\pi < 1$ because this is the parameter range for which (3.26) is convex.

In mathematical terms this is a new type of central limit theorem. Central limit theorems are usually a statement about sums of independent random variables. In the statistical mechanics of lattice spin systems in the high temperature phase the spins are somewhat independent and one expects a central limit theorem that the sum of the spins in a large block of side ℓ normalized by $\ell^{-\nu/2}$ is almost Gaussian and independent of similar sums over disjoint blocks. A beautiful theorem of this type has been proved (Newman, 1980; Newman and Wright, 1981; Newman and Wright, 1982). The most gentle way to encode high temperature (approximate independence) is to require only a finite susceptibility which remarkably is the assumption made by Newman, together with a type of ferromagnetism. In the case of the anharmonic bedspring the susceptibility is not finite; correlations decay with non-integrable power laws and the variables ϕ and their gradients are very far from independent. Now we no longer have a standard central limit theorem; indeed the right normalization for a block is now $\ell^{-\nu/2+1}$ but nevertheless these block sums become Gaussian.

From the point of view of the renormalization group the central limit theorem is the case of a high temperature fixed point obtained by scaling keeping the mass fixed so that the renormalization group dynamics drives the system to a white noise Gaussian fixed point. Theorem III.4 instead describes a massless Gaussian fixed point. Notice that the convexity hypothesis permits interactions that are not small.

The proof sharpens the estimates of (Brascamp and Lieb, 1975; Brascamp and Lieb, 1976), in particular the Brascamp–Lieb bounds:

Theorem III.5. Let $F=F(\phi)$ be any continuously differentiable function of fields. Under the convexity assumption (3.30),

$$\langle F^2\rangle-\langle F\rangle^2\leqslant\sum_{\mathbf{r},\mathbf{r}'}\left\langle\frac{\partial F}{\partial\phi(\mathbf{r})}S''^{-1}(\phi;\mathbf{r},\mathbf{r}')\frac{\partial F}{\partial\phi(\mathbf{r}')}\right\rangle \tag{3.38}$$

and

$$\langle e^{\phi(f)}\rangle\leqslant\exp\left(\tfrac{1}{2}\sum_{\mathbf{r},\mathbf{r}'}f(\mathbf{r})(-\delta\Delta)^{-1}(\mathbf{r},\mathbf{r}')f(\mathbf{r}')\right) \tag{3.39}$$

It is a corollary of Theorem III.4 that all reasonable functions of fields $\phi(f_\ell)$ converge to massless free field expectations. Unfortunately the standard observables are not included in this class, being local functions of the unaveraged field $\phi(\mathbf{r})$. For example the dipole density is

$$\hat{\rho}(\mathscr{E};\phi)=ze^{-i\beta^{1/2}\mathbf{d}\cdot\nabla\phi(\mathbf{r})} \tag{3.40}$$

Theorem III.4 is more or less equivalent to

$$\left\langle\prod\alpha^{\nu/2-1}\phi(\alpha\mathbf{r}_i)\right\rangle\to\int d\mu_C(\phi)\prod\phi(\mathbf{r}_i)\qquad\text{as}\quad\alpha\to\infty \tag{3.41}$$

but to get at the density observables we need information on asymptotics when some but not all of the points $\mathbf{r}_1,\dots,\mathbf{r}_n$ are driven apart by a scaling. Theorem III.5 provides an upper bound but lower bounds are not yet proven. There is no physical reason to doubt that they hold, but we are interested in a proof because if the Naddaf–Spencer argument could be extended to prove that more general functionals of ϕ have power law decay then a complete proof that there is no exponential screening in quantum Coulomb systems is within reach using the strategy in (Brydges and Keller, 1994a). An alternative route was started by (Brydges and Keller, 1994b) but it is presently unreasonably complicated.

One further remark about dipole systems is that the pressure and dipole distributions are analytic in the activity in a small neighborhood of zero (Gawedzki and Kupiainen, 1983; Brydges and Yau, 1990). Thus the Mayer expansion is convergent at small activities. Both proofs are complicated and despite many efforts, no one has yet obtained the result by direct attack on the size of the Mayer coefficients.

IV. SEMI-CLASSICAL COULOMB GAS

A. The Feynman–Kac Representation

In this chapter, we give an introduction to some of the main effects produced by quantum mechanics in the Coulomb gas. These effects are most easily seen by perturbing around the classical gas, i.e., neglecting the quantum statistics and keeping the first relevant contributions to an expansion in powers of the Planck constant $\hbar$ (the Wigner–Kirkwood expansion).[20] We have no control on the possible convergence or asymptotic character of these $\hbar$-series, but the examination of the lowest order terms gives immediately a prediction to the main issue: Debye screening-cannot survive if the quantum mechanical nature of the charges is taken into account. This serves as a gentle training for the reading of Section V where the fully quantum mechanical gas is considered, since most of the arguments and of the mathematical structure will be similar.

The formalism that is best adapted for both a semi-classical and a low density analysis of the quantum Coulomb gas is the Feynman–Kac functional integral representation. This representation is of course not new and goes back to (Ginibre, 1965; Ginibre, 1971) with his study of the low activity expansion of quantum fluids with short range forces. But, for quantum charges, the formalism shows its full capability and becomes particularly operational to deal with the long range of the Coulomb potential.

In Section IV.C we discuss the simpler situation of only two quantum charges immersed in a classical plasma. The model can be studied without

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[20] Note that to have stability of the classical reference system, the semi-classical analysis requires a regularization of the Coulomb potential at the origin, except for the one component plasma which remains well behaved in the classical limit.

recourse to $\hbar$ expansions and illustrates clearly how quantum fluctuations will irremediably destroy Debye screening: one finds an r^{-6} decay of the correlation between the two quantum charges. In Section IV.D we comment on the relation between this type of correlation between individual charges and the conventional van der Waals potential. Section IV.E comes back to a system of infinitely many quantum charges and summarizes the results obtained by the semi-classical analysis. In the last section, we combine the Sine–Gordon and the Feynman–Kac functional integrals: this gives an alternative view on the lack of exponential screening. Again a simplified model that captures the essence of quantum fluctuations illustrates how the occurrence of dipole (and higher multipole) fields will destroy Debye screening. In contrast, mixtures of classical particles that carry both charges and dipoles still show strong screening properties.

We start here and in Section IV.B by recalling familiar ideas about the representation of the quantum mechanical statistical operator by the Feynman–Kac functional integral. For the sake of simplicity, we consider first a single particle of mass m in three dimensions moving in an external potential $V(\mathbf{r})$. According to the original path integration (Feynman and Hibbs, 1965), the configurational matrix elements of the statistical operator associated with the one-particle Hamiltonian

$$H=-\frac{\hbar^2}{2m}\Delta+V,\qquad \Delta=\text{Laplacian in }\mathbb{R}^3 \tag{4.1}$$

read

$$\langle\mathbf{r}_1|\exp\left(-\beta\left(-\frac{\hbar^2}{2m}\Delta+V\right)\right)|\mathbf{r}_2\rangle=\sum_{paths}\exp\left(-\frac{1}{\hbar}S(\mathbf{r}(\cdot))\right) \tag{4.2}$$

In (4.2) $S(\mathbf{r}(\cdot))$ is the classical action corresponding to the potential $-V$ (the Euclidean action)

$$S(\mathbf{r}(\cdot))=\int_0^{\beta\hbar}dt\left(\frac{m}{2}\left|\frac{d\mathbf{r}(t)}{dt}\right|^2+V(\mathbf{r}(t))\right) \tag{4.3}$$

associated with the path $\mathbf{r}(t)$ starting from $\mathbf{r}_1$ at "time" $t=0$ and ending in $\mathbf{r}_2$ at "time" $\beta\hbar$. The summation in (4.2) runs over all such paths.

It is very useful to parameterize the path $\mathbf{r}(t)$ by dimensionless variables, making the change

$$\begin{gathered}s=\frac{t}{\beta\hbar},\qquad 0\leqslant s\leqslant 1\\ \mathbf{r}_{1,2}(s)=(1-s)\,\mathbf{r}_1+s\mathbf{r}_2+\lambda\xi(s),\qquad \xi(0)=\xi(1)=0\end{gathered} \tag{4.4}$$

where

$$\lambda = \hbar \sqrt{\frac{\beta}{m}} \tag{4.5}$$

is the de Broglie thermal wave length. In (4.4) $\boldsymbol{\xi}(s)$ represents now a closed path, called the Brownian bridge, starting and returning to the origin within the "time" $s=1$. In terms of these dimensionless variables, the matrix element (4.2) can be written in the precise form (Simon, 1979; Roepstorff, 1994)

$$\begin{aligned}\langle \mathbf{r}_1 | \exp\left(-\beta\left(-\frac{\hbar^2}{2m}\Delta + V\right)\right) | \mathbf{r}_2 \rangle \\ = \left(\frac{1}{2\pi\lambda^2}\right)^{3/2} \exp\left(-\frac{|\mathbf{r}_1-\mathbf{r}_2|^2}{2\lambda^2}\right) \\ \times \int D(\boldsymbol{\xi}) \exp\left(-\beta \int_0^1 ds\, V((1-s)\,\mathbf{r}_1 + s\mathbf{r}_2 + \lambda\boldsymbol{\xi}(s))\right)\end{aligned} \tag{4.6}$$

In (4.6) $D(\boldsymbol{\xi})$ is a Gaussian measure (the Brownian bridge measure) with weight formally represented (up to normalization) by $\exp(-\frac{1}{2}\int_0^1 |(d\boldsymbol{\xi}(s))/ds|^2)$. It has zero mean and is entirely defined by its covariance

$$\int D(\boldsymbol{\xi})\, \xi_\mu(s_1)\, \xi_\nu(s_2) = \delta_{\mu,\nu}(\min(s_1, s_2) - s_1 s_2) \tag{4.7}$$

where $\xi_\mu(s)$ are the Cartesian coordinates of $\boldsymbol{\xi}(s)$.

The representation (4.6) has several advantages: physical parameters $\mathbf{r}_1$, $\mathbf{r}_2$, β, $\hbar$, λ appear explicitly in the formula. Moreover the diagonal matrix elements

$$\begin{aligned}\langle \mathbf{r} | \exp\left(-\beta\left(-\frac{\hbar^2}{2m}\Delta + V\right)\right) | \mathbf{r} \rangle \\ = \left(\frac{1}{2\pi\lambda^2}\right)^{3/2} \int D(\boldsymbol{\xi}) \exp\left(-\beta \int_0^1 ds\, V(\mathbf{r} + \lambda\boldsymbol{\xi}(s))\right)\end{aligned} \tag{4.8}$$

have the form of an integral over a certain $\boldsymbol{\xi}$-dependent Boltzmann factor $\exp(-\beta V(\mathbf{r}, \boldsymbol{\xi}))$ with $V(\mathbf{r}, \boldsymbol{\xi}) = \int_0^1 ds\, V(\mathbf{r} + \lambda\boldsymbol{\xi}(s))$, as in classical statistical mechanics. In this view, one can think of a quantum point particle as a classical extended object, the closed filament $\boldsymbol{\xi}(s)$ located at $\mathbf{r}$. This closed filament, which plays formally the same role as a classical internal degree of freedom, represents the intrinsic quantum fluctuation with size controlled by the de Broglie wave length λ. The statistical weight of a filament having extension R behaves as $\exp(-R^2/\lambda^2)$; thus, in the semi-classical regime (λ small), only short filaments contribute to the integral (4.8). Obviously one recovers the genuine classical Boltzmann factor $\exp(-\beta V(\mathbf{r}))$ in (4.8) as $\lambda \to 0$. For these reasons, the Feynman–Kac representation is particularly suitable to study the semi-classical aspects of equilibrium quantities.

B. The Gas of Charged Filaments

The extension of the representation (4.8) to the many particle system is straightforward. In the sequel, $V(\mathbf{r}_1 - \mathbf{r}_2)$ represents a two-body regularized Coulomb potential, for instance of the form (1.8). To each particle labeled by i, $i = 1,..., N$, we associate an independent Brownian bridge $\xi_i(s)$, distributed with the Gaussian measure $D(\xi_i)$, and the diagonal elements of the N-particles statistical operator read

$$\begin{aligned}\langle \{\mathbf{r}_i\} |\, \exp(-\beta H_{\Lambda, N}) \,| \{\mathbf{r}_i\} \rangle &= \prod_{i=1}^{N} \frac{1}{(2\pi\lambda_{\alpha_i}^2)^{3/2}} \int \prod_{i=1}^{N} D(\xi_i) \\ &\quad \times \exp\left(-\frac{\beta}{2} \sum_{i \neq j}^{N} e_{\alpha_i} e_{\alpha_j} \int_0^1 ds\, V(\mathbf{r}_i + \lambda_{\alpha_i} \xi_i(s) - \mathbf{r}_j - \lambda_{\alpha_j} \xi_j(s)) \right) \end{aligned} \tag{4.9}$$

The Dirichlet boundary conditions on $H_{N,\Lambda}$ are implemented by the constraint that all paths in the integrand of (4.9) have to remain inside Λ for all s, $0 \leqslant s \leqslant 1$. We do not write this constraint explicitly since it will be trivially removed in the infinite volume limit. The grand-canonical Maxwell–Boltzmann partition function is defined by keeping in (1.40) only the term corresponding to the trivial permutation. Denoting it still by Ξ_Λ in this section, it is given by the sum

$$\begin{aligned}\Xi_\Lambda = \sum_{\{N_\alpha\}}^{\infty} \prod \frac{((2\sigma_\alpha + 1)\exp(\beta\mu_\alpha))^{N_\alpha}}{N_\alpha!} \\ \times \int_\Lambda d\mathbf{r}_1 \cdots d\mathbf{r}_N \langle \{\mathbf{r}_i\} |\, \exp(-\beta H_{\Lambda, N}) \,| \{\mathbf{r}_i\} \rangle \end{aligned} \tag{4.10}$$

The factor $2\sigma_\alpha + 1$ is the spin degeneracy, since the Hamiltonian (1.36) is independent of the spin.

A look at the Boltzmann-like factor in (4.9) suggests naturally the introduction of an enlarged classical phase space whose elements $\mathcal{F}$ are

$$\mathcal{F} = (\alpha, \mathbf{r}, \xi) \tag{4.11}$$

where α is the species and ξ is the filament shape of a particle at position $\mathbf{r}$. We shall call a point $\mathcal{F}$ in this phase space a "filament." Since the Hamiltonian is invariant under the permutations of the particles of the same species, we can use again the summation identity (1.14) to write the partition function (4.10) in the form

$$\Xi_\Lambda = \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{k=1}^{N} d\mathcal{F}_k \, z(\mathcal{F}_k) \exp(-\beta U(\mathcal{F}_1,..., \mathcal{F}_N)) \tag{4.12}$$

where the phase space integration means

$$\int d\mathcal{F} \cdots = \sum_{\alpha=1}^{\mathcal{S}} \int_\Lambda d\mathbf{r} \int D(\xi) \cdots \tag{4.13}$$

In (4.12) we have set

$$z(\mathcal{F}) = (2\sigma_\alpha + 1) \, z_\alpha, \qquad z_\alpha = \frac{\exp(\beta\mu_\alpha)}{(2\pi\lambda_\alpha^2)^{3/2}} \tag{4.14}$$

$$U(\mathcal{F}_1,..., \mathcal{F}_N) = \sum_{1=i<j}^{N} e_{\alpha_i} e_{\alpha_j} V(\mathcal{F}_i, \mathcal{F}_j) \tag{4.15}$$

with

$$V(\mathcal{F}_1, \mathcal{F}_2) = \int_0^1 ds \, V(\mathbf{r}_1 + \lambda_{\alpha_1} \xi_1(s) - \mathbf{r}_2 - \lambda_{\alpha_2} \xi_2(s)) \tag{4.16}$$

It is clear that the system defined by the relations (4.12)–(4.16) has the structure of a classical statistical mechanical system of objects having internal degrees of freedom α, ξ (the species and the shape of a filament), with activity (4.14) and two-body interaction (4.16). We call it "the system of filaments" and can apply to it all the standard methods of classical statistical mechanics.

In particular, one can define correlations between filaments in the usual way (see (1.19) and (1.20)). Introducing the "δ-function" which identifies the points $\mathcal{F}_1$ and $\mathcal{F}_2$ in phase space, i.e.

$$\int d\mathcal{F}_2 \, \delta(\mathcal{F}_1, \mathcal{F}_2) \, F(\mathcal{F}_2) = F(\mathcal{F}_1), \qquad \delta(\mathcal{F}_1, \mathcal{F}_2) = \delta_{\alpha_1, \alpha_2} \, \delta(\xi_1, \xi_2) \, \delta(\mathbf{r}_1 - \mathbf{r}_2) \tag{4.17}$$

the density of filaments and the two filament distribution are

$$\rho(\mathcal{F}) = \langle \hat{\rho}(\mathcal{F}) \rangle, \qquad \rho(\mathcal{F}_a, \mathcal{F}_b) = \langle \hat{\rho}(\mathcal{F}_a)\, \hat{\rho}(\mathcal{F}_b) \rangle \tag{4.18}$$

where

$$\hat{\rho}(\mathcal{F}) = \sum_i \delta(\mathcal{F}_i, \mathcal{F}) \tag{4.19}$$

and $\langle \cdots \rangle$ denotes the grand-canonical average in the system of filaments (the contribution of coincident filaments, included in (4.18), will be specified later if needed). However, one should remember that the shapes (of the filaments are not directly observable quantities: the physical particle distributions are obtained by integrating them out in (4.18) and (4.19). Thus the density of particles of type α is

$$\rho(\alpha, \mathbf{r}) = \int D(\xi)\, \rho(\mathcal{F}) \tag{4.20}$$

the two particle distribution is

$$\rho(\alpha_a, \mathbf{r}_a, \alpha_b, \mathbf{r}_b) = \int D(\xi_a)\, D(\xi_b)\, \rho(\mathcal{F}_a, \mathcal{F}_b) \tag{4.21}$$

and in the same way for the truncated distributions,

$$\begin{gathered} \rho_T(\mathcal{F}_a, \mathcal{F}_b) = \rho(\mathcal{F}_a, \mathcal{F}_b) - \rho(\mathcal{F}_a)\, \rho(\mathcal{F}_b) \\ \rho_T(\alpha_a, \mathbf{r}_a, \alpha_b, \mathbf{r}_b) = \int D(\xi_a)\, D(\xi_b)\, \rho_T(\mathcal{F}_a, \mathcal{F}_b) \end{gathered} \tag{4.22}$$

At this point, one has to make a fundamental observation. Although the system of filaments can be treated with the rules of classical statistical mechanics, it differs from a genuine assembly of classical charged random wires (distributed according to the Gaussian measure $D(\xi)$) on an important point: *the interaction (4.16) inherited from the quantum mechanical nature of the charges is not the standard electrostatic potential between two closed wires of shapes* ξ_1 *and* ξ_2. The latter potential, denoted $V_{\mathrm{cl}}(\mathcal{F}_1, \mathcal{F}_2)$, is

$$V_{\mathrm{cl}}(\mathcal{F}_1, \mathcal{F}_2) = \int_0^1 ds_1 \int_0^1 ds_2\, V(\mathbf{r}_1 + \lambda_{\alpha_1} \xi_1(s_1) - \mathbf{r}_2 - \lambda_{\alpha_2} \xi_2(s_2)) \tag{4.23}$$

since every element of charge $\xi_1(s_1)\,ds_1$ carried by the first filament has to interact with every element $\xi_2(s_2)\,ds_2$ of the other by the Coulomb law, and the corresponding total electrostatic energy is

$$U_{\mathrm{cl}}(\mathscr{F}_1,\ldots,\mathscr{F}_k)=\sum_{i<j=1}^{k} e_{\alpha_i}e_{\alpha_j}V_{\mathrm{cl}}(\mathscr{F}_i,\mathscr{F}_j) \tag{4.24}$$

Although the filaments are quantum mechanical in origin, we will use this subscript cl *to denote the filament system with interaction* U_{cl}. Replacing the interaction (4.16) by (4.23) would indeed lead to a genuine system of charged filaments obeying exponential Debye screening in the appropriate low density or high temperature regime, according to the theorems quoted in Section II and the discussion in Section IV.F. Hence different behaviors between quantum and classical charges in thermal equilibrium must be traced back to the difference between the interactions (4.16) and (4.23)

$$\begin{aligned} W(\mathscr{F}_1,\mathscr{F}_2) &= e_{\alpha_1}e_{\alpha_2}(V(\mathscr{F}_1,\mathscr{F}_2)-V_{\mathrm{cl}}(\mathscr{F}_1,\mathscr{F}_2)) \\ &= e_{\alpha_1}e_{\alpha_2}\int_0^1 ds_1\int_0^1 ds_2(\delta(s_1-s_2)-1) \\ &\qquad\times V(\mathbf{r}_1+\lambda_{\alpha_1}\xi_1(s_1)-\mathbf{r}_2-\lambda_{\alpha_2}\xi_2(s_2)) \end{aligned} \tag{4.25}$$

The large distance behavior of $W(\mathscr{F}_1,\mathscr{F}_2)$ is obtained from the multipolar expansion of the potential V written in the form

$$\begin{aligned} &V(\mathbf{r}_1+\lambda_{\alpha_1}\xi_1(s_1)-\mathbf{r}_2-\lambda_{\alpha_2}\xi_2(s_2)) \\ &\quad= V(\mathbf{r}_1-\mathbf{r}_2)+M_1(s_1)\,V(\mathbf{r}_1-\mathbf{r}_2) \\ &\qquad+M_2(s_2)\,V(\mathbf{r}_1-\mathbf{r}_2)+M_1(s_1)\,M_2(s_2)\,V(\mathbf{r}_1-\mathbf{r}_2) \end{aligned} \tag{4.26}$$

where $M_i(s)$ are the multipolar differential operators

$$M_i(s)=\sum_{k=1}^{\infty}\frac{(\lambda_{\alpha_i}\xi_i(s)\cdot\nabla_{\mathbf{r}_i})^k}{k!},\qquad i=1,2 \tag{4.27}$$

In the decomposition (4.26), the three first terms correspond to the charge–charge and charge–multipole interactions, whereas the last term represents the rest of the multipole–multipole interactions. Since

$$\int_0^1 ds_1(\delta(s_1-s_2)-1)=\int_0^1 ds_2(\delta(s_1-s_2)-1)=0 \tag{4.28}$$

we see that only this latter term contributes to W

$$W(\mathscr{F}_1, \mathscr{F}_2) = e_{\alpha_1} e_{\alpha_2} \int_0^1 ds_1 \int_0^1 ds_2 (\delta(s_1 - s_2) - 1)\, M_1(s_1)\, M_2(s_2)\, V(\mathbf{r}_1 - \mathbf{r}_2) \tag{4.29}$$

The dominant large distance behavior of W

$$W(\mathscr{F}_1, \mathscr{F}_2) \sim e_{\alpha_1} e_{\alpha_2} \int_0^1 ds_2 \int_0^1 ds_2 (\delta(s_1 - s_2) - 1) \\ \times (\lambda_{\alpha_1} \xi_1(s_1) \cdot \nabla_{\mathbf{r}_1})(\lambda_{\alpha_2} \xi_2(s_2) \cdot \nabla_{\mathbf{r}_2})\, V(\mathbf{r}_1 - \mathbf{r}_2), \qquad |\mathbf{r}_1 - \mathbf{r}_2| \to \infty \tag{4.30}$$

is typically a dipole–dipole potential, decaying as $|\mathbf{r}_1 - \mathbf{r}_2|^{-3}$, due to the dipole elements $e_{\alpha_1} \lambda_{\alpha_1} \xi_1(s_1)\, ds_1$ and $e_{\alpha_2} \lambda_{\alpha_2} \xi_1(s_2)\, ds_2$ associated with two filaments of arbitrary shapes. It will be shown (Section V) that the charge–charge and charge–multipole interactions have a fast screening in the quantum gas, but not the multipole–multipole interaction. This long range term will precisely be the cause for the breakdown of exponential screening in the quantum system for all values of the density and of the temperature. For the sake of pedagogy, we illustrate the above assertions in a simplified model involving only two quantum mechanical charges. This model presents already all the basic mechanisms which will be at work in the general case.

C. Quantum Fluctuations Destroy Exponential Screening

We consider the simplified situation where all particles are classical but two. For this it suffices to single out two filaments $\mathscr{F}_a = (\alpha_a, \mathbf{r}_a, \xi_a)$, $\mathscr{F}_b = (\alpha_b, \mathbf{r}_b, \xi_b)$ corresponding to two particles with nonvanishing de Broglie lengths λ_a, λ_b, and to set the de Broglie lengths of all the other particles equal to zero. Then the phase space variable of a classical particle reduces to $(\alpha, \mathbf{r})$ and its interaction with the quantum particle $\mathscr{F}_a$ to

$$V(\mathscr{F}_a, \mathbf{r}) = \int_0^1 ds\, V(\mathbf{r}_a + \lambda_a \xi_a(s) - \mathbf{r}) = V_{\mathrm{cl}}(\mathscr{F}_a, \mathbf{r}) \tag{4.31}$$

which is identical to the classical potential (4.23) with one λ set equal to 0, whereas the two quantum particles still interact with the potential (4.16). Here the quantum mechanical nature of the two specified particles will be treated non-perturbatively. The model is semiclassical only in the sense that their surrounding medium is now a classical plasma at density ρ and inverse temperature β.

As in (1.17) we denote by $\omega = (\alpha_1, \mathbf{r}_1,..., \alpha_n, \mathbf{r}_n)$ a configuration of the classical particles and by $\hat{c}(\mathbf{r}, \omega) = \sum_{j=1}^{n} e_{\alpha_j} \delta(\mathbf{r} - \mathbf{r}_j)$ the corresponding microscopic charge density. For this system, the total interaction (4.15) reads

$$U(\mathscr{F}_a, \mathscr{F}_b, \omega) = e_{\alpha_a} e_{\alpha_b} V(\mathscr{F}_a, \mathscr{F}_b) + e_{\alpha_a} \int d\mathbf{r}\, V(\mathscr{F}_a, \mathbf{r})\, \hat{c}(\mathbf{r}, \omega) + e_{\alpha_b} \int d\mathbf{r}\, V(\mathscr{F}_b, \mathbf{r})\, \hat{c}(\mathbf{r}, \omega) + U_0(\omega) \tag{4.32}$$

where $U_0(\omega)$ is the Coulomb energy of the classical particles.

The distribution of two filaments $\mathscr{F}_a$ and $\mathscr{F}_b$ in thermal equilibrium with the classical Coulomb gas enclosed in a finite volume Λ is defined by

$$\rho(\mathscr{F}_a, \mathscr{F}_b) = \frac{1}{\Xi_0} \int_\Lambda d\omega \exp(-\beta U(\mathscr{F}_a, \mathscr{F}_b, \omega)) \tag{4.33}$$

In (4.33), $\int_\Lambda d\omega$ means (canonical or grand canonical) summation on the configurations ω of the classical particles in Λ and $\Xi_0 = \int_\Lambda d\omega \exp(-\beta U_0(\omega))$ is the corresponding partition function (in this definition, there is no contribution of coincident filaments). For a single filament we define in the same way[21]

$$\rho(\mathscr{F}) = \frac{1}{\Xi_0} \int_\Lambda d\omega \exp(-\beta U(\mathscr{F}, \omega)) \tag{4.34}$$

with

$$U(\mathscr{F}, \omega) = e_\alpha \int d\mathbf{r}\, V(\mathscr{F}, \mathbf{r})\, \hat{c}(\mathbf{r}, \omega) + U_0(\omega) \tag{4.35}$$

Let us also introduce the auxiliary genuine classical distributions of charged filaments $\rho_{\mathrm{cl}}(\mathscr{F}_a, \mathscr{F}_b)$, $\rho_{\mathrm{cl}}(\mathscr{F})$ defined in the same way as (4.34), (4.35), but with V and U replaced by V_{cl} and U_{cl}. Comparing now the quantum and this classical system, we observe that in view of (4.31)

$$U(\mathscr{F}, \omega) = U_{\mathrm{cl}}(\mathscr{F}, \omega), \qquad \rho(\mathscr{F}) = \rho_{\mathrm{cl}}(\mathscr{F}) \tag{4.36}$$

---

[21] $-\beta^{-1} \ln \rho(\mathscr{F})$ and $-\beta^{-1} \ln \rho(\mathscr{F}_a, \mathscr{F}_b)$ are the excess free energies when one or two filaments are embedded in the classical plasma.

but taking into account the definitions (4.24) and (4.25)

$$\begin{aligned} U(\mathscr{F}_a, \mathscr{F}_b, \omega) &= W(\mathscr{F}_a, \mathscr{F}_b) + U_{\mathrm{cl}}(\mathscr{F}_a, \mathscr{F}_b, \omega) \\ \rho(\mathscr{F}_a, \mathscr{F}_b) &= \exp(-\beta W(\mathscr{F}_a, \mathscr{F}_b))\, \rho_{\mathrm{cl}}(\mathscr{F}_a, \mathscr{F}_b) \end{aligned} \tag{4.37}$$

We consider now these distributions in the thermodynamic limit, keeping the same notations. Because of translational invariance, $\rho(\mathscr{F}) = \rho_\alpha(\xi)$ is independent of $\mathbf{r}$ and $\rho(\mathscr{F}_a, \mathscr{F}_b)$ depends on $|\mathbf{r}_a - \mathbf{r}_b|$. In the Debye regime, we know that $\rho_{\mathrm{cl}}(\mathscr{F}_a, \mathscr{F}_b)$ clusters exponentially fast as $|\mathbf{r}_a - \mathbf{r}_b| \to \infty$ (with ξ_a, ξ_b fixed)

$$\begin{aligned} \rho_{\mathrm{cl}}(\mathscr{F}_a, \mathscr{F}_b) &= \rho_{\mathrm{cl}}(\mathscr{F}_a)\, \rho_{\mathrm{cl}}(\mathscr{F}_b) \\ &\quad + O\Big(\exp\Big(-C \inf_{0 \leqslant s_1, s_2 \leqslant 1} |\mathbf{r}_a + \lambda_{\alpha_a} \xi_a(s_1) - \mathbf{r}_b - \lambda_{\alpha_b} \xi_b(s_2)|\Big)\Big) \end{aligned} \tag{4.38}$$

Thus the asymptotic behavior of $\rho(\mathscr{F}_a, \mathscr{F}_b)$ in (4.37) is governed by that of $W(\mathscr{F}_a, \mathscr{F}_b)$, i.e., according to (4.30), $\rho(\mathscr{F}_a, \mathscr{F}_b)$ clusters as $|\mathbf{r}_a - \mathbf{r}_b|^{-3}$. The two-particle distribution is obtained by averaging $\rho(\mathscr{F}_a, \mathscr{F}_b)$ on the shapes of the filaments. Using (4.36), (4.38) and expanding the factor $\exp(-\beta W(\mathscr{F}_a, \mathscr{F}_b))$ yields

$$\begin{aligned} \rho(\mathbf{r}_a, \mathbf{r}_b) &= \int D(\xi_a)\, D(\xi_b) \exp(-\beta W(\mathscr{F}_a, \mathscr{F}_b))\, \rho_{\mathrm{cl}}(\mathscr{F}_a, \mathscr{F}_b) \\ &= \rho_a \rho_b - \beta \int D(\xi_a)\, D(\xi_b)\, W(\mathscr{F}_a, \mathscr{F}_b)\, \rho_a(\xi_a)\, \rho_b(\xi_b) \\ &\quad + \tfrac{1}{2} \beta^2 \int D(\xi_a)\, D(\xi_b)\, W^2(\mathscr{F}_a, \mathscr{F}_b)\, \rho_a(\xi_a)\, \rho_b(\xi_b) \\ &\quad + \cdots + O(\exp(-C\, |\mathbf{r}_a - \mathbf{r}_b|)) \end{aligned} \tag{4.39}$$

where $\rho_a = \rho(\alpha_a, \mathbf{r}_a)$. The remainder in (4.39) still gives an exponentially decreasing contribution since the probability of long filaments is Gaussian small. Let us show that the term linear in W in (4.39) does not contribute to the asymptotic behavior of $\rho(\mathbf{r}_a, \mathbf{r}_b)$. Indeed one notes that the measure $D(\xi)$ is invariant under reflections and rotations of the filament in three-dimensional space (see (4.7)). The same is true for $\rho(\xi)$ in an homogeneous phase of the classical plasma. Hence introducing the multipolar expansion of W with the help of (4.27), (4.29) one sees the occurrence of the ξ-averages

$$\int D(\xi_a)\, D(\xi_b)\, \rho(\xi_a)\, \rho(\xi_b)$$

$$[\lambda_a \xi_a(s_1) \cdot \nabla_{\mathbf{r}_a}]^k\, [\lambda_b \xi_b(s_2) \cdot \nabla_{\mathbf{r}_b}]^l\, V(\mathbf{r}_a - \mathbf{r}_b) \qquad k, l \geqslant 1 \tag{4.40}$$

In view of these symmetry considerations, the terms with k or l odd vanish, and the terms with both k and l even are necessarily proportional to $(\nabla^2_{\mathbf{r}})^{(k+l)/2}\, V(\mathbf{r})$, $\mathbf{r} = \mathbf{r}_a - \mathbf{r}_b$, which is a rapidly decreasing function since $\nabla^2_{\mathbf{r}}(1/|\mathbf{r}|) = 0$, $\mathbf{r} \neq 0$. Since all moments of the Gaussian measure $D(\xi)$ are finite, one concludes that the W-linear term in (4.39) decays faster than any power of $|\mathbf{r}_a - \mathbf{r}_b|$. The leading behavior is therefore determined by the quadratic term. According to (4.39) and (4.30) one finds for the normalized truncated distribution

$$\begin{aligned}
\frac{\rho_T(\mathbf{r}_a, \mathbf{r}_b)}{\rho_a \rho_b} &= \frac{\rho(\mathbf{r}_a, \mathbf{r}_b)}{\rho_a \rho_b} - 1 \\
&= \frac{\beta^2}{2\rho_a \rho_b} \int D(\xi_a)\, D(\xi_b)\, W^2(\mathscr{F}_a, \mathscr{F}_b)\, \rho_a(\xi_a)\, \rho_b(\xi_b) + \mathrm{O}(W^3) \\
&= \frac{B(\beta, \rho)}{|\mathbf{r}_a - \mathbf{r}_b|^6} + O\left(\frac{1}{|\mathbf{r}_a - \mathbf{r}_b|^8}\right)
\end{aligned} \tag{4.41}$$

where $B(\beta, \rho) > 0$ can be expressed, from (4.30), as the Brownian integral of a positive functional, depending on the temperature and density of the surrounding plasma. The correction $|r_a - r_b|^{-8}$ in (4.41) arises from the square of the dipole-quadrupole interaction. Note that the result (4.41) holds in any screening phase of the classical plasma and is nonperturbative in $\hbar$.

In the classical limit or in the high temperature limit, one finds that the dominant contribution to $B(\beta, \rho)$ is the same (Alastuey and Martin, 1989)

$$B(\beta, \rho) \simeq \hbar^4\, \frac{\beta^4}{240}\, \frac{e_a^2 e_b^2}{m_a m_b}, \qquad \hbar \to 0 \quad \text{or} \quad \beta \to 0 \tag{4.42}$$

The role of the quantum fluctuations is clearly demonstrated: the dipole-like interaction W, which originates from these intrinsic quantum fluctuations, can definitely not be shielded by the classical charges, even if the latter are in the Debye phase. Nevertheless a partial screening remains: the monopole is still screened and this, together with rotation invariance, reduces the bare Coulomb decay r^{-1} to r^{-6}. It will be shown in Section IV.E as well in Sections V and VI that these facts remain true in the full quantum gas.

D. Origin of the van der Waals Forces

One can interpret the result (4.41) by saying that there exists an effective potential $\Phi_1(r)$ between two individual quantum charges defined by $(\rho_T(\mathbf{r}_a, \mathbf{r}_b)/\rho_a \rho_b) = e^{-\beta\Phi_1(|\mathbf{r}_a - \mathbf{r}_b|)} - 1$. It is attractive at large distance and behaves as

$$\beta\Phi_1(r) \simeq -\frac{B(\beta, \rho)}{r^6}, \qquad r \to \infty \tag{4.43}$$

One may wonder if this potential between individual quantum charges is related to the van der Waals potential, also decaying as r^{-6}. The van der Waals forces are usually computed for preformed atoms and molecules in empty space, and are attributed to the dipole fluctuations in these bound entities.

To allow for the possibility of quantum mechanical binding in simple terms, we can generalize the model of Section IV.C by specifying four particles, say two electron-proton (e-p) pairs, in equilibrium with a classical plasma (Martin, 1996). The information about the correlations between these four particles is contained in the fully truncated four point correlation function $\rho_T(\mathbf{r}_a, \mathbf{r}_b, \mathbf{R}_1, \mathbf{R}_2)$ where $\mathbf{r}_a, \mathbf{r}_b$ designate the coordinates of the electrons and $\mathbf{R}_1, \mathbf{R}_2$ those of the protons. This correlation is defined by the natural generalization of the expressions (4.33)–(4.37) to four particles immersed in the plasma. We are interested in the amount of correlation that exists between the two (e-p) pairs as their centers of mass are taken far apart, but ignoring the relative positions of the particles. Assuming for simplicity that the two protons are infinitely heavy (i.e., classical), the center of mass of the pairs coincide with $\mathbf{R}_1, \mathbf{R}_2$ and the desired normalized correlation is

$$F(R) = \frac{1}{2}\frac{\int d\mathbf{r}_a \int d\mathbf{r}_b\, \rho_T(\mathbf{r}_a, \mathbf{r}_b, \mathbf{R}_1, \mathbf{R}_2)}{\int d\mathbf{r}_a\, \rho_T(\mathbf{r}_a, \mathbf{R}_1) \int d\mathbf{r}_b\, \rho_T(\mathbf{r}_b, \mathbf{R}_2)}, \qquad R = |\mathbf{R}_1 - \mathbf{R}_2| \tag{4.44}$$

The factor 1/2 takes into account that the electrons, treated here as identical particles, can be found in the neighborhood of either one of the protons (the contribution of coincident particles is omitted in (4.44)[22]). We define the effective (temperature and density dependent) potential $\Phi_2(R)$ between the two pairs by

$$F(R) = e^{-\beta\Phi_2(R)} - 1 \simeq -\beta\Phi_2(R), \qquad R \to \infty \tag{4.45}$$

In contrast to the standard calculation of van der Waals forces, Φ_2 incorporates now the effects of the thermal fluctuations of the electrons and of the screening provided by the medium.

As in (4.39), the asymptotic form of $\Phi_2(R)$ is determined by the quadratic term in the quantum potential W, namely

$$-\beta\Phi_2(R) \simeq \int \bar{D}(\xi_a)\, \bar{D}(\xi_b)\, W^2(\mathscr{F}_a, \mathscr{F}_b)$$

where now $\bar{D}(\xi_a)$, $\bar{D}(\xi_b)$ are dressed Brownian measures involving the single (e-p) pair correlation. One finds

$$\beta\Phi_2(R) \simeq -\frac{C(\beta, \rho)}{R^6}, \qquad R \to \infty, \quad C(\beta, \rho) > 0 \tag{4.46}$$

There are two situations of interest, the high temperature limit ($\beta \to 0$, ρ fixed) and the atomic limit. The atomic limit is obtained by simultaneously lowering the temperature ($\beta \to \infty$) to favor binding and reducing the density at an exponential rate ($\rho \simeq e^{-\delta\beta} \to 0, \delta > 0$) to get independent atoms. In this limit (e-p) pairs form noninteracting hydrogen atoms in their ground states (the atomic limit will be discussed in Section VII for the full quantum gas).

In the high temperature limit, one recovers the result (4.42), i.e.,

$$C(\beta, \rho) \simeq \hbar^4 \frac{\beta^4 e^4}{240 m^2}, \qquad \beta \to 0 \tag{4.47}$$

As $\beta \to 0$, the electrons tend to be fully ionized and the correlation becomes that found between individual charges.

In the atomic limit, for $\delta > 0$ not too large, one has

$$\lim_{\beta \to \infty,\, \rho \to 0} \beta^{-1} C(\beta, \rho) = -C_{\text{van der Waals}} \tag{4.48}$$

---

[22] As before, exchange effects due to the Fermi statistics of the electrons are neglected. Exchange correlations have a short range.

where $C_{\text{van der Waals}} < 0$ is the usual coefficient found in text books from a second order perturbation calculation of the residual Coulomb interaction between two hydrogen atoms in their ground states.

A similar analysis has now been carried out in the full quantum mechanical electron-proton gas with the diagrammatic methods of Section V. One finds indeed that the coefficient of the r^{-6} tail of the proton–proton correlation approaches the value $C_{\text{van der Waals}}$ in the scaling limit where hydrogen atoms form (Alastuey, Cornu, and Martin, 1998). In the medium, density and temperature effects modify the amplitude of the usual van der Waals potential, but not its r^{-6} range. In particular, the free charges that are always present in the medium only partially screen the dipole interaction between atoms, contrary to a naive mean field description that would lead to an exponential screening of these interactions. The partial screening of protons is due in part to collective effects, and also to individual electrons that will bind with the proton. As the temperature goes to zero the former effects vanish, and the screening is eventually entirely due to the formation of a neutral bound state. Hence the atomic limit coincides with a zero density calculation with two preformed neutral atoms in empty space. In fact, the coefficient $C(\beta, \rho)$ interpolates continuously between the high temperature and atomic regimes. There is no qualitative difference between the mechanism producing the van der Waals forces between bound entities and that causing the r^{-6} tail (4.41) between individual charges. Both have their common origin in the same basic quantum fluctuations put into evidence in the preceding section. One sees that the difference is only quantitative. In the atomic regime, the coefficient $C(\beta, \rho)$ has a non-zero value close to $|C_{\text{van der Waals}}|$ whereas it becomes vanishingly small at high temperature.

E. Semi-classical Analysis of Coulombic Correlations

We come now to the full quantum mechanical gas, but treated semi-classically as a whole. We use again the classical gas as a reference system by splitting the interaction between the filaments (4.15) into

$$U(\mathcal{F}_1,..., \mathcal{F}_n) = U_0(\alpha_1, \mathbf{r}_1,..., \alpha_n, \mathbf{r}_n) + U_m(\mathcal{F}_1,..., \mathcal{F}_n) \tag{4.49}$$

where

$$U_0(\alpha_1, \mathbf{r}_1,..., \alpha_n, \mathbf{r}_n) = \sum_{i<j}^{n} e_{\alpha_i} e_{\alpha_j} V(\mathbf{r}_i - \mathbf{r}_j) \tag{4.50}$$

is the Coulomb energy of n classical point particles and U_m is the residual multipolar interaction. It is defined as the sum of two-body interactions $V_m(\mathscr{F}_1, \mathscr{F}_2) = V(\mathscr{F}_1, \mathscr{F}_2) - V(\mathbf{r}_1 - \mathbf{r}_2)$ obtained from (4.16) by removing the charge–charge potential:

$$V_m(\mathscr{F}_1, \mathscr{F}_2) = \int_0^1 ds (M_1(s) + M_2(s))\, V(\mathbf{r}_1 - \mathbf{r}_2) + \int_0^1 ds\, M_1(s)\, M_2(s)\, V(\mathbf{r}_1 - \mathbf{r}_2) \tag{4.51}$$

$$U_m(\mathscr{F}_1,..., \mathscr{F}_n) = \sum_{i<j}^{n} e_{\alpha_i} e_{\alpha_j} V_m(\mathscr{F}_i, \mathscr{F}_j) \tag{4.52}$$

Since the Planck constant occurs only through the de Broglie lengths λ_α, it is clear that V_m and U_m are power series in $\hbar$ starting with a linear term (see (4.5) and (4.27)). Thus considering $\hbar$ as a small parameter, we are left with the standard problem of perturbing the classical equilibrium state (in the framework of the system of filaments) by the small modification (4.52) of the potential. This will generate formally power series in $\hbar$ for the distributions of filaments, and in turn, after averaging on their shapes, for the truncated distributions of the quantum charges

$$\rho_T(\alpha_1, \mathbf{r}_1,..., \alpha_n, \mathbf{r}_n) = \sum_{k \geqslant 0} \hbar^k \rho_T^{(k)}(\alpha_1, \mathbf{r}_1,..., \alpha_n, \mathbf{r}_n) \tag{4.53}$$

We shall not give here the rather complex algorithm for calculating the coefficients $\rho_T^{(k)}$ of this expansion, but only describe some qualitative aspects and state results.

From now on we assume that the classical reference system is in the Debye phase: its correlations $\rho_{\text{cl}, T}(\alpha_1, \mathbf{r}_1,..., \alpha_n, \mathbf{r}_n)$ cluster exponentially fast and obey the multipolar sum rule (2.16). By expanding around the classical gas, each $\rho_T^{(k)}$ involves combinations of convolutions of classical correlations with the multipole potentials coming from (4.51), so that the $\rho_T^{(k)}$ are expressed in terms of the supposedly known correlations $\rho_{\text{cl}, T}$ of the reference system. The main point is that although the classical correlations have an exponential fall-off, the law of formation of the $\rho_T^{(k)}$ is such that some of these convolutions decay only algebraically (there are two exceptions, namely if the potential is convoluted with the total charge density, then multipolar sum rules insure a fast decay, or if derivatives of the Coulomb potential are contracted to form a Laplacian $\nabla^2 V(\mathbf{r})$).

The results are as follows (Alastuey and Martin, 1988; Alastuey and Martin, 1989). Obviously

$$\rho_T^{(0)}(\alpha_1, \mathbf{r}_1, ..., \alpha_n, \mathbf{r}_n) = \rho_{\mathrm{cl},\, T}(\alpha_1, \mathbf{r}_1, ..., \alpha_n, \mathbf{r}_n) \tag{4.54}$$

$$\rho_T^{(k)}(\alpha_1, \mathbf{r}_1, ..., \alpha_n, \mathbf{r}_n) = 0, \qquad k \text{ odd} \tag{4.55}$$

This is because, according to (4.27), odd powers of $\hbar$ in the expansion (4.53) correspond to odd moments of filaments. Such odd moments have zero Gaussian average.

The coefficients $\rho_T^{(2)}(\alpha_1, \mathbf{r}_1, ..., \alpha_n, \mathbf{r}_n)$ are decreasing faster than any inverse power for large spatial separations of the arguments (for the two point function see (Jancovici, 1976)).

At the order $\hbar^4$ the truncated two particle correlation behaves as

$$\begin{aligned} &\langle \hat{\rho}(\alpha_1, \mathbf{r}_1)\, \hat{\rho}(\alpha_2, \mathbf{r}_2) \rangle_T^{(4)} \\ &\quad = \rho_T^{(4)}(\alpha_1, \mathbf{r}_1, \alpha_2, \mathbf{r}_2) \\ &\quad \sim \frac{2}{5}\left(\frac{\beta^2}{24}\right)^2 \int d\mathbf{r} \int d\mathbf{r}'\, f(\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{r} - \mathbf{r}')\, G(\mathbf{r}, \alpha_1)\, G(\mathbf{r}', \alpha_2) \end{aligned} \tag{4.56}$$

In (4.56) $f(\mathbf{r})$ is the square of the dipole–dipole potential

$$f(\mathbf{r}) = \sum_{\mu, \nu = 1}^{3} (\partial_\mu \partial_\nu V(\mathbf{r}))^2 \tag{4.57}$$

and

$$G(\mathbf{r}, \alpha_i) = \sum_{\alpha} \frac{e_\alpha^2}{m_\alpha} \langle \hat{\rho}(\alpha, \mathbf{0})\, \hat{\rho}(\alpha_i, \mathbf{r}) \rangle_{\mathrm{cl},\, T}, \qquad i = 1, 2 \tag{4.58}$$

where $\langle \cdots \rangle_{\mathrm{cl}}$ means equilibrium average with respect to the classical reference system. Since $f(\mathbf{r}) \sim 6/|\mathbf{r}|^6$, $|\mathbf{r}| \to \infty$, the leading contribution to (4.56) is

$$\langle \hat{\rho}(\alpha_1, \mathbf{r}_1)\, \hat{\rho}(\alpha_2, \mathbf{r}_2) \rangle_T^{(4)} \sim \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|^6} \frac{\beta^4}{240} \left(\int d\mathbf{r}\, G(\mathbf{r}, \alpha_1) \right) \left(\int d\mathbf{r}\, G(\mathbf{r}, \alpha_2) \right) \tag{4.59}$$

If one examines the correlation of a particle with the total charge density $\hat{c}(\mathbf{r})$, one must replace $\hat{\rho}(\alpha, \mathbf{r})$ in one factor G by the charge $\hat{c}(\mathbf{r})$. Then the coefficient of $|\mathbf{r}_1-\mathbf{r}_2|^{-6}$ vanishes in (4.59) because of the charge sum rule (2.16), and one has to carry the asymptotic expansion of $f(r)$ further on. For the particle-charge correlation, one finds

$$\langle \hat{\rho}(\alpha_1, \mathbf{r}_1)\, \hat{c}(\alpha_2, \mathbf{r}_2)\rangle_T^{(4)} = \sum_{\alpha_2} e_{\alpha_2} \rho_T^{(4)}(\alpha_1, \mathbf{r}_1, \alpha_2, \mathbf{r}_2) \sim \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|^8} \frac{\beta^4}{16} \left(\int d\mathbf{r}\, G(\mathbf{r}, \alpha_1) \right) \left(\frac{1}{3} \int d\mathbf{r}\, |\mathbf{r}|^2\, K(\mathbf{r}) \right) \tag{4.60}$$

and for the charge–charge correlation

$$\langle \hat{c}(\alpha_1, \mathbf{r}_1)\, \hat{c}(\alpha_2, \mathbf{r}_2)\rangle_T^{(4)} = \sum_{\alpha_1, \alpha_2} e_{\alpha_1} e_{\alpha_2} \rho_T^{(4)}(\alpha_1, \mathbf{r}_1, \alpha_2, \mathbf{r}_2) \sim \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|^{10}} \frac{7\beta^4}{4} \left(\frac{1}{3} \int d\mathbf{r}\, |\mathbf{r}|^2\, K(\mathbf{r}) \right)^2 \tag{4.61}$$

with

$$K(\mathbf{r}) = \sum_\alpha \frac{e_\alpha^2}{m_\alpha} \langle \hat{\rho}(\alpha, \mathbf{0})\, \hat{c}(\mathbf{r})\rangle_{\mathrm{cl},\, T} \tag{4.62}$$

In fact, as discussed in Sections VI.A.2 and VI.A.3, the formulae (4.59), (4.60) and (4.61) become asymptotically exact for the quantum Coulomb gas in the low density limit. In this limit the functions $G(\mathbf{r})$ and $K(\mathbf{r})$ are given by their Debye–Hückel approximation.[23]

The formulae simplify in the case of the jellium when one has only one species of charges. Then there is no distinction between particle and charge correlations up to a factor e ($eG(\mathbf{r}) = K(\mathbf{r}) = (e/m)\langle \hat{c}(0)\, \hat{c}(\mathbf{r})\rangle_{\mathrm{cl},\, T}$), so (4.61) applies in all cases. Furthermore, in view of the second moment condition (1.33), the correlation at order $\hbar^4$ in the jellium behaves as

$$\rho_T^{(4)}(\mathbf{r}_1, \mathbf{r}_2) \sim \frac{7}{16\pi^2} \left(\frac{\beta}{m} \right)^2 \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|^{10}}, \qquad |\mathbf{r}_1-\mathbf{r}_2| \to \infty \tag{4.63}$$

For the jellium, (Gombert and Leger, 1994) have given the complete formula for $\rho_T^{(4)}(\mathbf{r}_1, \mathbf{r}_2)$ at the order $\hbar^4$ including the short range contributions.

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[23] Note that the exchange contributions vanish exponentially fast with $\hbar$, so leading contributions in $\hbar$ can be obtained from Maxwell–Boltzmann statistics.

Correlations involving more than two particles also have slow decays at order $\hbar^4$. For instance $\rho_T^{(4)}(\alpha_1, \mathbf{r}_1, \alpha_2, \mathbf{r}_2, \alpha_3, \mathbf{r}_3)$ decays also as $|\mathbf{r}|^{-6}$ when the particle 1 is sent to infinity, the others being kept fixed. If the three particles are taken simultaneously far apart (say, $|\mathbf{r}_1 - \mathbf{r}_2| = r$, $|\mathbf{r}_1 - \mathbf{r}_3| = ar$, $|\mathbf{r}_2 - \mathbf{r}_3| = br$, $r \to \infty$), this function decays as r^{-9}. Moreover, the four point function $\rho_T^{(4)}(\alpha_1, \mathbf{r}_1, \alpha_2, \mathbf{r}_2, \alpha_3, \mathbf{r}_3, \alpha_4, \mathbf{r}_4)$ decays only as r^{-3} when two pairs of particles are sent far away (say, $|\mathbf{r}_1 - \mathbf{r}_2|$, $|\mathbf{r}_3 - \mathbf{r}_4|$ fixed, $r = |\mathbf{r}_1 - \mathbf{r}_3| \to \infty$). This slow decay is due to the breaking of rotational invariance around the points $\mathbf{r}_1$ and $\mathbf{r}_2$ when the directions $\mathbf{r}_1 - \mathbf{r}_2$ and $\mathbf{r}_3 - \mathbf{r}_4$ are fixed. It is precisely because of rotation invariance that the pure dipolar decay r^{-3} is reduced to r^{-6} in the two point function, as in the model of Section IV.C.

We have reported on the semi-classical tails (4.59)–(4.61) in some detail with the purpose of illustrating the following points. There is definitely no exponential screening in the quantum gas, even in the high temperature phase and whatever the density may be. Moreover, in contrast with a fluid with short range forces, various types of decay laws have to be expected depending on what type of observables are concerned, and what cluster of particles are taken far apart. The occurrence of these different types of decay are due to the underlying multipolar forces displayed in the filament formalism in conjunction with the effect of screening sum rules (2.16).

We finally discuss the possible observable implications of these findings. Since the calculations pertain to the semi-classical regime, we only consider real systems under conditions that the quantum effects are small. We determine the crossover distance r_0 above which quantum algebraic tails dominate the classical behavior by equating (4.63) to the usual Debye law

$$\frac{\rho e^{-r_0/l_D}}{4\pi l_D^2 r_0} = \frac{7}{16\pi^2} \left(\frac{\beta}{m}\right)^2 \frac{\hbar^4}{r_0^{10}} \tag{4.64}$$

The classical exponential is normalized in order to obey the charge sum rule. For instance, for sodium chloride at room temperature, one finds $r_0 \sim 60 l_D$. For a white dwarf under prevailing conditions, one has $r_0 \sim 40 l_D$. In both cases, the quantum effects on the clustering turn out to be very small and the use of the Debye potential is still legitimate from a quantitative point of view. However if we apply crudely (4.64) (disregarding its semiclassical nature) to the electrons in a metal (replacing l_D by the Thomas–Fermi screening length λ_{TF}), one finds r_0 of the order of λ_{TF}. This indicates that the use of the exponential potential might be less reliable in this case.

F. Breakdown of Exponential Screening in the Quantum Sine–Gordon Representation

In this section we show how the Sine–Gordon transformation of Section II.C extends to the quantum mechanical system (Fröhlich and Park, 1978). We saw in (2.24) that the classical partition function is a Gaussian superposition of ideal gas partition functions in external fields $i\phi(\mathbf{r})$. The same holds for quantum mechanics except that one must use time dependent fields $i\phi(\mathbf{r}, s)$.

After the Sine–Gordon transformation is discussed we use it to illustrate the natural appearance of dipole forces in the quantum system and make some comparisons with classical systems of particles that simultaneously have charge and dipole moments.

We consider a quantum Coulomb system as in (1.36), but replace the Coulomb interaction (1.1) by

$$U_{\infty, L} = \tfrac{1}{2} \sum_{i, j}^{N} e_{\alpha_i} e_{\alpha_j} V_{\infty, L}(\mathbf{r}_i - \mathbf{r}_j) \tag{4.65}$$

where $V_{\infty, L}$ is the potential defined in (1.9) whose singularity at the origin is smoothed out on length scale L. Note also that self-energies are included in $U_{\infty, L}$ which simplifies the Sine–Gordon transformation, but gives rise to $\exp(\pm\beta/2L)$ discrepancies with our previous formulae. We assume $L \gg \beta$. It should be possible to reduce the $1/r$ to this case by a Mayer expansion as was done in the classical case in Section II.D because the Mayer expansion is known to converge (Brydges and Federbush, 1976; Brydges and Federbush, 1977).

From (1.40) with external field ϕ set to zero and using the Trotter product formula

$$\begin{aligned} \Xi_\Lambda &= \operatorname{Tr} P \exp(-\beta(H_{\Lambda, N} - \underline{\boldsymbol{\mu}} \cdot \underline{\mathbf{N}})) \\ &= \operatorname{Tr} P \lim_{n \to \infty} \prod_{1}^{n} \left(e^{-(\beta/n)[H^0_{\Lambda, N} - \underline{\boldsymbol{\mu}} \cdot \underline{\mathbf{N}}]} e^{-(\beta/n)\, U_{\infty, L}}\right) \end{aligned} \tag{4.66}$$

where the $H^0_{\Lambda, N}$ is the free Hamiltonian and $\underline{\boldsymbol{\mu}} \cdot \underline{\mathbf{N}} = \sum_\alpha \mu_\alpha N_\alpha$. We insert

$$e^{-(\beta/n)\, U_{\infty, L}} = \int d\mu_L(\phi)\, e^{-i(\beta/n)^{1/2} \int d\mathbf{r}\, \hat{c}(\mathbf{r})\, \phi(\mathbf{r})} \tag{4.67}$$

Each factor $e^{-(\beta/n)\, U_{\infty, L}}$ requires its own auxiliary field $\phi_i(\mathbf{r})$, $i = 1, ..., n$, so that the right hand side of (4.66) contains

$$\int d\mu_L(\phi_1) \cdots d\mu_L(\phi_n) \operatorname{Tr} P \prod_{1}^{n} \left({}^{-(\beta/n)\, H^0_{\Lambda, N}} e^{-(\beta/n)^{1/2}\, i \int d\mathbf{r}\, \hat{c}(\mathbf{r})\, \phi_j(\mathbf{r})}\right) \tag{4.68}$$

By scaling the fields $\phi_j \to n^{-1/2}\phi_j$ and uniting them into one time dependent field $\phi(\mathbf{r}, s) \equiv \phi_j(\mathbf{r})$ when $s \in [(j-1)/n, j/n)$, we obtain

$$\Xi_\Lambda = \int d^{[0,1]}\mu_L(\phi)\, \Xi_{\text{ideal}, \Lambda}(\beta^{1/2} i\phi) \tag{4.69}$$

where $\int d^{[0,1]}\mu_L(\phi)$ is the Gaussian defined by

$$\int d^{[0,1]}\mu_L(\phi)\, \phi(\mathbf{r}, s)\, \phi(\mathbf{r}', s') = \delta(s-s')\, V_{\infty, L}(\mathbf{r}-\mathbf{r}'); \qquad 0 \leqslant s \leqslant 1 \tag{4.70}$$

and

$$\Xi_{\text{ideal}, \Lambda}(\phi) = \operatorname{Tr} P \exp\left(-\int_0^1 \left(\beta H^0_{\Lambda, N} - \beta \underline{\boldsymbol{\mu}} \cdot \underline{\mathbf{N}} + \int d\mathbf{r}\, \hat{c}(\mathbf{r})\, \phi(\mathbf{r}, s) \right) ds \right) \tag{4.71}$$

is the ideal gas partition function for a time-dependent external field and the exponential is time-ordered. In the case of Boltzmann statistics, which means omitting the sum over permutations in the projection P, the trace factors over particles so that

$$\begin{aligned} &\Xi_{\text{ideal, Bolt}, \Lambda}(\beta\phi) \\ &\quad = \sum_{\{N_\alpha\}} \prod_\alpha \frac{1}{N_\alpha!} \operatorname{Tr} \exp\left(-\beta \int_0^1 \left(H^0_{\Lambda, N} - \underline{\boldsymbol{\mu}} \cdot \underline{\mathbf{N}} + \int d\mathbf{r}\, \hat{c}(\mathbf{r})\, \phi(\mathbf{r}, s) \right) ds \right) \\ &\quad = \exp\left(\sum_\alpha \operatorname{Tr} e^{-\beta \int_0^1 ds [h_\alpha(s) - \mu_\alpha]} \right) \end{aligned} \tag{4.72}$$

where $h_\alpha(s) = (\hbar^2/2m_\alpha)(-\Delta) + e_\alpha \phi(\mathbf{r}, s)$ is the one-particle Hamiltonian for species α in the time-dependent external field and the exponential is still time-ordered. Without making the simplification of Boltzmann statistics one has, instead,

$$\Xi_{\text{ideal}, \Lambda}(\beta\phi) = \exp\left(\sum_\alpha \sum_{q=1}^\infty \frac{\eta_\alpha^{q-1}}{q} \operatorname{Tr} e^{-\beta \int_0^q ds [h_\alpha(s) - \mu_\alpha]} \right) \tag{4.73}$$

where $\phi(\mathbf{r}, s)$ is extended periodically in s. This formula will be proved in Section V.A.4.

Notice that this quantum ideal gas is invariant under

$$\phi(\mathbf{r}, \tau) \to \phi(\mathbf{r}, \tau) + f(\tau) \tag{4.74}$$

where f is any function independent of $\mathbf{r}$ such that $\int_0^1 d\tau\, f(\tau) = 0$. The Gaussian $d^{[0,1]}\mu$ is also formally invariant under this transformation. This "Goldstone mode" is a signal that there are long range correlations in the ϕ field, whereas in the classical system ϕ correlations are exponentially decaying.

By the Feynman–Kac formula,

$$\begin{gathered} \Xi_{\text{ideal, Bolt}, \Lambda}(\beta\phi) = \exp\left(\int d\mathscr{F}\, z(\mathscr{F})\, e^{-\beta e_\alpha \phi(\mathscr{F})}\right) \\ \phi(\mathscr{F}) = \int_0^1 \phi(\mathbf{r} + \lambda_\alpha \xi(s), s)\, ds \end{gathered} \tag{4.75}$$

where $\mathscr{F}$, $d\mathscr{F}$ were defined in (4.11), (4.13). There is a similar formula for the ideal gas (4.73) without the Boltzmann statistics simplification and it is given in Section V.A.4. It could be used in the following considerations, but would not change the discussion in any important way. Furthermore we set the spins $s_\alpha = 0$.

When $\lambda_\alpha = 0$ the phase space integration $d\mathscr{F}$ reduces to $\sum_\alpha \int d\mathbf{r}$ and (4.75) reduces to the classical ideal gas. This suggests (Brydges and Keller, 1994a) the following model. We replace the integration $\int d\mathscr{F}$ over all Wiener paths by integration concentrated on just one kind of path which oscillates about the initial point by a distance $O(\lambda_\alpha)$ (the size of the wave packet) in a random direction: let $d\sigma(\vec{e})$ be a spherically symmetric integration on vectors $\vec{e}$. Then $\int d\mathscr{F}$ is replaced by

$$\sum_\alpha \int d\mathbf{r} \int d\sigma(\vec{e}) \tag{4.76}$$

and each $(\mathbf{r}, \vec{e})$ labels a path: $\mathbf{r} + \lambda_\alpha \xi(s)$ with $\xi(s) = \vec{e} \sin(2\pi s)$. We chose $\sin(2\pi s)$ because it is orthogonal to 1.

The consequence of this and another minor approximation (Brydges and Keller, 1994a) is that the dependence of (4.72) on $\phi(\mathbf{r}, s)$ is only through two modes

$$\phi_1(\mathbf{r}) = \int_0^1 \phi(\mathbf{r}, s)\, ds; \qquad \phi_2(\mathbf{r}) = \sqrt{2} \int_0^1 \phi(\mathbf{r}, s) \sin(2\pi s)\, ds$$

Since ϕ_1, ϕ_2 are Gaussian and $\int d^{[0,1]}\mu_L \phi_i(\mathbf{r})\, \phi_j(\mathbf{r}') = V_{\infty, L}(\mathbf{r}-\mathbf{r}')\, \delta_{ij}$, the integral $\int d^{[0,1]}\mu_L$ can be replaced by $\int d\mu_L(\phi_1) \int d\mu_L(\phi_2)$ and the partition function becomes

$$\Xi_\Lambda = \int d\mu_L(\phi_2) \int d\mu_L(\phi_1) \exp\left(\sum_\alpha e^{\beta\mu_\alpha} \int d\mathbf{r} \int d\sigma(\vec{e})\, e^{-i\beta^{1/2} e_\alpha (\phi_1 + 2^{-1/2}\lambda_\alpha \vec{e} \cdot \nabla\phi_2)} \right) \tag{4.77}$$

Notice that if $d\sigma(\vec{e})$ is set to $\delta(\vec{e})$ we revert to the classical Coulomb gas. If ϕ_1 is set to zero then by reversing the Sine–Gordon transformation we obtain the partition function of a classical dipole gas with dipole moments $\vec{e}$ distributed according to $d\sigma$. Furthermore part of the Goldstone mode (4.73) survives as

$$\phi_2(\mathbf{r}) \to \phi_2(\mathbf{r}) + \text{const} \tag{4.78}$$

If the fields $\phi = \phi_1 = \phi_2$ are set equal, this becomes exactly the Sine–Gordon transform of a classical gas of particles that are simultaneously carrying charge and a dipole moment. *But in this case the symmetry* (4.78) *no longer holds and the methods of Section* II *prove that correlations decay exponentially near the Debye–Hüclem limit.*

Indeed consider the Debye–Hückel approximation wherein the exponent in (4.77) is replaced by the quadratic approximation

$$\begin{aligned} Q &= -\tfrac{1}{2} \sum_\alpha e^{\beta\mu_\alpha} \int d\mathbf{r} \int d\sigma(\vec{e}) (\beta^{1/2} e_\alpha \phi + (\beta/2)^{1/2}\, e_\alpha \lambda_\alpha \vec{e} \cdot \nabla\phi)^2 \\ &= -\tfrac{1}{2} \sum_\alpha \beta e_\alpha^2 e^{\beta\mu_\alpha} \int d\mathbf{r} (\phi^2 + \tfrac{1}{6} (\lambda_\alpha \nabla\phi)^2) \end{aligned} \tag{4.79}$$

The Gaussian $d\mu_L \exp(-Q)$ has a covariance whose Fourier transform is

$$4\pi(\mathbf{k}^2 + L^2\mathbf{k}^4 + l_D^{-2} + a\mathbf{k}^2)^{-1} \tag{4.80}$$

where $l_D^{-2} = 4\pi \sum_\alpha \beta e_\alpha^2 e^{\beta\mu_\alpha}$ and $a = 4\pi \sum_\alpha \beta e_\alpha^2 \lambda_\alpha^2 e^{\beta\mu_\alpha}$. There is no pole for any real $\mathbf{k}$ which indicates exponential decay of all correlations. It has been wrongly said (Martin, 1988, Section II.G) that classical ions with structure might have weaker screening properties than pure charges. The present discussion shows that such systems have Debye screening near the Debye–Hückel limit.

The model defined by (4.76) and (4.77) exemplifies again that the breakdown of exponential screening is really due to quantum mechanics, manifested here by the existence of the two fields ϕ_1 and ϕ_2 (and more generally by the time-dependent field $\phi(\mathbf{r}, s)$ in the Sine–Gordon representation). Reconsider indeed that $\phi_1 \neq \phi_2$ are independent Gaussian fields. The quadratic approximation is misleading here because the cross-terms coupling ϕ_1, ϕ_2 are lost in this approximation but they are present at cubic and higher order in (4.77). In (Brydges and Keller, 1994a) it is argued that these higher order couplings allow the long range correlations of ϕ_2 to creep into the correlations of both ϕ_1 and ϕ_2. This gives an alternative but more qualitative derivation of the no-screening results. The massive zero frequency field ϕ_1 mediates (parts of) the electrostatic potential V_{cl} defined in (4.23) whereas the non-zero frequency field ϕ_2 mediates (part of) the non-electrostatic part W defined in (4.25) that cannot be screened.

All these discussions show that screening is destroyed because lack of commutativity of momentum and position bring time dependent phenomena in through the back door (e.g., the imaginary time ordering mentioned below (4.71)). It is in fact easy to prove that imaginary time dependent observables are not screened (Brydges and Seiler, 1986).

We should also mention that another class of semiclassical models has been introduced, to deal with polarizability effects in dielectrics (Høye and Stell, 1981; Brevik and Høye, 1988). In these models, internal atomic degrees of freedom are treated quantum mechanically (e.g., harmonically bound pairs of charges) while the center of mass of atoms behave in a classical manner with pair-wise dipolar forces. These models capture physically interesting effects but do not incorporate all the effects stemming from the Coulomb potential (binding, ionization, collective screening) in an equally consistent and fundamental footing. Hopefully the loop formalism developed in Section V does provide a way to treat all these effects in a fully coherent way.

V. THE GAS OF CHARGED LOOPS

A. The Statistical Mechanics of Loops

1. The Magic Formula. We are ready to develop the general Feynman–Kac representation of the Coulomb gas. The first step (Section V.A) is to include the Fermi statistics of the electrons and the Bose or Fermi statistics of the nuclei. This can be done with some combinatorial effort by a rearrangement of the sums in the partition function (1.40), leading to the "magic formula" (5.16), that has a marvelous effect: as in the preceding section, the gas appears as a classical-like assembly of extended objects, the charged loops, and the diagrammatic techniques of classical statistical mechanics will apply. The magic formula has been known at least implicitly for a long time, starting from (Ginibre, 1965), see also (Ginibre, 1971). A combinatorial proof of it, following the lines of (Ginibre, 1965) can be found in (Cornu, 1996a). It has been also retrieved recently in (Hóye and Stell, 1994). In Subsection V.A.4 we give the main lines of a derivation that does not make use of combinatorial arguments. From now on, $V(\mathbf{r}_1-\mathbf{r}_2)=1/|\mathbf{r}_1-\mathbf{r}_2|$ is the exact Coulomb potential on all scales: a short range regularization is no more needed sience the latter is henceforth provided by quantum mechanics that will be now fully taken into account.

The rest of the chapter is devoted to the development of a Mayer diagrammatic for this system, following mainly (Cornu, 1996a). In Section V.B the monopole and multipole interactions are singled out in close analogy to what was done in Section IV.B, in order to isolate the part $W(\mathscr{L}_1, \mathscr{L}_2)$ (5.36) that will ultimately be responsible for the non-exponential decay. Then, following the classical treatment of Coulomb divergences, one sums the Coulomb chains, providing thus the screening length κ^{-1} (5.56) (a comparison of this screening length with that of the standard RPA theory is postponed to Section VI.A.4). Finally in Section V.B.3 the class of resummed diagrams is reorganized in prototype graphs involving four types of bonds. Prototype graphs are finite, decay at least as r^{-3} at large separation and will serve as the starting point of low density calculations. The content of this chapter as well as the next one is mathematically formal since nothing is known about the asymptotic nature of the infinite series of prototype diagrams.

We now come back to the partition function (1.40). We first represent the matrix element in (1.40) by a Feynman–Kac integral. Since $H_{\Lambda,N}$ is independent of the spins, the spin scalar product $\prod_{i=1}^{N}\langle\sigma_{\alpha_{p(i)}}\mid\sigma_{\alpha_i}\rangle$ factorizes out in this matrix element, and according to (4.6) its positional part is represented by the functional integral

$$\begin{aligned}\langle\{\mathbf{r}_{p(i)}\}\mid\exp(-\beta H_{\Lambda,N})\mid\{\mathbf{r}_i\}\rangle\\ =\prod_{i=1}^{N}\left(\frac{1}{2\pi\lambda_{\alpha_i}^2}\right)^{3/2}\exp\left(-\frac{|\mathbf{r}_{p(i)}-\mathbf{r}_i|^2}{2\lambda_{\alpha_i}^2}\right)\\ \times\int\prod_{i=1}^{N}D(\xi_i)\exp\left(-\frac{\beta}{2}\sum_{i\neq j}^{N}e_{\alpha_i}e_{\alpha_j}\int_0^1 ds\, V(\mathbf{r}_{i,\,p(i)}(s)-\mathbf{r}_{j,\,p(j)}(s))\right)\end{aligned}\tag{5.1}$$

We have kept the notation (4.4) for a path with extremities $\mathbf{r}_{i,\,p(i)}(s=0)=\mathbf{r}_i$ and $\mathbf{r}_{i,\,p(i)}(s=1)=\mathbf{r}_{p(i)}$

$$\mathbf{r}_{i,\,p(i)}(s)=(1-s)\,\mathbf{r}_i+s\,\mathbf{r}_{p(i)}+\lambda_{\alpha_i}\xi_i(s)\tag{5.2}$$

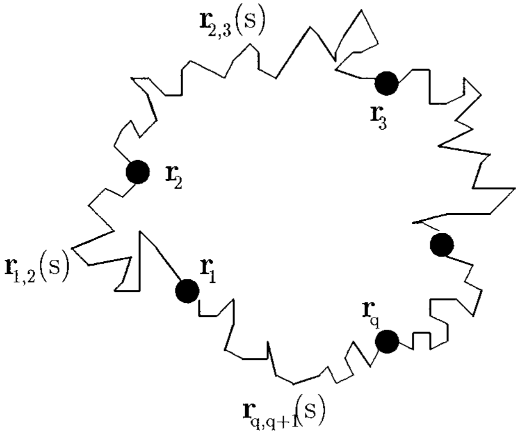

Fig. 1. A q particle loop.

The same remark made after (4.9) concerning the implementation of the boundary conditions remains valid: all paths are constrained to stay inside Λ.

The main observation to be made at this point is that by a rearrangement of the sums, the partition function (1.40) can be formally written in the same classical form as (4.12), provided that one introduces a suitably enlarged phase space. This rearrangement exploits the fact that any permutation can uniquely be decomposed into a product of cycles. A cycle of length q, $1 \leqslant q \leqslant N_\alpha$, is a subset of the N_α particle indices that are permuted among themselves in a cyclic way under p_α, for instance

$$(1, 2,..., q-1, q) \to (2, 3,..., q, 1) \tag{5.3}$$

The objects constituting the enlarged phase space are precisely associated with such cycles in the following way. The permutations p in (5.1) involve now open paths (except for the trivial one). However the set of open paths belonging to a cycle of q elements occurring in p can be joined together to form a closed loop $\mathscr{L}$ (sometimes also called a polymer) with q particle coordinates. The loop $\mathscr{L}$ corresponding to the cycle (5.3) is made of the collection of paths $\{\mathbf{r}_{k,k+1}(s)\}_{k=1,...,q}$, with $q+1$ identified to 1 (see Fig. 1).

Thus a loop is specified by the variables

$$(\alpha, q, \{\mathbf{r}_k\}_{k=1,...,q}, \{\xi_k\}_{k=1,...,q}) \tag{5.4}$$

It is convenient to unite the q filaments constituting the loop into a single path parameterized by a time parameter s running from 0 to q setting

$$\mathbf{R}(s)=\mathbf{r}_{k,\,k+1}(\tilde{s}), \qquad k=[s]+1, \qquad 0\leqslant s\leqslant q \tag{5.5}$$

where $[s]=$ integer part of s and $\tilde{s}=s\ (\mathrm{mod}1)=s-[s]$. One can then locate the loop at $\mathbf{R}$ by selecting the position of one of the particles, say $\mathbf{r}_1=\mathbf{R}$, and write

$$\mathbf{R}(s)=\mathbf{R}+\lambda_\alpha \mathbf{X}(s), \qquad \mathbf{X}(0)=\mathbf{X}(q)=0 \tag{5.6}$$

Then the particles are located at the points

$$\mathbf{r}_k=\mathbf{R}+\lambda_\alpha \mathbf{X}_k, \qquad \mathbf{X}_k=\mathbf{X}(k-1) \tag{5.7}$$

In (5.6), $\mathbf{X}(s)$ is the shape of the loop $\mathscr{L}$ at $\mathbf{R}$, as $\xi(s)$ was describing the shape of a filament at $\mathbf{r}$: it is again a dimensionless Brownian bridge starting and returning to the origin within the time q. Its normalized Gaussian measure $D(\mathbf{X})$ is the composition of that of the q open filaments that constitute the loop (see (4.6))

$$D(\mathbf{X})=(2\pi q)^{3/2}\prod_{k=1}^{q}\frac{\exp(-\frac{1}{2}(\mathbf{X}_{k+1}-\mathbf{X}_k)^2)}{(2\pi)^{3/2}}\,d\mathbf{X}_2\cdots d\mathbf{X}_q\,D(\xi_1)\cdots D(\xi_q) \tag{5.8}$$

where one sets $\mathbf{X}_1=\mathbf{X}_{q+1}=0$. One can calculate its covariance from the definitions (5.5)–(5.6)

$$\int D(\mathbf{X})\,X_\mu(s_1)\,X_\nu(s_2)=\delta_{\mu\nu}q\left[\min\left(\frac{s_1}{q},\frac{s_2}{q}\right)-\frac{s_1}{q}\frac{s_2}{q}\right] \tag{5.9}$$

Thus one can think of a loop $\mathscr{L}$ either as a set of particle coordinates (as in (5.4)) or again as a single Brownian path, setting

$$\mathscr{L}=(\alpha,q,\mathbf{R},\mathbf{X}(s),0\leqslant s\leqslant q) \tag{5.10}$$

It is now possible, generalizing also (4.14)–(4.16), to define activities and interactions of loops. The interaction between two loops $\mathscr{L}_i$, $i=1,2$, is the sum of those of the particles constituting the two loops

$$\begin{aligned}V(\mathscr{L}_1,\mathscr{L}_2)&=\sum_{k_1=1}^{q_1}\sum_{k_2=1}^{q_2}\int_0^1 ds\,V(\mathbf{r}_{1,k_1,k_1+1}(s)-\mathbf{r}_{2,k_2,k_2+1}(s))\\&=\int_0^{q_1}ds_1\int_0^{q_2}ds_2\,\delta(\tilde{s}_1-\tilde{s}_2)\,V(\mathbf{R}_1+\lambda_{\alpha_1}\mathbf{X}_1(s_1)-\mathbf{R}_2-\lambda_{\alpha_2}\mathbf{X}_2(s_2))\end{aligned} \tag{5.11}$$

and for n loops

$$U(\mathscr{L}_1,..., \mathscr{L}_n)=\sum_{1=i<j}^{n} e_{\alpha_i} e_{\alpha_j} V(\mathscr{L}_i, \mathscr{L}_j) \tag{5.12}$$

The activity $z(\mathscr{L})$ of a loop incorporates the effects of quantum statistics, the spin degeneracy as well as the internal interaction $U(\mathscr{L})$ of the particles in the same loop

$$z(\mathscr{L})=(2s_\alpha+1)\,\frac{(\eta_\alpha)^{q-1}}{q}\,\frac{\exp(\beta\mu_\alpha q)}{(2\pi q\lambda_\alpha^2)^{3/2}}\exp(-\beta U(\mathscr{L})) \tag{5.13}$$

with

$$\begin{aligned} U(\mathscr{L}) &= \frac{e_\alpha^2}{2}\sum_{k\neq k'}^{q}\int_0^q ds\; V(\mathbf{r}_{k,k+1}(s)-\mathbf{r}_{k',k'+1}(s)) \\ &= \frac{e_\alpha^2}{2}\int_0^q ds_1\int_o^q ds_2(1-\delta_{[s_1],[s_2]})\,\delta(\tilde{s}_1-\tilde{s}_2)\;V(\lambda_\alpha(\mathbf{X}(s_1)-\mathbf{X}(s_2))) \end{aligned} \tag{5.14}$$

Clearly, all the above quantities are invariant under cyclic permutations of the particles in the same loop. Notice also that particles in the same loop have the same charge; thus their mutual Coulomb interactions are positive and this implies the bound

$$|z(\mathscr{L})|\leqslant\frac{2s_\alpha+1}{q}\,\frac{\exp(\beta\mu_\alpha q)}{(2\pi q\lambda_\alpha^2)^{3/2}} \tag{5.15}$$

Considering now the phase space of loops together with the above definitions, it can be shown (see Section V.A.4) that the partition function can be written in the same form as (4.12) (*the magic formula*)

$$\Xi_\Lambda=\sum_{n=0}^{\infty}\frac{1}{n!}\int\prod_{i=1}^{n} d\mathscr{L}_i\, z(\mathscr{L}_i)\exp(-\beta U(\mathscr{L}_1,..., \mathscr{L}_n)) \tag{5.16}$$

where the phase space integration means here

$$\int d\mathscr{L}\cdots=\sum_{\alpha=1}^{\mathscr{S}}\sum_{q=1}^{\infty}\int_\Lambda d\mathbf{R}\int D(\mathbf{X}) \tag{5.17}$$

We call the system defined by the relations (5.9)–(5.17) the "system of loops."[24] It reduces to the system of filaments (i.e., charges with Maxwell–Boltzmann statistics) if all loops with more than one particle are omitted. This view of the quantum Coulomb system as a gas of loops is well-suited to the low density regime, when loops remain well localized objects.

2. Loop and Particle Correlations. It is clear that the statistical mechanical system of loops defined by the above relations has a classical structure. Therefore, introducing the "δ-function" which identifies two loops,

$$\delta(\mathscr{L}_1, \mathscr{L}_2) = \delta_{\alpha_1, \alpha_2} \delta_{q_1, q_2} \delta(\mathbf{R}_1 - \mathbf{R}_2)\, \delta(\mathbf{X}_1, \mathbf{X}_2) \tag{5.18}$$

one can define the density of loops $\rho(\mathscr{L})$ and the two loop distribution function $\rho(\mathscr{L}_1, \mathscr{L}_2)$ by the formulae (4.18)–(4.19) with $\mathscr{L}$ replacing $\mathscr{F}$.

In order to obtain the particle distributions from those of the loops, some care has to be exercised because loops are constituted of several particles. For a configuration of particles distributed on a set of loops $\mathscr{L}_i$, we can write the particle density and distributions as a summation on the loop index i

$$\hat{\rho}(\alpha, \mathbf{r}) = \sum_i \delta_{\alpha_i, \alpha} \sum_{k=1}^{q_i} \delta(\mathbf{r}_{(k, i)} - \mathbf{r}) \tag{5.19}$$

where, according to (5.7), $\mathbf{r}_{(k, i)} = \mathbf{R}_i + \lambda_{\alpha_i} \mathbf{X}_i(k-1)$, $k = 1,..., q_i$ are the positions of the particles belonging to the loop i. For $\mathbf{r}_a \neq \mathbf{r}_b$ one writes also

$$\begin{aligned}\hat{\rho}(\alpha_a, \mathbf{r}_a)\, \hat{\rho}(\alpha_b, \mathbf{r}_b) = {} & \sum_{i \neq j} \delta_{\alpha_i, \alpha_a} \delta_{\alpha_j, \alpha_b} \sum_{k=1}^{q_i} \sum_{k'=1}^{q_j} \delta(\mathbf{r}_{(k, i)} - \mathbf{r}_a)\, \delta(\mathbf{r}_{(k', j)} - \mathbf{r}_b) \\ & + \delta_{\alpha_a, \alpha_b} \sum_i \delta_{\alpha_i, \alpha_a} \sum_{k \neq k'}^{q_i} \delta(\mathbf{r}_{(k, i)} - \mathbf{r}_a)\, \delta(\mathbf{r}_{(k', i)} - \mathbf{r}_b)\end{aligned} \tag{5.20}$$

In (5.19) and (5.20), k (k') runs on particles belonging to the same loop. The first term in (5.20) refers to particles in different loops and the second term to particles within the same loop. Then a comparison between the

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[24] Our definitions of the weight of a loop (5.8), the activity (5.13) and the self-energy (5.14) differ slightly from those found in (Cornu, 1996a). It is natural to define the loop measure (5.8) again as that of the Brownian bridge process in time $[0, q]$.

density of loops $\hat{\rho}(\mathscr{L})=\sum_i \delta(\mathscr{L}_i, \mathscr{L})$ and the particle density (5.19) shows that

$$\hat{\rho}(\alpha, \mathbf{r})=\sum_{q=1}^{\infty} \int d\mathbf{R} \int D(\mathbf{X}) \sum_{k=1}^{q} \delta(\mathbf{r}_k-\mathbf{r})\, \hat{\rho}(\mathscr{L}) \tag{5.21}$$

Taking the average of the above relation on the ensemble of loops gives the number density

$$\rho(\alpha, \mathbf{r})=\sum_{q=1}^{\infty} q \int D(\mathbf{X})\, \rho(\alpha, q, \mathbf{r}, \mathbf{X}) \tag{5.22}$$

where $\rho(\alpha, q, \mathbf{r}, \mathbf{X})=\rho(\mathscr{L})$ with $\mathscr{L}=(\alpha, q, \mathbf{r}, \mathbf{X})$. We have used the fact that $\rho(\mathscr{L})$ is invariant under cyclic permutations of the q particles in the loop. The two particle distributions are obtained by averaging the relation (5.20) where we distinguish again between pairs belonging to different loops or exchanged in the same loop ($\mathbf{r}_a \neq \mathbf{r}_b$)

$$\rho(\alpha_a, \mathbf{r}_a, \alpha_b, \mathbf{r}_b)=\rho^{(nex)}(\alpha_a, \mathbf{r}_a, \alpha_b, \mathbf{r}_b)+\delta_{\alpha_a, \alpha_b}\, \rho^{(ex)}(\alpha_a, \mathbf{r}_a, \mathbf{r}_b) \tag{5.23}$$

with

$$\begin{aligned}\rho^{(nex)}&(\alpha_a, \mathbf{r}_a, \alpha_b, \mathbf{r}_b)\\ &=\sum_{q_a=1}^{\infty} \sum_{q_b=1}^{\infty} q_a q_b \int D(\mathbf{X}_a) \int D(\mathbf{X}_b)\, \rho(\alpha_a, q_a, \mathbf{r}_a, \mathbf{X}_a; \alpha_b, q_b, \mathbf{r}_b, \mathbf{X}_b)\end{aligned} \tag{5.24}$$

and

$$\rho^{(ex)}(\alpha_a, \mathbf{r}_a, \mathbf{r}_b)=\sum_{q=2}^{\infty} \int d\mathbf{R} \int D(\mathbf{X}) \sum_{k \neq k'}^{q} \delta(\mathbf{r}_k-\mathbf{r}_a)\, \delta(\mathbf{r}_{k'}-\mathbf{r}_b)\, \rho(\alpha_a, q, \mathbf{R}, \mathbf{X}) \tag{5.25}$$

For a translation invariant state ($\rho(\alpha, q, \mathbf{R}, \mathbf{X})$ independent of $\mathbf{R}$), one has, using (5.7)

$$\begin{aligned}\rho^{(ex)}(\alpha_a, \mathbf{r}_a, \mathbf{r}_b)&=\sum_{q=2}^{\infty} \int D(\mathbf{X}) \sum_{k \neq k'}^{q} \delta(\lambda_{\alpha_a}(\mathbf{X}_k-\mathbf{X}_{k'})+\mathbf{r}_b-\mathbf{r}_a)\, \rho(\alpha_a, q, \mathbf{X})\\ &=\sum_{q=2}^{\infty} \int D(\mathbf{X})\, q \sum_{k=2}^{q} \delta(\lambda_{\alpha_a} \mathbf{X}_k+r_b-\mathbf{r}_a)\, \rho(\alpha_a, q, \mathbf{X})\end{aligned} \tag{5.26}$$

The second line follows again from the invariance of $\rho(\alpha_a, q, \mathbf{X})$ under cyclic permutations of the particles in the loop.

One can also write the corresponding similar representations for the truncated distributions.

3. Loop Interactions. The same fundamental observation made for the system of filaments remains valid here: the interaction (5.11) is not the standard electrostatic Coulomb energy of two charged loops, which would be

$$V_{\mathrm{cl}}(\mathcal{L}_1, \mathcal{L}_2) = \int_0^{q_1} ds_1 \int_0^{q_2} ds_2\; V(\mathbf{R}_1 + \lambda_{\alpha_1} \mathbf{X}_1(s_1) - \mathbf{R}_2 - \lambda_{\alpha_2} \mathbf{X}_2(s_2)) \qquad (5.27)$$

and the discussion following (4.23) can be reproduced word by word. In particular, the Coulomb potential has the multipolar expansion

$$\begin{aligned} &V(\mathbf{R}_1 + \lambda_{\alpha_1} \mathbf{X}_1(s_1) - \mathbf{R}_2 - \lambda_{\alpha_2} \mathbf{X}_2(s_2)) \\ &\quad = V(\mathbf{R}_1 - \mathbf{R}_2) + M_1(s_1)\, V(\mathbf{R}_1 - \mathbf{R}_2) + M_2(s_2)\, V(\mathbf{R}_1 - \mathbf{R}_2) \\ &\qquad + M_1(s_1)\, M_2(s_2)\, V(\mathbf{R}_1 - \mathbf{R}_2) \end{aligned} \qquad (5.28)$$

with now

$$M_i(s) = \sum_{k=1}^{\infty} \frac{(\lambda_{\alpha_i} \mathbf{X}_i(s) \cdot \nabla_{\mathbf{R}_i})^k}{k!}, \qquad i = 1, 2 \qquad (5.29)$$

and hence the loop interaction can be decomposed into its charge–charge, charge–multipole and multipole–multipole components

$$\begin{aligned} V(\mathcal{L}_1, \mathcal{L}_2) = {} & V_{cc}(\mathcal{L}_1, \mathcal{L}_2) + V_{cm}(\mathcal{L}_1, \mathcal{L}_2) \\ & + V_{mc}(\mathcal{L}_1, \mathcal{L}_2) + V_{mm}(\mathcal{L}_1, \mathcal{L}_2) \end{aligned} \qquad (5.30)$$

$$V_{cc}(\mathcal{L}_1, \mathcal{L}_2) = q_1 q_2\, V(\mathbf{R}_1 - \mathbf{R}_2) \qquad (5.31)$$

$$V_{cm}(\mathcal{L}_1, \mathcal{L}_2) = q_1 \int_0^{q_2} ds_2\, M_2(s_2)\, V(\mathbf{R}_1 - \mathbf{R}_2) \qquad (5.32)$$

$$V_{mc}(\mathcal{L}_1, \mathcal{L}_2) = q_2 \int_0^{q_1} ds_1\, M_1(s_1)\, V(\mathbf{R}_1 - \mathbf{R}_2) \qquad (5.33)$$

$$V_{mm}(\mathcal{L}_1, \mathcal{L}_2) = \int_0^{q_1} ds_1 \int_0^{q_2} ds_2\, \delta(\tilde{s}_1 - \tilde{s}_2)\, M_1(s_1)\, M_2(s_2)\, V(\mathbf{R}_1 - \mathbf{R}_2) \qquad (5.34)$$

The relevant quantity which will again embody the long range effects is the difference between the quantum and classical interaction

$$W(\mathscr{L}_1, \mathscr{L}_2) = e_{\alpha_1} e_{\alpha_2} (V(\mathscr{L}_1, \mathscr{L}_2) - V_{\text{cl}}(\mathscr{L}_1, \mathscr{L}_2)) \tag{5.35}$$

It depends only on the multipole-multipole part of the interaction as in (4.29)

$$W(\mathscr{L}_1, \mathscr{L}_2) = e_{\alpha_1} e_{\alpha_2} \int_0^{q_1} ds_1 \int_0^{q_2} ds_2 (\delta(\tilde{s}_1 - \tilde{s}_2) - 1)\, M_1(s_1)\, M_2(s_2)\, V(\mathbf{R}_1 - \mathbf{R}_2) \tag{5.36}$$

and has the asymptotic dipolar character (4.30) as $|\mathbf{R}_1 - \mathbf{R}_2| \to \infty$

$$\begin{aligned} W(\mathscr{L}_1, \mathscr{L}_2) \sim e_{\alpha_1} e_{\alpha_2} \int_0^{q_1} ds_1 \int_0^{q_2} ds_2 (\delta(\tilde{s}_1 - \tilde{s}_2) - 1)(\lambda_{\alpha_1} \mathbf{X}_1(s_1) \cdot \nabla_{\mathbf{R}_1}) \\ \times (\lambda_{\alpha_2} \mathbf{X}_2(s_2) \cdot \nabla_{\mathbf{R}_2})\, V(\mathbf{R}_1 - \mathbf{R}_2) \end{aligned} \tag{5.37}$$

4. Derivation of the Magic Formula. We derive first the formula (5.16) in the special case where there is an external field $\phi(\mathbf{r})$ and no two-body interaction. In this case the magic formula is essentially the same as (4.73).

It is enough to consider just one species with charge e_α and spin s_α because the partition function factors. In terms of annihilation and creation operators $\hat{a}_\sigma(\mathbf{r})$, $\hat{a}_\sigma^*(\mathbf{r})$ the many-body Hamiltonian for the external field case is

$$H_\alpha = \sum_\sigma \int \hat{a}_\sigma^*(\mathbf{r})\, h_\alpha \hat{a}_\sigma(\mathbf{r})\, d\mathbf{r}; \qquad h_\alpha = \frac{\hbar^2}{2m_\alpha}(-\Delta) + e_\alpha \phi \tag{5.38}$$

We begin with the averaged particle number

$$\langle N \rangle = \frac{d}{d(\beta\mu)} \ln \Xi_\Lambda = \frac{1}{\Xi_\Lambda} \sum_\sigma \int d\mathbf{r}\, \mathrm{Tr}(\hat{a}_\sigma^*(\mathbf{r})\, \hat{a}_\sigma(\mathbf{r})\, e^{-\beta(H_\alpha - \mu N)})$$

$$N = \sum_\sigma \int \hat{a}_\sigma^*(\mathbf{r})\, \hat{a}_\sigma(\mathbf{r})\, d\mathbf{r}; \qquad \Xi_\Lambda = \mathrm{Tr}\, e^{-\beta(H_\alpha - \mu N)} \tag{5.39}$$

The canonical commutation relations for the annihilation and creation operators $\hat{a}_\sigma(\mathbf{r})$, $\hat{a}_\sigma^*(\mathbf{r})$ imply that

$$\hat{a}_\sigma(\mathbf{r})\, e^{-\beta H_\alpha} = e^{-\beta H_\alpha} \int e^{-\beta h_\alpha}(\mathbf{r}, \mathbf{r}')\, \hat{a}_\sigma(\mathbf{r}')\, d\mathbf{r}' \tag{5.40}$$

where $\exp(-\beta h_\alpha)(\mathbf{r}, \mathbf{r}')$ is the kernel of the operator $\exp(-\beta h_\alpha)$. Inserting this relation in (5.39), using the cyclicity of the trace and the canonical commutation relations gives

$$\frac{d}{d(\beta\mu)} \ln \Xi_\Lambda = \sum_{q=1}^{\infty} \eta^{q-1} \operatorname{Tr} e^{-q\beta[h_\alpha - \mu]} \tag{5.41}$$

where Tr is now the one-particle trace and it includes the sum over spin. In the case of zero external field this is the standard formula for the density of an ideal Bose or Fermi gas by summing the geometric series.

Integrating (5.41) from $-\infty$ to $\beta\mu$ yields

$$\Xi_\Lambda = \exp\left(\sum_{q=1}^{\infty} \frac{\eta^{q-1}}{q} \operatorname{Tr} e^{-q\beta[h_\alpha - \mu]} \right) \tag{5.42}$$

If we replace q in the exponent by $\int_0^q \cdots ds$ and time-order the exponential then this formula and our derivation remain valid for a periodic time-dependent external field $\phi(\mathbf{r}, s)$, and we obtain (4.73).

The "magic formula" in the case of external field, no two-body interaction and one particle species follows by substituting in the Feynman–Kac representation

$$\begin{gathered} \sum_{q=1}^{\infty} \frac{\eta^{q-1}}{q} \operatorname{Tr} e^{-\beta \int_0^q [h_\alpha(s) - \mu]\, ds} = \int d\mathscr{L}\, z(\mathscr{L})\, e^{-\beta e_\alpha \phi(\mathscr{L})} \\ \phi(\mathscr{L}) = \int_0^q \phi(\mathbf{R}(s), s)\, ds \end{gathered} \tag{5.43}$$

where we use the notation described in Subsection V.A.1.

The "magic formula" (5.16) in the case of two-body interactions follows by integrating over imaginary time-dependent fields $i\phi(\mathbf{r}, s)$ with a Gaussian measure. According to our discussion of the quantum Sine–Gordon transform in Section IV.F this reconstructs the two-body interaction with self-energies. The formulas (5.13), (5.14) follow by absorbing the self-energies into the activities.

B. The Loop Mayer Expansion

1. The Loop Ursell Function. Since the system of loops has a classical structure, it can be treated by the well known methods of classical statistical mechanics. In this section we apply the standard techniques of the virial expansion to the two-point Ursell function $h(\mathcal{L}_a, \mathcal{L}_b)$ together with the partial resummations needed to deal with the long range of the Coulomb potential.

The Ursell function is defined in terms of the two-loops truncated distribution $\rho_T(\mathcal{L}_a, \mathcal{L}_b)$ by

$$\rho_T(\mathcal{L}_a, \mathcal{L}_b) = \rho(\mathcal{L}_a)\, \rho(\mathcal{L}_b)\, h(\mathcal{L}_a, \mathcal{L}_b) \tag{5.44}$$

Although loops are extended objects, we still call them "points" and represent them graphically by points in the diagrammatic language. The non-integrated loop variables $\mathcal{L}_a$, $\mathcal{L}_b$ are called root points. We recall that the Ursell function has the following simple loop-density expansion (Hansen and McDonald, 1976)

$$h(\mathcal{L}_a, \mathcal{L}_b) = \sum_{\Gamma} \frac{1}{S_\Gamma} \int \prod_{n=1}^{N} d\mathcal{L}_n\, \rho(\mathcal{L}_n) \left[\prod f \right]_\Gamma \tag{5.45}$$

In (5.45), the sum runs over all unlabeled topologically different connected diagrams Γ with two root points $\mathcal{L}_a$, $\mathcal{L}_b$ and N internal points $N = 0$, 1, 2,..., without articulations (an articulation point is such that, when removed, the diagram splits into two pieces, at least one of which is disconnected from any root point). To each bond $(\mathcal{L}_i, \mathcal{L}_j)$ in the diagram is associated the Mayer factor (called f-bond)

$$f(\mathcal{L}_i, \mathcal{L}_j) = \exp(-\beta_{i,j} V(\mathcal{L}_i, \mathcal{L}_j)) - 1, \qquad \beta_{i,j} = \beta e_{\alpha_i} e_{\alpha_j} \tag{5.46}$$

and $[\prod f]_\Gamma$ is the product of all f-bonds in the Γ-diagram; the symmetry factor S_Γ is the number of permutations of internal points $\mathcal{L}_n$ that leave this product invariant.

It is clear from (5.30) and (5.31) that the loop potential $V(\mathcal{L}_i, \mathcal{L}_j)$ is Coulombic at large distances, so that the bond (5.46) is not integrable. In the classical case it is known that by resumming appropriate classes of graphs (the convolution chains leading to the Debye–Hückel potential), one can introduce new bonds and diagrams (the prototype diagrams) that are free of divergences. One applies here the same procedure to the quantum gas in the loop formalism. The main guidance comes from the fact that the pure monopole part (5.31) would lead to Debye screening. Therefore the subsequent operations aim at disentangling the monopole from the multipolar effects, and then extracting as much classical screening as possible in order to reduce the range of the interaction. When all these steps are completed, no bond will decay lower than $|\mathbf{r}|^{-3}$, thus converting the gas of Coulombic loops into a certain gas of dipoles (together with higher order multipoles).

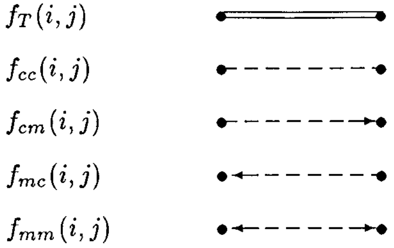

Fig. 2. Graphical definitions for bonds.

2. Summing the Coulomb Chains. The basic f-bond (5.46) is split into the sum of five contributions according to

$$f = f_T + f_{cc} + f_{cm} + f_{mc} + f_{mm} \tag{5.47}$$

with the following analytical and graphical definitions (Fig. 2) (abbreviating $f(\mathscr{L}_i, \mathscr{L}_j) = f(i, j)$)

$$f_T(i, j) = f(i, j) + \beta_{i,j} V(i, j) \tag{5.48}$$

$$f_{cc}(i, j) = -\beta_{i,j} V_{cc}(i, j) \tag{5.49}$$

$$f_{cm}(i, j) = -\beta_{i,j} V_{cm}(i, j) \tag{5.50}$$

$$f_{mc}(i, j) = -\beta_{i,j} V_{mc}(i, j) \tag{5.51}$$

$$f_{mm}(i, j) = -\beta_{i,j} V_{mm}(i, j) \tag{5.52}$$

Then, the Ursell function is given by the same formula as (5.45), summing now diagrams $\tilde{\Gamma}$ with the same topological structure as the Γ-diagrams, but where the bonds can be any one of the quantities (5.48)–(5.52). Points without arrows in a $\tilde{\Gamma}$-diagram and to which are attached only two dashed lines are called Coulomb points (Fig. 3). A Coulomb point involves only interactions with the total charge qe_α of the loop (considered as a point like object) without multipolar effects.

A Coulomb chain is a convolution chain where all intermediate points are Coulomb points. There are four types of Coulomb chains associated with the four bonds (5.49)–(5.52) (Coulomb chains without intermediate points are defined as the bonds themselves). As in the classical theory, we

Fig. 3. A Coulomb point.

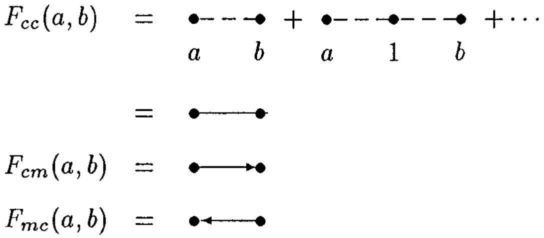

Fig. 4. Resummed Coulomb chains.

sum all Coulomb chains of a given type, and denote these sums F_{cc}, F_{cm}, F_{mc}, F_{mm} (Figs. 4 and 5). One has

$$F_{cc}(\mathscr{L}_a, \mathscr{L}_b) = f_{cc}(\mathscr{L}_a, \mathscr{L}_b) + \sum_{N=1}^{\infty} \int \prod_{i=1}^{N} d\mathscr{L}_i\, \rho(\mathscr{L}_i)\, f_{cc}(\mathscr{L}_a, \mathscr{L}_1)\, f_{cc}(\mathscr{L}_1, \mathscr{L}_2) \cdots f_{cc}(\mathscr{L}_N, \mathscr{L}_b) \tag{5.53}$$

Since by (5.31) $f_{cc}(\mathscr{L}_i, \mathscr{L}_j) = -\beta_{i,j} q_i q_j V(\mathbf{R}_i - \mathbf{R}_j)$ does not depend on the configurations $\mathbf{X}_i$, $\mathbf{X}_j$ of the loops, the summation on the internal variables can immediately be performed, giving a factor $\sum_\alpha \sum_q \int D(\mathbf{X})\, q^2 e_\alpha^2 \rho(\alpha, q, \mathbf{X})$ for each intermediate point in (5.53). Because of translation invariance the loop-density $\rho(\mathscr{L}) = \rho(\alpha, q, \mathbf{X})$ does not depend on the location $\mathbf{R}$ of the loop, therefore the multiple convolution (5.53) in the $\mathbf{R}$ variables sum up as in the classical chains to

$$F_{cc}(a, b) = -\beta_{a,b} q_a q_b \Phi(\mathbf{R}_a - \mathbf{R}_b) \tag{5.54}$$

where $\Phi(\mathbf{R})$ is a Debye-like potential

$$\Phi(\mathbf{R}) = \frac{\exp(-\kappa\, |\mathbf{R}|)}{|\mathbf{R}|} \tag{5.55}$$

with inverse screening length κ given by

$$\kappa^2 = 4\pi\beta \sum_\alpha \sum_q \int D(\mathbf{X})\, q^2 e_\alpha^2 \rho(\alpha, q, \mathbf{X}) \tag{5.56}$$

Fig. 5. Multipole–multipole resummed bond.

From the definitions (5.32)–(5.33) and (5.50)–(5.51), the sum of Coulomb chains corresponding to the charge-multipole bonds are obtained from (5.54) by application of the multipolar operator (5.29) on $\Phi(\mathbf{R}_1-\mathbf{R}_2)$ (Fig. 4)

$$F_{cm}(1,2)=-\beta_{1,2}q_1\int_0^{q_2}ds_2\,M_2(s_2)\,\Phi(\mathbf{R}_1-\mathbf{R}_2)\tag{5.57}$$

$$F_{mc}(1,2)=-\beta_{1,2}q_2\int_0^{q_1}ds_1\,M_1(s_1)\,\Phi(\mathbf{R}_1-\mathbf{R}_2)\tag{5.58}$$

Obviously the resummed bonds (5.57) and (5.58) have a short range. Let us have a closer look at the multipole-multipole resummed bond (Fig. 5)

$$\begin{aligned}F_{mm}(1,2)&=f_{mm}(1,2)+f_{mc}*f_{cm}(1,2)+f_{mc}*f_{cc}*f_{cm}(1,2)+\cdots\\&=-\beta_{1,2}V_{mm}(1,2)\qquad(5.59)\\&\quad-\beta_{1,2}\int_0^{q_1}ds_1\,M_1(s_1)\int_0^{q_2}ds_2\,M_2(s_2)(\Phi(\mathbf{R}_1-\mathbf{R}_2)-V(\mathbf{R}_1-\mathbf{R}_2))\\&=-\beta W(1,2)-\beta_{1,2}\int_0^{q_1}ds_1\,M_1(s_1)\int_0^{q_2}ds_2\,M_2(s_2)\,\Phi(\mathbf{R}_1-\mathbf{R}_2)\qquad(5.60)\end{aligned}$$

The first term in (5.59) is the multipole-multipole quantum potential that has only "equal time" contributions whereas the rest of the chain can be obtained by an application of multipolar operators at both ends (omitting here the term with no intermediate Coulomb points). The expression (5.60) results from (5.36), showing the asymptotic dipolar character of F_{mm} (see (5.37)). Notice that the sum of the resummed bonds equals

$$\begin{aligned}F(1,2)&\equiv F_{cc}(1,2)+F_{cm}(1,2)+F_{mc}(1,2)+F_{mm}(1,2)\\&=-\beta W(1,2)-\beta_{1,2}\Phi_{\text{cl}}(1,2)\end{aligned}\tag{5.61}$$

where $\Phi_{\text{cl}}(1,2)$ is a short-range interaction defined as in (5.27)

$$\Phi_{\text{cl}}(\mathscr{L}_1,\mathscr{L}_2)=\int_0^{q_1}ds_1\int_0^{q_2}ds_2\,\Phi(\mathbf{R}_1+\lambda_{\alpha_1}\mathbf{X}_1(s_1)-\mathbf{R}_2-\lambda_{\alpha_2}\mathbf{X}_2(s_2))\tag{5.62}$$

representing the screened classical interaction between loops.

The screening length κ^{-1} in (5.56) can be written in a more familiar form by noting the identity coming from (5.26)

$$\int d\mathbf{r}\, \rho_T^{(ex)}(\alpha, \mathbf{r}, \mathbf{0}) = \sum_{q=2}^{\infty} \int D(\mathbf{X})\, q(q-1)\, \rho(\alpha, q, \mathbf{X}) \tag{5.63}$$

hence, using also (5.22)

$$\kappa^2 = 4\pi\beta \sum_{\alpha} e_\alpha^2 \left(\rho_\alpha + \int d\mathbf{r}\, \rho_T^{(ex)}(\alpha, \mathbf{r}, \mathbf{0}) \right) \tag{5.64}$$

An alternative expression for κ^2 follows from the quantum charge sum rule (2.16)

$$\int d\mathbf{r}\, c_T(\mathbf{r}, \mathbf{0}) = \sum_{\alpha_1 \alpha_2} e_{\alpha_1} e_{\alpha_2} \int d\mathbf{r} (\rho_T(\alpha_1, \mathbf{r}, \alpha_2, \mathbf{0}) + \rho_{\alpha_1}\, \delta_{\alpha_1 \alpha_2}\, \delta(\mathbf{r})) = 0 \tag{5.65}$$

which leads to the following relation, once expressed in terms of the loop distributions by (5.23)

$$\sum_{\alpha} e_\alpha^2 \left(\rho_\alpha + \int d\mathbf{r}\, \rho_T^{(ex)}(\alpha, \mathbf{r}, \mathbf{0}) \right) = -\sum_{\alpha_1, \alpha_2} e_{\alpha_1} e_{\alpha_2} \int d\mathbf{r}\, \rho_T^{(nex)}(\alpha_1, \mathbf{r}, \alpha_2, \mathbf{0}) \tag{5.66}$$

and thus

$$\kappa^2 = -4\pi\beta \sum_{\alpha_1, \alpha_2} e_{\alpha_1} e_{\alpha_2} \int d\mathbf{r}\, \rho_T^{(nex)}(\alpha_1, \mathbf{r}, \alpha_2, \mathbf{0}) \tag{5.67}$$

In the integrals in (5.66) and (5.67), the contribution of coincident points is not included. On physically reasonable grounds, κ^2 is indeed a positive quantity. One sees from (5.64) that κ^2 reduces to the classical Debye value when exchange effects can be neglected, and it will coincide with the RPA value at high density (Section VI.A.4), both quantities being positive. Moreover, the screening cloud $\sum_{\alpha_2} e_{\alpha_2} \int d\mathbf{r}\, \rho_T^{(nex)}(\alpha_1, \mathbf{r}, \alpha_2, \mathbf{0})$ of charges of different species around the charge e_{α_1}, should have the sign opposite to e_{α_1}, implying that the right hand side of (5.67) is positive.

3. The Prototype Diagrams. The $\tilde{\Gamma}$-diagrams can be divided into classes such that all diagrams in a class lead to the same so-called prototype Π-diagram when all the Coulomb points are integrated out. Points in a $\tilde{\Gamma}$-diagram that survive as points in a Π-diagram are either

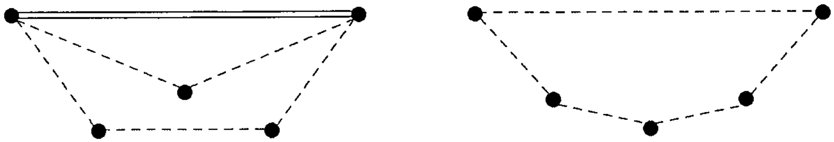

Fig. 6. f-bonds with Coulomb chains in parallel.

convolutions which do not involve Coulomb points, or points linked to three or more other points of $\tilde{\Gamma}$. There will be four different bonds (called F-bonds) in prototype diagrams:

(i) the screened charge–charge bond (5.54) and the two charge–multipole bonds (5.57)–(5.58). Since Coulomb points cannot occur in prototype graphs, the use of these bonds is subjected to the excluded convolution rule: in a Π-diagram, convolutions $F_{cc} * F_{cc}$, $F_{mc} * F_{cc}$, $F_{cc} * F_{cm}$, $F_{mc} * F_{cm}$ are forbidden.

(ii) a bound F_l that incorporates all the bonds that are not taken into account in (i).

Let us now construct the bond F_l. We distinguish two cases:

(a) f_T and F_{mm} occur as individual bonds in Π-diagrams since they are never attached to Coulomb points in $\tilde{\Gamma}$-diagrams,

(b) single bonds in a Π-diagram attached to points that had more than two links in a $\tilde{\Gamma}$-diagram, as the result of the suppression of Coulomb points.

The latter situation is obtained when two points in a diagram were linked

(b.1) by any one of the f-bonds together with Coulomb chains in parallel (Fig. 6)

(b.2) by several Coulomb chains (Fig. 7).

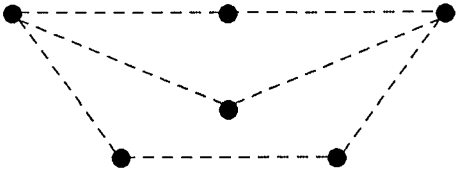

Fig. 7. Coulomb chains in parallel.

$$F_l(a,b) =$$

Fig. 8. Graphical symbol for right hand side of (5.70) bond.

The Coulomb chains occurring in (b.1) and (b.2) must have intermediate points since there is at most one f-bond between two points in a $\tilde{\Gamma}$-diagram. The sum of such Coulomb chains, F_{ch}, is obtained by removing from F (5.61) the single bonds (5.49)–(5.52). Thus, with (5.30)

$$F_{ch}(i, j) = F(i, j) + \beta_{i,j} V(i, j) = -\beta W(i, j) + \beta_{i,j}(V(i, j) - \Phi_{\mathrm{cl}}(i, j)) \tag{5.68}$$

The contributions described in (a) and (b) sum up to

$$F_l = f_T + F_{mm} + f(\exp(F_{ch}) - 1) + \exp(F_{ch}) - 1 - F_{ch} \tag{5.69}$$

The last two parts of (5.69) correspond to the contributions (b.1) and (b.2) (for the combinatorial aspects, see (Cornu 1996a). Combining the definitions (5.46), (5.48), (5.61) and (5.68) in (5.69) leads to the final result (Fig. 8)

$$F_l(i, j) = \exp(-\beta W(i, j) - \beta_{i,j}\Phi_{\mathrm{cl}}(i, j)) - 1 - F_{cc}(i, j) - F_{cm}(i, j) - F_{mc}(i, j) \tag{5.70}$$

Eventually the loop-Ursell function is given by a sum of prototype graphs Π

$$h(\mathscr{L}_1, \mathscr{L}_2) = \sum_{\Pi} \frac{1}{S_\Pi} \int \prod_{n=1}^{N} d\mathscr{L}_n\, \rho(\mathscr{L}_n) \left[\prod F \right]_{\Pi} \tag{5.71}$$

with F-bonds F_{cc}, F_{mc}, F_{cm}, and F_l. The Π-diagrams have the same structure as the Γ-diagrams, with the additional excluded convolution rule formulated in (i).

All F-bonds are rapidly decreasing except F_l. Obviously the asymptotic behavior of F_l is dominated by that of $W(\mathscr{L}_1, \mathscr{L}_2)$

$$\begin{aligned} F_l(\mathscr{L}_1, \mathscr{L}_2) &\sim \exp(-\beta W(\mathscr{L}_1, \mathscr{L}_2)) - 1 \\ &\sim -\beta W(\mathscr{L}_1, \mathscr{L}_2), \qquad |\mathbf{R}_1 - \mathbf{R}_2| \to \infty \end{aligned} \tag{5.72}$$

which is of dipole type as shown by (5.37). It is interesting to note that each F_l bond has the same form (up to short range contributions) as that found in the model of Section IV.C when only two quantum mechanical charges are present. The long range part W depends solely on the intrinsic quantum fluctuations of the two particles (or the two loops), and not on the temperature and density of the state.

There are of course several ways of reorganizing the diagrams with bare Coulomb bonds (5.46) into prototype graphs by partial resummations. Other resummations may be more adequate depending on the density and temperature regime and the physical quantity to be computed. The present reorganization appears to be optimal in the following sense. The remaining long range part has been isolated in the single bond F_l. The decay cannot be improved any more by chain resummations. By (5.72) and (5.37), the longest range part of such chains would arise from convolutions of W-bonds, but such convolutions keep their dipolar character (Cornu, 1996b); the same is true for classical dipoles, see for instance (Høye and Stell, 1974). Moreover, our prototype diagrams are the natural generalization of those used in the classical case. Indeed, if we set the de Broglie lengths equal to zero, the multipolar operator (5.29) vanishes as well as W, F_{cm} and F_{mc}. The effects of the quantum statistics disappear, and both Φ (5.55) and Φ_{cl} (5.62) reduce to the usual Debye potential Φ_D. Hence one finds that the only surviving bonds are

$$\lim_{\hbar \to 0} F_{cc}(1, 2) = -\beta_{1,2} \Phi_D(1, 2)$$

and from (5.70)

$$\lim_{\hbar \to 0} F_l = e^{-\beta_{1,2}\Phi_D(1,2)} - 1 + \beta_{1,2} \Phi_D(1, 2)$$

They are precisely the two bonds occurring in the Meeron theory of the classical plasma (Meeron, 1958; Meeron, 1961).

4. Integrability of Prototype Diagrams. Let us present some crude arguments for the integrability of Π-diagrams; they can be substantiated by the more thorough analysis of (Cornu, 1996a), but a proof is still missing. Each internal point involves a density factor $\rho(\mathscr{L}) = \rho(\alpha, q, \mathbf{X})$ which depends only on the internal variables of the loop and not on its location in space because of translation invariance. Integration on an internal point $\mathscr{L}$ will be of the form

$$\int d\mathbf{R} \sum_{\alpha} \sum_{q=1}^{\infty} \int D(\mathbf{X})\, \rho(\alpha, q, \mathbf{X})\, G(\alpha, q, \mathbf{R}, \mathbf{X}; ...) \tag{5.73}$$

where $G(\mathscr{L}; ...)$ denotes the $\mathscr{L}$-dependence of the bonds attached to this point. It can be argued that the loop-density $\rho(\mathscr{L})$ is bounded in the shape variables $\mathbf{X}$ and inherits a prefactor $\exp(\beta\mu_\alpha q)$ from the activity of the loop (see (5.13), (5.15) and (5.74) below). Thus for a sufficiently negative chemical potential this factor should insure convergence for the q summation on the size of the loops. If these conditions are met, the integrability of Π-diagrams, when the distance between the loops becomes large, is determined by the the decay of the F-bonds. Because of the absence of articulation points, any cluster of points is linked by at least two bonds to the remaining points of the diagram. Hence the product $[\prod F]_\Pi$, once integrated on the internal variables, decays at least as $|\mathbf{R}|^{-6}$ in the loop distances, showing the integrability for the whole diagram. One should add that the splitting (5.47) of the original f-bond may introduce spurious non-integrable singularities at the origin in some diagrams. These singularities will cancel out when suitably collecting together such dangerous diagrams (the f-bond (5.46) gives a finite contribution at the origin because of the smoothing provided by the functional integration on the filaments).

To summarize the situation, once the topological reduction to prototype diagrams has been performed, the two-particle correlation is reduced, in the sense of the formal diagrammatic cluster expansion (5.71), to a system that resembles a classical gas of multipoles described in the loop formalism by the four types of bonds F_{cc}, F_{mc}, F_{cm} and F_l.

5. The Density Expansion. An important remark has to be made when one comes down to computations, in particular when one seeks to obtain explicit low density expansions of physical quantities. The diagrammatic representation (5.71) of the loop Ursell function is a straightforward expansion in the density of loops, but not in the particle densities ρ_α themselves, for two reasons:

- the resummed F-bonds depend on the particle densities through the density dependent screened potential Φ (5.55),
- the loop densities entering as weights of the internal points in Π-diagrams are not simply proportional to the particle densities.

The first point is not new and occurs of course already in the diagrammatic treatment of the classical gas. The second point is more delicate: the loop and particle densities are related by the formula (5.22); hence the particle–particle distributions (5.23) calculated from (5.71) have a very implicit dependence on the ρ_α. In principle this dependence can be extracted as follows. According to the standard rules of the Mayer diagrammatics, the loop density is represented by the activity expansion

$$\rho(\mathscr{L}) = z(\mathscr{L}) \sum_G \frac{1}{S_G} \int \prod_{n=1}^{N} d\mathscr{L}_n \, z(\mathscr{L}_n) \left[\prod f \right]_G \tag{5.74}$$

The G-diagrams are defined as the Γ-diagrams (with one root point) except that articulation points are allowed and weights are given by activities. The integrals diverge in (5.74) because of the long range of the f-bonds, but after a suitable topological reduction (resumming Coulomb chains), the representation of $\rho(\mathscr{L})$ becomes a series of prototype graphs, each of them being finite. The procedure is similar to that given above for the Ursell function and will not be described here in detail, see (Cornu, 1996a). Once this is done, formula (5.22) yields in principle the particle densities as functions of the activities

$$\rho_\alpha = \rho_\alpha(z_1, ..., z_{\mathscr{S}}), \qquad \alpha = 1, ..., \mathscr{S} \tag{5.75}$$

Because of the overall neutrality $\sum_{\alpha=1}^{\mathscr{S}} e_\alpha \rho_\alpha = 0$ the system (5.75) consists only of $\mathscr{S} - 1$ independent relations, and so does not determine the z_α uniquely. A unique determination of the z_a is usually made by imposing the convenient additional relation (already discussed in Section I.D)

$$\sum_{\alpha=1}^{\mathscr{S}} e_\alpha z_\alpha = 0 \tag{5.76}$$

Thus by inverting the system (5.75)–(5.76) one can express first $\rho(\mathscr{L})$ and then the particle-particle correlations in terms of the ρ_α. Explicit calculations in this formalism can of course only be performed in the low density regime. Applications to the determination of the asymptotic behavior of the correlations and to the virial equation of state will be presented in the next section.

VI. CORRELATIONS AND THE EQUATION OF STATE

A. Asymptotic Behavior of Particle and Charge Correlations

The first application of the general formalism concerns the determination of the large distance behavior of the correlations without recourse to $\hbar$-expansions, including the quantum statistics and using the exact Coulomb potential on all scales. The calculation remains perturbative in the sense that we examine the large distance behavior of each Π-diagram in the series (5.71) representing the Ursell function, but, as before, without control on the sum of these series.

The semi-classical analysis of Section IV.C has revealed that the two particle correlation, at order $\hbar^4$, decay as r^{-6} at large distance. We show that the same result holds for each of the Π-diagrams contributing to the particle-particle correlation $\rho_T(\alpha_a, \mathbf{r}_a, \alpha_b, \mathbf{r}_b)$, i.e.,

$$\rho_T(\alpha_a, \mathbf{r}_a, \alpha_b, \mathbf{r}_b) \sim \frac{A_{ab}(\beta, \{\rho_\alpha\})}{|\mathbf{r}_a - \mathbf{r}_b|^6}$$

where the coefficient $A_{ab}(\beta, \{\rho_\alpha\})$ is the formal sum of the asymptotic contributions of the Π-diagrams as $|\mathbf{r}_a - \mathbf{r}_b| \to \infty$ at densities ρ_α and inverse temperature β. It is then possible to calculate the lowest order contributions in the densities ρ_α to $A_{ab}(\beta, \{\rho_\alpha\})$ leading to the explicit formula (6.22) below. We will describe the general strategy and illustrate some key points by explicit calculations, details can be found in (Cornu, 1996b). A short review can be found in (Alastuey and Cornu, 1997b).

1. Large Distance Behavior of the Loop Ursell Function. The first task is to study the behavior of the Ursell function (5.71) in the space of loops as the loops are separated. This large distance behavior will be determined by that of the four bonds F_{cc}, F_{cm}, F_{mc} and F_l, once integration on the internal loop variables has been performed in prototype graphs. Among these bonds, only F_l has the long range multipolar character (5.72) that may induce a slow decay of the graph as the two loops are separated.

Therefore one has to keep track of the effects of F_l-bonds (and more specifically of the basic quantum interaction W (5.35)) in the convolutions occurring in prototype diagrams. For this it is appropriate to recall some facts on the asymptotic form of convolutions in three dimensional space.

The forthcoming analysis depends on the assumption (made throughout the whole Section VI.A) that the leading asymptotic term has a monotone decay, whose behavior is governed by that of the small wave numbers $\mathbf{k} \sim 0$ of the Fourier transform. Possible decay with oscillation, due to singularities at non-zero values of $\mathbf{k}$, is not considered. Such oscillating decays are not expected to occur at positive temperature and low density.

Consider a (non-oscillating) function $g(\mathbf{r})$ which decays as $r = |\mathbf{r}| \to \infty$ (up to a multiplicative constant)

$$g(\mathbf{r}) \sim \frac{(\ln r)^m}{r^n}, \qquad n, m \text{ integers}, \quad n \geqslant 3, \quad m \geqslant 0 \tag{6.1}$$

This type of decay is reflected by the existence of a non-analytic part $\tilde{g}_{sing}(\mathbf{k})$ in its Fourier transform $\tilde{g}(\mathbf{k})$ as $\mathbf{k} \to 0$. One can split the low $\mathbf{k}$-expansion of $\tilde{g}(\mathbf{k})$ into $\tilde{g}(\mathbf{k}) = \tilde{g}_{reg}(\mathbf{k}) + \tilde{g}_{sing}(\mathbf{k})$ where $\tilde{g}_{reg}(\mathbf{k}) = a_0 + \sum_{\mu=1}^{3} a_\mu k_\mu + \sum_{\mu,\nu=1}^{3} a_{\mu\nu} k_\mu k_\nu + \cdots$ has a Taylor expansion around $\mathbf{k} = \mathbf{0}$ and $\tilde{g}_{sing}(\mathbf{k})$ behaves (up to multiplicative constants) as (Gel'fand and Shilov, 1964)

$$\tilde{g}_{sing}(\mathbf{k}) \sim \begin{cases} |\mathbf{k}|^{n-3} (\ln |\mathbf{k}|)^{m+1}, & n \text{ odd} \\ |\mathbf{k}|^{n-3} (\ln |\mathbf{k}|)^{m}, & n \text{ even} \end{cases}, \qquad \mathbf{k} \to 0 \tag{6.2}$$

The singular part of Fourier transforms of derivatives $\partial_{\mu_1} \cdots \partial_{\mu_j} g(\mathbf{r})$ is $k_{\mu_1} \cdots k_{\mu_j} \tilde{g}_{sing}(\mathbf{k})$. Since the Fourier transform of the convolution $(g_1 * g_2)(\mathbf{r})$ is the product $\tilde{g}_1(\mathbf{k})\, \tilde{g}_2(\mathbf{k})$, one deduces from the above correspondence rules that for $n_1, n_2 > 3$

$$(g_1 * g_2)(\mathbf{r}) \sim g_1(\mathbf{r}) \int d\mathbf{r}'\, g_2(\mathbf{r}') + g_2(\mathbf{r}) \int d\mathbf{r}'\, g_1(\mathbf{r}'), \qquad r \to \infty \tag{6.3}$$

In particular, if $n_2 > n_1 > 3$, the convolution decays as the slowest of the two functions

$$(g_1 * g_2)(\mathbf{r}) \sim g_1(\mathbf{r}) \int d\mathbf{r}'\, g_2(\mathbf{r}'), \qquad r \to \infty \tag{6.4}$$

At the border $n_1 = n_2 = 3$ of the integrability domain one has

$$(g_1 * g_2)(\mathbf{r}) \sim \frac{(\ln r)^{m_1 + m_2 + 1}}{r^3} \tag{6.5}$$

One sees from (6.5) that convolutions of r^{-3} functions can generate in principle logarithmic factors in the power law decays. To simplify the discussion we abbreviate (6.1) by $g(\mathbf{r}) \approx r^{-n}$, omitting from the notation the possible logarithmic dependence. Since F_l decays as r^{-3}, it is clear from the above convolution rules that no Π-diagram (or subdiagram) decays slower than $\approx r^{-3}$. The slowest possible decay comes then from diagrams where the two root points can be disconnected by cutting a single F_l-bond: otherwise chains containing a F_l-bond will be multiplied by another chain (or subdiagram) decaying at least as $\approx r^{-3}$ so the decay of the whole diagram will be at least as $\approx r^{-6}$. To put this idea at work, one splits the F_l-bond into two pieces

$$F_l = -\beta W + \tilde{F}_l, \qquad \tilde{F}_l \equiv F_l + \beta W \tag{6.6}$$

and enlarge accordingly the set of Π-diagrams to $\tilde{\Pi}$-diagrams equipped with the new bonds $-\beta W$ and $\tilde{F}_l$. One has from (5.72)

$$\tilde{F}_l(1,2) \sim \exp(-\beta W(1,2)) - 1 + \beta W(1,2) \sim \frac{1}{2}(\beta W(1,2))^2 \quad \text{and}$$
$$(W(1,2))^2 \sim \frac{C}{|\mathbf{R}_1 - \mathbf{R}_2|^6}, \qquad |\mathbf{R}_1 - \mathbf{R}_2| \to \infty \tag{6.7}$$

thus $\tilde{F}_l$ is integrable and W is the slowest bond in the new set of $\tilde{\Pi}$-diagrams. Introduce now the subclass of $\tilde{\Pi}_C$-diagrams that remain connected when one removes a W-bond, and denote $H(\mathscr{L}_a, \mathscr{L}_b)$ the value of the sum of these diagrams. With this definition, the loop truncated distribution function (5.44) can be expressed as an exact Dyson equation in terms of convolution chains involving H and W

$$\rho_T(\mathscr{L}_a, \mathscr{L}_b) = \rho(\mathscr{L}_a)\, \rho(\mathscr{L}_b)\, H(\mathscr{L}_a, \mathscr{L}_b)$$
$$-\beta \int d\mathscr{L}_1\, d\mathscr{L}'_1\, G(\mathscr{L}_a, \mathscr{L}_1)\, W(\mathscr{L}_1, \mathscr{L}'_1)\, G(\mathscr{L}'_1, \mathscr{L}_b) \tag{6.8}$$
$$+\beta^2 \int d\mathscr{L}_1\, d\mathscr{L}'_1 \int d\mathscr{L}_2\, d\mathscr{L}'_2\, G(\mathscr{L}_a, \mathscr{L}_1)\, W(\mathscr{L}_1, \mathscr{L}'_1)$$
$$\times G(\mathscr{L}'_1, \mathscr{L}_2)\, W(\mathscr{L}_2, \mathscr{L}'_2)\, G(\mathscr{L}'_2, \mathscr{L}_b) + \cdots \tag{6.9}$$

In (6.8)–(6.9) we have set

$$G(\mathscr{L}_1, \mathscr{L}_2) = \rho(\mathscr{L}_1)\, \rho(\mathscr{L}_2)\, H(\mathscr{L}_1, \mathscr{L}_2) + \delta(\mathscr{L}_1, \mathscr{L}_2)\, \rho(\mathscr{L}_1) \tag{6.10}$$

where the term $\delta(\mathscr{L}_1, \mathscr{L}_2)\, \rho(\mathscr{L}_1)$ takes into account the case when W-bonds are in direct convolution with themselves. By construction, no diagram in $H(\mathscr{L}_a, \mathscr{L}_b)$ decays slower than $\approx |\mathbf{R}_a - \mathbf{R}_b|^{-6}$. Indeed if a $\tilde{\Pi}_C$-diagram contains no W-bonds, the slowest possible decay is determined by that of $\tilde{F}_l$ according to (6.7). If it contains a W-bond, this W bond (or the chain where it belongs to) is necessarily multiplied by another chain that decays not slower than $\approx r^{-3}$, hence the overall decay of the diagram is at least $\approx r^{-6}$. In this way we have isolated the origin of decays that are slower than $\approx r^{-6}$ in the chains of W-bonds (6.8)–(6.9). Since (6.8) contains in particular the term $\rho(\mathscr{L}_a)\, \rho(\mathscr{L}_b)\, W(\mathscr{L}_a, \mathscr{L}_b)$ the loop correlation decays indeed as $\approx r^{-3}$.

2. Large Distance Behavior of the Two-Particle Correlation. In the loop formalism, the two-particle distribution consists of the two terms displayed in (5.23)–(5.25). The dominant part at large distances will come from $\rho^{(nex)}$ involving particles belonging to different loops. The contribution $\rho^{(ex)}$ of particles exchanged in the same loop will be discussed at the end of this subsection. To obtain $\rho^{(nex)}$ we have to integrate $\rho_T(\mathscr{L}_a, \mathscr{L}_b) = \rho(\mathscr{L}_a)\, \rho(\mathscr{L}_b)\, h(\mathscr{L}_a, \mathscr{L}_b)$ over the internal variables of the root loops $\mathscr{L}_a, \mathscr{L}_b$ according to (5.24):

$$\rho^{(nex)}(\alpha_a, \mathbf{r}_a, \alpha_b, \mathbf{r}_b) = \sum_{q_a, q_b} q_a q_b \int D(\mathbf{X_a})\, D(\mathbf{X_b})\, \rho(\mathscr{L}_a)\, \rho(\mathscr{L}_b)\, h(\mathscr{L}_a, \mathscr{L}_b) \tag{6.11}$$

The point to be made below is that, once these integrations have been performed, the asymptotic contribution of the chains of W-bonds (6.8)–(6.9) is strictly faster than $\approx |\mathbf{R}_a - \mathbf{R}_b|^{-6}$. Hence the decay of $\rho^{(nex)}$ is entirely determined by that of the $\tilde{\Pi}_C$-diagrams constituting the function H, i.e., $\approx \mathbf{r}^{-6}$ according to the analysis of the preceding subsection.

Consider for simplicity the diagram consisting of a single W-bond in (6.8): its contribution to $\rho^{(nex)}(\mathbf{r}_a, \mathbf{r}_b)$ is

$$-\beta \sum_{q_a=1}^{\infty} \sum_{q_b=1}^{\infty} q_a q_b \int D(\mathbf{X}_a) \int D(\mathbf{X}_b)\, \rho(\alpha_a, q_a, \mathbf{X}_a)\, \rho(\alpha_b, q_b, \mathbf{X}_b)\, W(\mathscr{L}_a, \mathscr{L}_b) \tag{6.12}$$

The same mechanism that was put forward in the model of Section IV.C to show that the term linear in W was in fact short-ranged works also in the present case. Since in a homogeneous phase of the Coulomb gas the loop-density $\rho(\alpha, q, \mathbf{X})$ as well as the measure $D(\mathbf{X})$ are invariant under global rotations of the shape $\mathbf{X}$ of the loop, the expressions

$$\int D(\mathbf{X})\, \rho(\alpha, q, \mathbf{X})\, \frac{(\mathbf{X}(s) \cdot \nabla_{\mathbf{R}})^k}{k!}, \qquad k = 1, 2,.. \tag{6.13}$$

occurring in (6.12) according to the multipole expansion (5.36) of W have to vanish for k odd and are necessarily proportional to $(\nabla^2_{\mathbf{R}})^{k/2}$ for k even. Then the contribution (6.13) to (6.12) is strictly local since $\nabla^2_{\mathbf{R}}(1/|\mathbf{R}|) = 0$, $\mathbf{R} \neq \mathbf{0}$: thus (6.12) decays faster than any inverse power. More generally, it can be shown that as a consequence of the rotational symmetry and of the harmonicity of the Coulomb potential, all chains (6.9) involving more than one W-bond decay also strictly faster than $\approx |\mathbf{r}_a - \mathbf{r}_b|^{-6}$.

As an example, we give the argument for the term (6.9) involving a two W-bond convolution and keeping only the slowest part of these

W-bonds, i.e., the dipole-dipole interaction (5.37). Once (5.37) has been inserted in (6.9) one obtains convolutions relative to the loop positional variables $\mathbf{R}$ of the form

$$(G_{\nu_1} * \partial_{\nu_1}\partial_{\mu_1} V * G_{\mu_1\nu_2} * \partial_{\nu_2}\partial_{\mu_2} V * G_{\mu_2})(\mathbf{R}_a - \mathbf{R}_b) \tag{6.14}$$

with

$$G_\nu(\mathbf{R}) = \int D(\mathbf{X}_a) \int D(\mathbf{X})\, X_\nu(s)\, G(\mathbf{R}, \mathbf{X}_a, \mathbf{X}) \tag{6.15}$$

$$G_{\mu\nu}(\mathbf{R}) = \int D(\mathbf{X}') \int D(\mathbf{X})\, X'_\mu(s')\, X_\nu(s)\, G(\mathbf{R}, \mathbf{X}', \mathbf{X}) \tag{6.16}$$

where we write

$$G(\mathscr{L}_1, \mathscr{L}_2) = G(\mathbf{R}_1 - \mathbf{R}_2, \mathbf{X}_1, \mathbf{X}_2) \tag{6.17}$$

because of translation invariance. In (6.14)–(6.17) we have omitted the loop indices α, q and the times s as well as the corresponding summations. The loop internal variables have been integrated and sums on repeated Cartesian indices are understood. To analyze the long distance behavior of (6.14) it is convenient to first consider its Fourier transform

$$\tilde{G}_{\nu_1}(\mathbf{k})\, \frac{k_{\nu_1} k_{\mu_1}}{|\mathbf{k}|^2}\, \tilde{G}_{\mu_1\nu_2}(\mathbf{k})\, \frac{k_{\nu_2} k_{\mu_2}}{|\mathbf{k}|^2}\, \tilde{G}_{\mu_2}(\mathbf{k}) \tag{6.18}$$

Since the measure $D(\mathbf{X})$ as well as $G(\mathbf{R}, \mathbf{X}_1, \mathbf{X}_2)$ are invariant under spatial rotations, $\tilde{G}(\mathbf{k})$ and $\tilde{G}_{\mu\nu}(\mathbf{k})$ transform as tensors: hence they are necessarily of the form

$$\begin{aligned} \tilde{G}_\nu(\mathbf{k}) &= k_\nu a(|\mathbf{k}|) \\ \tilde{G}_{\mu\nu}(\mathbf{k}) &= \delta_{\mu\nu} b(|\mathbf{k}|) + k_\mu k_\nu c(|\mathbf{k}|) \end{aligned} \tag{6.19}$$

for some functions a, b, and c of $|\mathbf{k}|$. We know that $G(\mathbf{R}, \mathbf{X}_1, \mathbf{X}_2)$ and hence $G_\nu(\mathbf{R})$, $G_{\mu\nu}(\mathbf{R})$ do not decay slower than $\approx |\mathbf{R}|^{-6}$. Taking the correspondence (6.1)–(6.2) into account, this implies that the small $|\mathbf{k}|$ expansion of $\tilde{G}_\nu(\mathbf{k})$ and $\tilde{G}_{\mu\nu}(\mathbf{k})$ must be of the form

$$\begin{aligned} \tilde{G}_\nu(\mathbf{k}) &= k_\nu(a + O(|\mathbf{k}|^2\, (\ln |\mathbf{k}|)^{m_1+1}) \\ \tilde{G}_{\mu\nu}(\mathbf{k}) &= \delta_{\mu\nu}(b_1 + b_2\, |\mathbf{k}|^2 + O(|\mathbf{k}|^3\, (\ln |\mathbf{k}|)^{m_2}) + k_\mu k_\nu(c + O(|\mathbf{k}|\, (\ln |\mathbf{k}|)^{m_3}) \end{aligned} \tag{6.20}$$

for some $m_1, m_2, m_3 \geqslant 0$. Upon inserting (6.20) into (6.18) one sees that the Coulomb singularities $|\mathbf{k}|^{-2}$ are compensated and (6.18) behaves as $C\,|\mathbf{k}|^2 + O(|\mathbf{k}|^4\,(\ln|\mathbf{k}|)^{m+1})$ as $|\mathbf{k}| \to 0$, hence (6.14) decays strictly faster than $\approx |\mathbf{R}|^{-6}$ (possibly as $\approx |\mathbf{R}|^{-7}$). The same argument extends to all higher order multipoles and chains in (6.9) with arbitrary numbers of W-bonds, showing that $\rho^{(nex)}(\alpha_a, \mathbf{r}_a, \alpha_b, \mathbf{r}_b)$ decays at least as $\approx |\mathbf{r}_a - \mathbf{r}_b|^{-6}$.

We briefly comment about the exchange part $\rho^{(ex)}(\alpha_a, \mathbf{r}_a, \mathbf{r}_b)$ of the particle-particle distribution. One sees from (5.25) that this exchange part involves the loop density $\rho(\mathscr{L})$ with the position of two particles fixed at $\mathbf{r}_a$ and $\mathbf{r}_b$. The Mayer expansion of the loop density (5.74) has an activity factor $z(\mathscr{L})$ that has the bound (5.15). One can show that after the needed resummation of Coulomb chains, all prototype graphs representing $\rho(\mathscr{L})$ inherit the same activity factor $z(\mathscr{L})$. Furthermore prototype graphs are bounded functions of the loop variables $\mathbf{r}_1,\ldots, \mathbf{r}_q$. Taking these facts into account in (5.26), the contribution of a prototype graph to $\rho^{(ex)}(\alpha_a, \mathbf{r}_a, \mathbf{r}_b)$ will be majorized by

$$\begin{aligned}
&\sum_{q=2}^{\infty} q \int D(\mathbf{X})\, |z(\mathscr{L})| \sum_{k=2}^{q} \delta(\lambda_{\alpha_a}\mathbf{X}_k + \mathbf{r}_a - \mathbf{r}_b) \leqslant \frac{2s_{\alpha_a}+1}{\lambda^3_{\alpha_a}} \\
&\sum_{q=2}^{\infty} e^{\beta\mu_{\alpha_a} q} \int d\mathbf{X}_2 \cdots d\mathbf{X}_q \prod_{k=1}^{q} \frac{\exp(-\frac{1}{2}\,|\mathbf{X}_{k+1}-\mathbf{X}_k|^2)}{(2\pi)^{3/2}} \sum_{k=2}^{q} \delta(\lambda_{\alpha_a}\mathbf{X}_k + \mathbf{r}_a - \mathbf{r}_b) \\
&= (2s_{\alpha_a}+1)\left[\frac{1}{(2\pi)^3}\int d\mathbf{k}\, \exp(-i\mathbf{k}\cdot(\mathbf{r}_a-\mathbf{r}_b))\, \frac{1}{\exp(\beta((\hbar^2/2m)\,|\mathbf{k}|^2-\mu_{\alpha_a}))-1}\right]^2
\end{aligned} \tag{6.21}$$

The integral in (6.21) is nothing else than the off-diagonal part of the one-body density matrix of a free Bose gas (the Bose distribution occurs because we have replaced the fermionic sign η_{α_a} by 1 in the bound). At sufficiently low density ($\exp(\beta\mu_{\alpha_a} < 1$), this function, the Fourier transform of an infinitely differentiable function, decays faster than any inverse power of $|\mathbf{r}_a - \mathbf{r}_b|$. Under the assumption that the same property remains true for the sum of all prototype graphs, we conclude that the asymptotic behavior of the particle-particle distribution is dominated by its non-exchange part previously discussed.

The diagrams contributing to the coefficient of the r^{-6} tail can also be analyzed in the low density regime (Cornu, 1997a). At the lowest order in the densities, one finds that the tail has the same form (4.59) as in the semi-classical gas

$$\rho_T(\alpha_a, \mathbf{r}_a, \alpha_b, \mathbf{r}_b) \sim \frac{1}{|\mathbf{r}_a - \mathbf{r}_b|^6}\,\frac{\hbar^4\beta^4}{240} \int d\mathbf{r}\, G^{D.H.}(\mathbf{r}, \alpha_a) \int d\mathbf{r}\, G^{D.H.}(\mathbf{r}, \alpha_b) \tag{6.22}$$

where $G^{D.H.}(\mathbf{r}, \alpha)$ is defined as in (4.58), but calculated in the Debye–Hückel approximation

$$\int d\mathbf{r}\, G^{D.H.}(\mathbf{r}, \alpha) = \rho_\alpha \left(\frac{e_\alpha^2}{m_\alpha} - \frac{4\pi\beta e_\alpha}{\kappa^2} \sum_\gamma \frac{e_\gamma^3 \rho_\gamma}{m_\gamma} \right) \tag{6.23}$$

This is to be expected, since at lowest order in the densities, the particles surrounding the two fixed charges at $\mathbf{r}_a$ and $\mathbf{r}_b$ are fully ionized and will behave as a classical plasma. It is interesting to specialize (6.22) to the electron-proton system. In this case one finds from (6.22) and (6.23) with $\alpha =$ electron or proton, $e_{\mathrm{el}} = -e_{\mathrm{pr}} = e$, $\rho_{\mathrm{el}} = \rho_{\mathrm{pr}} = \rho$

$$\rho_T(\alpha_a, \mathbf{r}_a, \alpha_b, \mathbf{r}_b) \sim \frac{\rho^2}{|\mathbf{r}_a - \mathbf{r}_b|^6} \frac{\hbar^4 \beta^4}{240} \frac{e^4}{4} \left(\frac{1}{m_{\mathrm{el}}} + \frac{1}{m_{\mathrm{pr}}} \right)^2 \tag{6.24}$$

showing that in this system all tails have exactly the same decay rate at low density.

The tail of the particle correlation in presence of a uniform magnetic field $\mathbf{B}$ has also been calculated (Cornu, 1997b; Cornu, 1998a). Because of breaking of the full rotation invariance, it has the slower decay $\sim P_4(\cos\theta)/|\mathbf{r}_a - \mathbf{r}_b|^5$ where $P_4(\cos\theta)$ is a Legendre polynomial and θ is the angle between $\mathbf{B}$ and $\mathbf{r}_a - \mathbf{r}_b$.

3. Correlations of the Total Charge Density. As in the semiclassical case, the total charge density enjoys better screening properties than individual particles. This is reflected by the fact that correlations involving the total charge density $\hat{c}(\mathbf{r}) = \sum_\alpha e_\alpha \hat{\rho}(\alpha, \mathbf{r})$ such as the charge-particle correlation

$$\langle \hat{c}(\mathbf{r}_a)\, \hat{\rho}(\alpha_b, \mathbf{r}_b)) \rangle_T = \sum_{\alpha_a} e_{\alpha_a} \rho_T(\alpha_a, \mathbf{r}_a, \alpha_b, \mathbf{r}_b) \tag{6.25}$$

will have a faster decay than the particle-particle correlation.

To illustrate the origin of this additional screening mechanism, it is convenient to construct a certain “dressing” of the root point $\mathscr{L}_a$ in the Ursell function. For this we call $\mathscr{L}_a$ a Coulomb root point in a Π-diagram if $\mathscr{L}_a$ is linked to the rest of the diagram by exactly one F_{cc} bond or one F_{cm} bond, and split the Ursell function accordingly

$$h(\mathscr{L}_a, \mathscr{L}_b) = h^c(\mathscr{L}_a, \mathscr{L}_b) + h^{nc}(\mathscr{L}_a, \mathscr{L}_b) \tag{6.26}$$

$h^c(\mathscr{L}_a, \mathscr{L}_b)$ ($h^{nc}(\mathscr{L}_a, \mathscr{L}_b)$) is the sum of Π-diagrams where $\mathscr{L}_a$ is (is not) a Coulomb point. This definition implies immediately the following integral equation

$$h^c = F_{cc} + F_{cc}\rho * h^{nc} + F_{cm} + F_{cm}\rho * h \tag{6.27}$$

and thus

$$h = F_{cc} + F_{cm} + (F_{cc}\rho + 1) * h^{nc} + F_{cm}\rho * h \tag{6.28}$$

where here the symbol $*$ means both integration on the internal variables and convolution with respect to the positions of the loops; $\rho = \rho(\mathscr{L})$ is the weight of intermediate points. Note that h^{nc} occurs in the second term of (6.27) because convolutions of F_{cc} bonds are forbidden in Π-diagrams. As we know the two first terms of (6.28) are rapidly decreasing; the third term contributes to $\rho_T(\mathscr{L}_a, \mathscr{L}_b)$ as

$$\begin{aligned}&\rho(\mathscr{L}_a) \int d\mathscr{L}(F_{cc}(\mathscr{L}_a, \mathscr{L})\, \rho(\mathscr{L}) + \delta(\mathscr{L}_a, \mathscr{L}))\, h^{nc}(\mathscr{L}, \mathscr{L}_b)\, \rho(\mathscr{L}_b)\\ &\quad = \int d\mathscr{L}\; S(\mathscr{L}_a, \mathscr{L})\, \rho(\mathscr{L})\, h^{nc}(\mathscr{L}, \mathscr{L}_b)\, \rho(\mathscr{L}_b)\end{aligned} \tag{6.29}$$

with "dressing" factor of the point $\mathscr{L}_a$ defined by

$$S(\mathscr{L}_a, \mathscr{L}) = \rho(\mathscr{L}_a)\, F_{cc}(\mathscr{L}_a, \mathscr{L}) + \delta(\mathscr{L}_a, \mathscr{L}) \tag{6.30}$$

When summed on the internal variables of the loop $\mathscr{L}_a$ and the charges, it is immediately seen, using (5.54) and (5.56) that (6.30) gives

$$\begin{aligned}&\sum_{\alpha_a} e_{\alpha_a} \sum_{q_a} q_a \int D(\mathbf{X}_a)\, S(\mathscr{L}_a, \mathscr{L})\\ &\quad = e_\alpha q_\alpha \left(\delta(\mathbf{r}) - \kappa^2 \frac{\exp(-\kappa r)}{4\pi r} \right), \qquad \mathbf{r} = \mathbf{R}_a - \mathbf{R}\end{aligned} \tag{6.31}$$

with Fourier transform

$$e_\alpha q_\alpha \left(1 - \frac{\kappa^2}{\kappa^2 + |\mathbf{k}|^2} \right) = e_\alpha q_\alpha \frac{|\mathbf{k}|^2}{\kappa^2 + |\mathbf{k}|^2} \tag{6.32}$$

Hence the convolution (6.29) will contribute to the Fourier transform of the charge-particle correlation as

$$\frac{|\mathbf{k}|^2}{\kappa^2+|\mathbf{k}|^2}\times\left\{\begin{matrix}\text{Fourier transform of } \Pi\text{-diagrams constituting } h^{nc} \\ \text{integrated on the internal variables of their root points}\end{matrix}\right\} \tag{6.33}$$

Since the singular term of these diagrams is $|\mathbf{k}|^3\,(\ln|\mathbf{k}|)^m$ (corresponding to a $\approx r^{-6}$ decay as seen in Section VI.A.2), the singular term in (6.33) is $|\mathbf{k}|^5 \ln|\mathbf{k}|^m$ implying a $\approx r^{-8}$ decay. The same conclusion can be drawn for the contribution of the last term of (6.28) on the grounds of rotational invariance and of the short range of F_{cm}. The final result is that the charge-particle has the following large distance behavior in the low density regime (Cornu 1997a)

$$\langle \hat{\rho}(\alpha_a,\mathbf{r}_a)\,\hat{c}(\mathbf{r}_b)\rangle_T \sim \frac{1}{|\mathbf{r}_a-\mathbf{r}_b|^8}\frac{\hbar^4\beta^4}{16}\int d\mathbf{r}\; G^{D.H.}(\mathbf{r},\alpha_a)\left(\frac{1}{3}\int d\mathbf{r}\;|\mathbf{r}|^2\,K^{D.H.}(\mathbf{r})\right) \tag{6.34}$$

where the last factor is the expression (4.62) calculated in the Debye–Hückel approximation

$$\frac{1}{3}\int d\mathbf{r}\;|\mathbf{r}|^2\,K^{D.H.}(\mathbf{r}) = -\frac{2}{\kappa^2}\sum_\alpha \frac{e_\alpha^3\rho_\alpha}{m_\alpha} \tag{6.35}$$

For the charge-charge correlation, both root points $\mathscr{L}_a$ and $\mathscr{L}_b$ can be dressed as before, leading to a $\approx r^{-10}$ decay with

$$\begin{aligned}\langle \hat{c}(\mathbf{r}_a)\,\hat{c}(\mathbf{r}_b)\rangle_T &\sim \frac{1}{|\mathbf{r}_a-\mathbf{r}_b|^{10}}\frac{7\hbar^4\beta^4}{4}\left(\frac{1}{3}\int d\mathbf{r}\;|\mathbf{r}|^2\,K^{D.H.}(\mathbf{r})\right)^2 \\ &\sim \frac{1}{|\mathbf{r}_a-\mathbf{r}_b|^{10}}\frac{7\hbar^4\beta^4}{\kappa^4}\left(\sum_\alpha \frac{e_\alpha^3\rho_\alpha}{m_\alpha}\right)^2\end{aligned} \tag{6.36}$$

The fact that the space integral of (6.31) vanishes (or equivalently (6.32) vanishes at $\mathbf{k}=0$) is the elementary form of the classical charge sum rule in the Debye–Hückel theory (see (2.9)). In the quantum gas, this vestige of classical screening can still operate to improve the decay of the charge–charge correlation from $\approx r^{-6}$ to $\approx r^{-10}$, but not beyond.

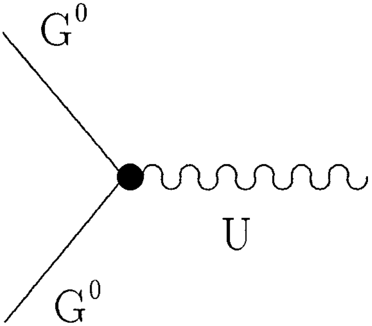

Fig. 9. Vertex with two propagator lines and one interaction line.

Finally the susceptibility (1.45) (i.e., the response to an external classical charge) decays as r^{-8}. Its tail at low density is given by

$$\chi(r) \sim \frac{4\pi}{r^8} \frac{\hbar^4 \beta^5}{8\kappa^4} \left(\sum_{\alpha} \frac{e_\alpha^3 \rho_\alpha}{m_\alpha} \right)^2 \tag{6.37}$$

We emphasize that (6.22), (6.34), (6.36) and (6.37) are exact asymptotic results for the multicomponent quantum gas.

4. A Comparison with the Standard Many-Body Perturbation Theory. The standard finite temperature many-body perturbation theory is an expansion in powers of the coupling constant (the charge e^2). Here we adopt the definitions and normalizations of (Fetter and Walecka, 1971) and (Cornu and Martin, 1991).[25] We recall a few facts. The terms of the expansion are represented by Feynman graphs in which bonds $(\alpha_1, \mathbf{r}_1, s_1; \alpha_2, \mathbf{r}_2, s_2)$ are joined either by free propagators $\delta_{\alpha_1, \alpha_2} G^0_{\alpha_1}(\mathbf{r}_2 - \mathbf{r}_1, s_1 - s_2)$ or by interaction lines $U_{\alpha_1, \alpha_2}(\mathbf{r}_2 - \mathbf{r}_1, s_1 - s_2)$ (Fig. 9). At each vertex $(\alpha, \mathbf{r}, s)$ are attached two propagator lines and one interaction line.

A basic link between physical quantities and perturbation theory can be established through the imaginary time displaced charge correlation (1.43) by

$$c_T(\mathbf{r}, s, \mathbf{0}) = -\sum_{\alpha\gamma} e_\alpha e_\gamma \mathscr{P}_{\alpha\gamma}(\mathbf{r}, s) \tag{6.38}$$

The total polarization $\mathscr{P}_{\alpha\gamma}(\mathbf{r}, \tau)$ consists of all connected Feynman graphs in which the points $(\alpha, \mathbf{r}, s)$ and $(\gamma, \mathbf{0}, 0)$ are joined by internal lines. $\mathscr{P}_{\alpha\gamma}(\mathbf{r}, \tau)$

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[25] There is a minus sign missing in front of the right hand side of (Cornu and Martin 1991, formula (2.4)).

is a time periodic function of period β. Introducing its space and time Fourier transform $\mathscr{P}(\mathbf{k}, n)$, the structure factor (1.44) and the susceptibility (1.45) are given by (n indexes even Matsubara frequencies $\omega_n = \pi n/\beta$, n even)[26]

$$S(\mathbf{k}) = -\sum_{n=-\infty}^{\infty} \sum_{\alpha\gamma} e_\alpha e_\gamma \mathscr{P}_{\alpha\gamma}(\mathbf{k}, n) \tag{6.39}$$

$$\chi(\mathbf{k}) = \beta V(\mathbf{k}) \sum_{\alpha\gamma} e_\alpha e_\gamma \mathscr{P}_{\alpha\gamma}(\mathbf{k}, n=0), \qquad V(\mathbf{k}) = \frac{4\pi}{|\mathbf{k}|^2} \tag{6.40}$$

It is convenient to consider the proper polarization $\mathscr{P}^*_{\alpha\gamma}(\mathbf{k}, n)$, the set of all polarization parts that cannot be separated into two polarization parts by cutting a single interaction line. $\mathscr{P}_{\alpha\gamma}(\mathbf{k}, n)$ and $\mathscr{P}^*_{\alpha\gamma}(\mathbf{k}, n)$ are related by a Dyson equation

$$\mathscr{P}_{\alpha\gamma}(\mathbf{k}, n) = \frac{\mathscr{P}^*_{\alpha\gamma}(\mathbf{k}, n)}{1 - \beta V(\mathbf{k}) \sum_{\alpha\gamma} e_\alpha e_\gamma \mathscr{P}^*_{\alpha\gamma}(\mathbf{k}, n)} \tag{6.41}$$

An effective frequency dependent interaction can be defined by

$$U^{\text{eff}}(\mathbf{k}, n) = \frac{V(\mathbf{k})}{1 - \beta V(\mathbf{k}) \sum_{\alpha\gamma} e_\alpha e_\gamma \mathscr{P}^*_{\alpha\gamma}(\mathbf{k}, n)} \tag{6.42}$$

This definition is justified by the fact that its zero frequency component coincides with the static effective potential (1.30) (with $\varepsilon(\mathbf{k})$ given by (1.45))

$$U^{\text{eff}}(\mathbf{k}, n=0) = \varepsilon^{-1}(\mathbf{k})\, V(\mathbf{k}) \tag{6.43}$$

One has also the relation

$$\mathscr{P}_{\alpha\gamma}(\mathbf{k}, n) = \mathscr{P}^*_{\alpha\gamma}(\mathbf{k}, n) + \beta \sum_{\delta\eta} \mathscr{P}^*_{\alpha\delta}(\mathbf{k}, n)\, e_\delta e_\eta\, U^{\text{eff}}(\mathbf{k}, n)\, \mathscr{P}^*_{\eta\gamma}(\mathbf{k}, n) \tag{6.44}$$

The well known random phase approximation (RPA) amounts to replacing $\mathscr{P}^*_{\alpha\gamma}(\mathbf{r}, \tau)$ by the lowest order proper polarization term, i.e., the product of two free propagators

$$\begin{aligned} \mathscr{P}^*_{\mathrm{RPA},\,\alpha\gamma}(\mathbf{r}, s) &= -\eta_\alpha\, \delta_{\alpha\gamma} (2s_\alpha + 1)\, G^0_\alpha(\mathbf{r}, s)\, G^0_\alpha(-\mathbf{r}, -s) \\ &= \delta_{\alpha\gamma} \mathscr{P}^*_{\mathrm{RPA},\,\alpha}(\mathbf{r}, s) \end{aligned} \tag{6.45}$$

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[26] In general, n is odd for fermionic propagators and even for bosonic propagators, but the charge correlation (1.43) involves only quadratic expressions of the Fermi or Bose fields and only even frequencies occur in its time Fourier series.

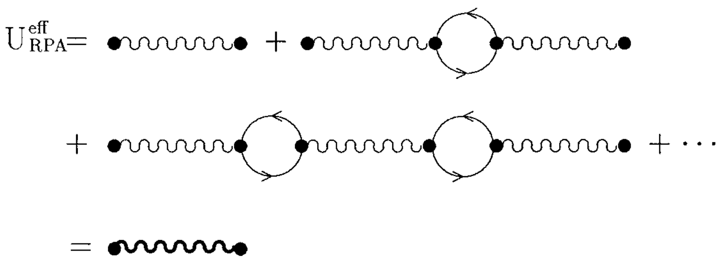

Fig. 10. The random phase approximation.

Hence from (6.41) and (6.42) (see Fig. 10)

$$\mathscr{P}_{\mathrm{RPA},\,\alpha\gamma}(\mathbf{k},n)=\frac{\delta_{\alpha\gamma}\mathscr{P}^{*}_{\mathrm{RPA},\,\alpha}(\mathbf{k},n)}{1-\beta V(\mathbf{k})\sum_{\alpha}e_{\alpha}^{2}\mathscr{P}^{*}_{\mathrm{RPA},\,\alpha}(\mathbf{k},n)} \tag{6.46}$$

$$U^{\mathrm{eff}}_{\mathrm{RPA}}(\mathbf{k},n)=\frac{V(\mathbf{k})}{1-\beta V(\mathbf{k})\sum_{\alpha}e_{\alpha}^{2}\mathscr{P}^{*}_{\mathrm{RPA},\,\alpha}(\mathbf{k},n)} \tag{6.47}$$

and with (6.39) and (6.40), this defines also $S_{\mathrm{RPA}}(\mathbf{k})$ and $\chi_{\mathrm{RPA}}(\mathbf{k})$.

Let us show that the RPA approximation fails to capture the algebraic tails in the correlations.[27] The free propagator has the form

$$G^{0}_{\alpha}(\mathbf{k},s)=\exp\left(-\beta s\left(\frac{\hbar^{2}\,|\mathbf{k}|^{2}}{2m_{\alpha}}-\mu_{\alpha}\right)\right)[n^{0}_{\alpha}(\mathbf{k})-\theta(s)] \tag{6.48}$$

where $n^{0}_{\alpha}(\mathbf{k})=(\exp(\hbar^{2}\beta\,|\mathbf{k}|^{2}/2m_{\alpha}-\beta\mu_{\alpha})\pm 1)^{-1}$ is the free Fermi or Bose distribution and $\theta(s)$ is the Heaviside function. It is clearly an infinitely differentiable function of $\mathbf{k}$ (if $\mu_{\alpha}<0$ for Bose particles). One can deduce from (6.45) that the same is true for $\mathscr{P}^{*}_{\mathrm{RPA},\,\alpha}(\mathbf{r},n)$ and one finds the small $\mathbf{k}$ behaviour

$$\begin{aligned}\mathscr{P}^{*}_{\mathrm{RPA},\,\alpha}(\mathbf{k},n=0)&=-\frac{\partial\rho^{0}_{\alpha}}{\partial(\beta\mu_{\alpha})}+O(|\mathbf{k}|^{2})\neq 0\\ \mathscr{P}^{*}_{\mathrm{RPA},\,\alpha}(\mathbf{k},n\neq 0)&=O(|\mathbf{k}|^{2}),\qquad \mathbf{k}\to 0\end{aligned} \tag{6.49}$$

where $\rho^{0}_{\alpha}=(2s_{a}+1)\int d\mathbf{k}\,n^{0}_{\alpha}(\mathbf{k})$ is the density of the free gas. With (6.46) this implies that the $\mathscr{P}^{*}_{\mathrm{RPA},\,\alpha}(\mathbf{k},n)$ are infinitely differentiable at $\mathbf{k}=0$ and by (6.39) and (640) $S_{\mathrm{RPA}}(\mathbf{k})$ and $\chi_{\mathrm{RPA}}(\mathbf{k})$ inherit the same property. Thus, in

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[27] The present considerations apply only if the temperature is different from zero. At zero temperature, the effective potential shows the long range Friedel oscillations $\cos(2k_{F}r)/r^{3}$ due to the sharpness of the Fermi surface.

space, these functions decay faster than any inverse power of the distance. From (6.46) and (6.49) one sees that $\chi_{\mathbf{RPA}}(\mathbf{k})$ can be approximated for small $\mathbf{k}$ by the Debye-like form

$$\chi_{\mathbf{RPA}}(\mathbf{k}) \simeq -\frac{\kappa^2_{\mathbf{RPA}}}{|\mathbf{k}|^2 + \kappa^2_{\mathbf{RPA}}} \tag{6.50}$$

with

$$\kappa^2_{\mathbf{RPA}} = 4\pi\beta \sum_{\alpha} e^2_{\alpha} \frac{\partial \rho^0_{\alpha}}{\partial(\beta\mu_{\alpha})} \tag{6.51}$$

so defining the RPA screening length $\kappa^{-1}_{\mathbf{RPA}}$. It is instructive to compare it with the loop screening length κ^{-1} (5.64). For this, we introduce the general relation

$$\begin{aligned}\frac{\partial}{\partial(\beta\mu_{\alpha})}\,\rho_{\alpha} &= \rho_{\alpha} + \int d\mathbf{r}\,\rho_T(\alpha, \mathbf{r}, \alpha, \mathbf{0})\\ &= \rho_{\alpha} + \int d\mathbf{r}\,\rho^{(ex)}_T(\alpha, \mathbf{r}, \mathbf{0}) + \int d\mathbf{r}\,\rho^{(nex)}_T(\alpha, \mathbf{r}, \alpha, \mathbf{0})\end{aligned} \tag{6.52}$$

in (5.64), so that κ^2 can also be written as

$$\kappa^2 = 4\pi\beta\left(\sum_{\alpha} e^2_{\alpha}\,\frac{\partial\rho_{\alpha}}{\partial(\beta\mu_{\alpha})} - \sum_{\alpha} e^2_{\alpha}\int d\mathbf{r}\rho^{(nex)}_T(\alpha, \mathbf{r}, \alpha, \mathbf{0})\right) \tag{6.53}$$

In the integrals in (6.52) and (6.53), there are no contributions of coincident points. The loop screening length interpolates between the classical Debye length at low density (as seen from (5.64) when exchange effects can be neglected) and the RPA length at high density. Indeed, in the high density regime, the kinetic energy dominates the Coulomb interaction energy: the gas becomes free so the non-exchange part of the correlation can now be neglected in (6.53) and κ^2 tends to the RPA value.

As far as the effective potential (6.42) is concerned, one finds in the RPA approximation that its zero frequency component $U^{\mathrm{eff}}_{\mathbf{RPA}}(\mathbf{k}, n=0)$ is also Debye-like for small $\mathbf{k}$ with a screening length slightly different from $\kappa^{-1}_{\mathbf{RPA}}$ (for explicit formulae see (Cornu and Martin, 1991; Cornu, 1996b)). However its non-zero frequency components $U^{\mathrm{eff}}_{\mathbf{RPA}}(\mathbf{k}, n\neq 0)$ are not shielded and keep a pure Coulombic singularity $|\mathbf{k}|^{-2}$, but within the RPA theory these singularities do not induce any algebraic tails in the particle and charge correlations. For instance, if $\mathscr{P}^{*}_{\alpha\gamma}(\mathbf{k}, n)$ is approximated by

$\mathscr{P}^*_{\mathrm{RPA},\,\alpha\gamma}(\mathbf{k}, n)$ in (6.44), the vanishing of the nonzero frequency components as $|\mathbf{k}| \to 0$ kills the $|\mathbf{k}|^{-2}$ singularity coming from $U^{\mathrm{eff}}_{\mathrm{RPA}}(\mathbf{k}, n \neq 0)$.

One may however wonder how these tails emerge in the framework of the many-body perturbation theory. The role played by $U^{\mathrm{eff}}_{\mathrm{RPA}}$ in Feynman graphs is analogous to that of the resummed bond F_l (5.70) in-loop prototype diagrams. F_l has a long range part W (see (6.6)), but this long range part generates tails in the correlations only if it occurs at least quadratically in prototype graphs (see Section VI.A.2). In the same way, $U^{\mathrm{eff}}_{\mathrm{RPA}}$ must enter quadratically in Feynman graphs to generate tails in the correlations. This leads to including as a first correction to the RPA approximation the proper polarization insertion $\mathscr{P}^*_1$ made of two propagator loops linked by two RPA lines of Fig. 11. The effect of this correction has been studied in the one component system (Cornu and Martin, 1991). The Coulombic singularities of $U^{\mathrm{eff}}_{\mathrm{RPA}}(\mathbf{k}, n \neq 0)$ come now non-trivially into the game and one finds that $\mathscr{P}^*_1(\mathbf{k}, n = 0)$ and $\mathscr{P}^*_1(\mathbf{k}, n \neq 0)$ have respectively a $|\mathbf{k}|^3$ and a $|\mathbf{k}|^7$ singular term in their small $\mathbf{k}$ expansion. One can then infer through the Dyson equation (6.41) that these singular terms induce r^{-10} and r^{-8} tails in $S(\mathbf{r})$ and $\chi(\mathbf{r})$ respectively, in accordance with the findings of Section VI.A.3. The graphs of Fig. 11 have been considered previously in (Maags and Ashcroft, 1987; Langreth and Vosko, 1987) in connection with calculating the cohesive energy of metals and inter-atomic potentials at zero temperature.

It is not possible to establish in general strict correspondence rules between the many-body perturbation algorithm and that of the loop formalism. Since the reference system of the many-body perturbation scheme is the noninteracting gas, any approximation there gives expressions in terms of free quantities. In the loop expansion, weights and bonds in Mayer diagrams contain already the coupling constant e^2 and the statistics in a non-perturbative way, and they involve the exact particle densities. This difference is clearly seen in the two screening lengths $\kappa^{-1}_{\mathrm{RPA}}$ and κ^{-1} that depend respectively on the free densities ρ^0_α and exact densities ρ_α. One can however establish a precise relation between the loop chain potential and the RPA effective potential in the Boltzmann limit when statistics are neglected (see (Cornu and Martin, 1991, Section IV)).

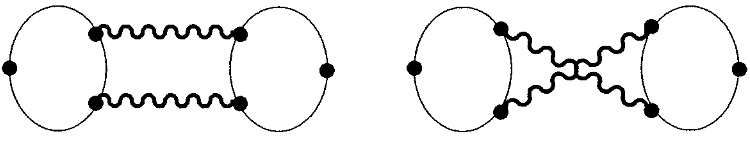


Fig. 11. A first correction to RPA.

The two formalisms play complementary roles. The many-body formalism is suitable for performing low temperature and ground state calculations. By analytic continuation in time it can also be used to compute real time displaced correlations. Information on ground state quantities in the loop formalism would necessitate applying the Feynman–Kac formula backwards at some point before taking the $\beta \to \infty$ limit. However the loop formalism provides a better insight into Coulombic correlations and screening. For instance the reduction to a gas of multipoles is not visible in the many-body framework where the effective potential $U_{\mathbf{RPA}}^{\mathrm{eff}}$ keeps an unscreened bare Coulomb part. Low density behaviors are much more conveniently obtained from the loop expansion: it would not be straightforward to recover the exact results of Section VI.A from an analysis of Feynman graphs. The next section offers another example of the usefulness of the loop formalism.

B. The Virial Equation of State

The derivation of the equation of state of a quantum mechanical plasma is an old problem of practical and theoretical interest. In particular, a precise knowledge of this equation plays an important role in astrophysical conditions, and it is not possible to give credit here to the large literature devoted to this question. We quote the thorough study of the quantum Coulomb gas undertaken by Ebeling and collaborators by the usual methods of the many-body problem. This work is reported in (Kraeft *et al.*, 1986) and some comments will be given at the end of this section. In the sequel, we put forward that the loop representation is also a convenient tool for calculating the equation of state at low density and fixed temperature. In particular the formalism enables simultaneously keeping track, in a coherent and systematic way, of the quantum effects and of the long range of the Coulomb potential, a notoriously difficult problem. A detailed presentation of all calculations can be found in (Alastuey and Perez, 1992; Alastuey, Cornu, and Perez, 1994; Alastuey, Cornu, and Perez, 1995; Alastuey and Perez, 1996) and a review on this subject is presented in (Alastuey, 1994). Here we outline the general computational scheme and illustrate some salient points.

To evaluate the density expansion of the thermodynamic functions, it is appropriate to start from a standard identity relating the free energy $f(\beta, \{\rho_\alpha\})$ per unit volume to the two-particle correlation with a variable coupling parameter

$$\beta f = \beta f_{\mathrm{ideal}} + \frac{\beta}{2} \sum_{\alpha_a \alpha_b} e_{\alpha_a} e_{\alpha_b} \int_0^1 dg \int d\mathbf{r}\, \rho_{T,\, g}(\alpha_a, \mathbf{r}, \alpha_b, 0)\, \frac{1}{|\mathbf{r}|} \tag{6.54}$$

Here $\rho_{T,\,g}(\alpha_a, \mathbf{r}, \alpha_b, \mathbf{0})$ is the truncated two-particle correlation (without the contribution of coincident points) for a system of charges interacting by the Coulomb potential $g/|\mathbf{r}|$ with a dimensionless coupling parameter g, $0 \leqslant g \leqslant 1$. For each g, $\rho_{T,\,g}(\alpha_a, \mathbf{r}, \alpha_b, 0)$ must be evaluated at the same values of the densities and temperature that occur as arguments of $f(\beta, \{\rho_\alpha\})$. The particle correlation $\rho_{T,\,g}(\alpha_a, \mathbf{r}_a, \alpha_b, \mathbf{r}_b)$ is in turn related to the loop correlations through (5.23), (5.24) and (5.25) and the loop correlations have the diagrammatic expansion discussed in Section V.B. Then one has to organize the contributions of this expansion in terms that are of increasing order in the particle densities and insert them in (6.54). This will yield the desired expansion for the free energy. Finally the pressure $P(\beta, \{\rho_\alpha\})$ follows from the usual formula

$$P = \sum_\alpha \rho_\alpha \frac{\partial}{\partial \rho_\alpha} f - f \tag{6.55}$$

The calculation has been carried out up to order $\rho^{5/2}$.

1. The Maxwell–Boltzmann Pressure.

At this point one can make the following comment about the treatment of exchange effects. It is clear from (5.13) that q-particle exchanges are of decreasing order $\exp(\beta\mu_\alpha q)$ as q grows (μ_α negative); hence they can also be treated perturbatively at low density. This is the view point adopted in (Alastuey *et al.* 1995) and that is reported here. One considers first the Maxwell–Boltzmann (MB) Coulomb gas, and one includes the exchange effects in a second perturbative stage. The MB system is simpler since loops reduce to filaments. Also the exchange part (5.25) of the correlation can be ignored in the first stage. Dropping here the Fermi statistics should not alarm the reader. All terms of the low density expansion remain well defined, since these terms involve only finitely many body Hamiltonians, and thus the stability of matter plays no role at any finite order. As already noted, the local singularity of the Coulomb potential is smoothed by the usual laws of quantum mechanics (the uncertainty principle) as in atomic physics.

In the works (Alastuey *et al.* 1994, Alastuey *et al.* 1995), prototype diagrams are constructed with a slightly different definition of resummed bonds than in Section V.B.3. One has here, keeping similar notations as in Section V.B.2 and V.B.3

$$\begin{gathered}\text{the charge–charge bond } F_{cc}\text{, the charge–dipole bonds } F_{cd}, F_{dc}\\ \text{the dipole–dipole bond } F_{dd}\text{, the residual bond } F_r\end{gathered} \tag{6.56}$$

The bond F_{cc} is identical to (5.54) (with $q_a = q_b = 1$); F_{cd} and F_{dc} are defined as in (5.57) and (5.58) but retaining only the dipole part

$$F_{cd}(1,2) = -\beta e_1 e_2 \int_0^1 ds_2 (\lambda_2 \xi_2(s_2) \cdot \nabla_2) \frac{\exp(-\kappa |\mathbf{R}_1 - \mathbf{R}_2|)}{|\mathbf{R}_1 - \mathbf{R}_2|} \tag{6.57}$$

The bond F_{dd} is equal to the dipole part of the second term in (5.60), i.e.,

$$\begin{aligned} F_{dd}(1,2) = -\beta e_1 e_2 \int_0^1 ds_1 \int_0^1 ds_2 (\lambda_1 \xi_1(s_1) \cdot \nabla_1) \\ \times (\lambda_2 \xi_2(s_2) \cdot \nabla_2) \left(\frac{\exp(-\kappa |\mathbf{R}_1 - \mathbf{R}_2|) - 1}{|\mathbf{R}_1 - \mathbf{R}_2|} \right) \end{aligned} \tag{6.58}$$

while F_r incorporates all the other contributions (higher order multipoles and quantum effects). Note that in this decomposition we have the two types of long range r^{-3}-bonds F_{dd} and F_r (in contrast to the prototype graphs of subsection V.B.3 where only F_l is dipolar).

As already explained in Subsection V.B.5, there are two sources for the density dependence: the weight $\rho(\alpha, \xi)$, that has itself an expansion in the particle densities ρ_α, and the screening length κ occurring in the resummed bonds. One performs first the activity expansion of ρ_α with the help of appropriate prototype graphs (here the bonds are as in (6.56) but weights are activities), and one eliminates activities in favor of densities with the help of the relation $\rho_\alpha = \int D(\xi)\, \rho(\alpha, \xi)$. The analysis shows that $\rho(\alpha, \xi)$ is given as double power series in $\rho^{1/2}$ and $\ln \rho$ with first terms

$$\begin{aligned} \rho(\alpha, \xi) = \rho_\alpha + \sum_\gamma \rho_\alpha \rho_\gamma \int d\mathbf{r} \int D(\xi_1) \\ \times \left[\exp\left(-\beta e_\alpha e_\gamma \int_0^1 ds\, V(|\mathbf{r} + \lambda_\gamma \xi_1(s) - \lambda_\alpha \xi(s)|) \right) \right. \\ \left. - \int D(\xi_2) \exp\left(-\beta e_\alpha e_\gamma \int_0^1 ds\, V(|\mathbf{r} + \lambda_\gamma \xi_1(s) - \lambda_\alpha \xi_2(s)|) \right) \right] \\ + O(\rho^{5/2}) \end{aligned} \tag{6.59}$$

These series are introduced in the statistical weights of the expansion of the Ursell function. Finally one obtains also the free energy (6.54) and the pressure (6.55) as double power series in $\rho^{1/2}$ and $\ln \rho$. Half powers of ρ come,from the Debye length $\kappa^{-1} \sim \rho^{-1/2}$ in the screened potential, while $\ln \rho$ terms occur because the r^{-3}-bonds F_{dd} and F_r are at the border line of integrability in three dimensions.

The density dependence contained in the Debye length can be extracted by a scaling analysis. Introducing the dimensionless variable $x=\kappa\,|\mathbf{R}_1-\mathbf{R}_2|$ one sees that F_{cc} scales as κ, $F_{cd}(F_{dc})$ as κ^2, and F_{dd} as κ^3. More generally a higher order multipole term of the form

$$(\xi_1(s_1)\cdot\nabla_1)^{k_1}\,(\xi_2(s_2)\cdot\nabla_2)^{k_2}\,\frac{\exp(-\kappa\,|\mathbf{R}_1-\mathbf{R}_2|)}{|\mathbf{R}_1-\mathbf{R}_2|}$$

scales as $\kappa^{k_1+k_2+1}$. In F_r the quantum effects (associated with the de Broglie length λ_α and classical screening (associated with the Debye length κ^{-1}) can be disentangled by a decomposition of the form

$$F_r=F_q(1+\kappa H_1+\kappa^2 H_2+\cdots)+\kappa^2 G_2+\kappa^3 G_3+\cdots \tag{6.60}$$

where F_q is the quantum (truncated) bond

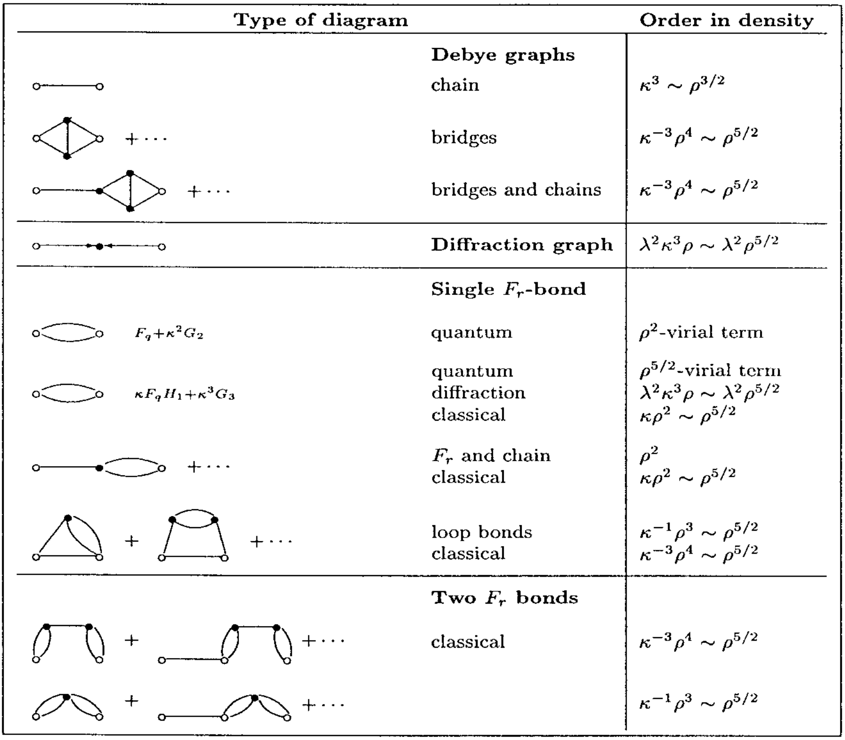
$$\begin{aligned}F_q(1,2)={}&\exp\left(-\beta_{12}\int_0^1 ds\;V(|\mathbf{r}+\lambda_{\alpha_1}\xi_1(s)-\lambda_{\alpha_2}\xi_2(s)|)\right)\\&-1+\frac{\beta_{12}}{r}-\frac{\beta_{12}^2}{2r^2}+\beta_{12}\int_0^1 ds[\lambda_{\alpha_1}\xi_1(s)\cdot\nabla-\lambda_{\alpha_2}\xi_2(s)\cdot\nabla]\left(\frac{1}{r}\right)\end{aligned} \tag{6.61}$$

and the H_i and G_i are scaled functions involving contributions of higher order multipoles. We distinguish three different types of effects in this game:

- classical screening manifested by the occurrence of the Debye length in the scaled bonds
- quantum diffraction effects due to the coupling of quantum fluctuations ξ to the classical Debye potential as in F_{cc}, F_{cd} and F_{dd}
- quantum bound and scattering states appearing through F_r.

As an illustration the table in Fig. 12 gives a (non exhaustive) list of examples of graphs contributing to different effects in the MB free energy. The calculations are tractable up to order $\rho^{5/2}$. There are two simplifications up to this order: internal weights $\rho(\alpha,\xi)$ can always be replaced by their lowest order ρ_α, and only low order multipoles contribute in view of the above mentioned scaling arguments. The MB pressure is given by the terms (6.66) to (6.69) in the final result stated in the next subsection.

2. The Exchange Contributions and the Final Result. To include the exchange contributions perturbatively, one has to come back to



Type of diagram		Order in density
	Debye graphs	
	chain	$\kappa^3 \sim \rho^{3/2}$
$+\cdots$	bridges	$\kappa^{-3}\rho^4 \sim \rho^{5/2}$
$+\cdots$	bridges and chains	$\kappa^{-3}\rho^4 \sim \rho^{5/2}$
	Diffraction graph	$\lambda^2\kappa^3\rho \sim \lambda^2\rho^{5/2}$
	Single F_r-bond	
$F_q+\kappa^2G_2$	quantum	ρ^2-virial term
$\kappa F_q H_1+\kappa^3 G_3$	quantum diffraction classical	$\rho^{5/2}$-virial term $\lambda^2\kappa^3\rho \sim \lambda^2\rho^{5/2}$ $\kappa\rho^2 \sim \rho^{5/2}$
$+\cdots$	F_r and chain classical	ρ^2 $\kappa\rho^2 \sim \rho^{5/2}$
$+$ $+\cdots$	loop bonds classical	$\kappa^{-1}\rho^3 \sim \rho^{5/2}$ $\kappa^{-3}\rho^4 \sim \rho^{5/2}$
	Two F_r bonds	
$+$ $+\cdots$	classical	$\kappa^{-3}\rho^4 \sim \rho^{5/2}$
$+$ $+\cdots$		$\kappa^{-1}\rho^3 \sim \rho^{5/2}$

Fig. 12. Examples of contributions to Maxwell–Boltzmann free energy.

the expression (1.40) of the grand-partition function with statistics and collect together all the terms involving the exchange of exactly n particles

$$\Xi_\Lambda = \Xi_\Lambda^{\mathrm{MB}} + \sum_{n=2}^{\infty} \Xi_\Lambda^{(n)} = \Xi_\Lambda^{\mathrm{MB}} \left(1 + \sum_{n=2}^{\infty} \frac{\Xi_\Lambda^{(n)}}{\Xi_\Lambda^{\mathrm{MB}}}\right) \tag{6.62}$$

where $\Xi_\Lambda^{\mathrm{MB}}$ is the Maxwell–Boltzmann partition function and the contribution with N_α exchanged particles has necessarily an activity factor $\exp(\beta\mu_\alpha N_\alpha)$. The expansion (6.62) generates in turn an expansion of the grand-canonical pressure

$$P = \beta^{-1} \lim_{|\Lambda| \to \infty} \frac{1}{|\Lambda|} \ln \Xi_\Lambda = P^{\mathrm{MB}} + \sum_{n=2}^{\infty} P^{(n)} \tag{6.63}$$

with P^{MB} the Maxwell–Boltzmann pressure and $P^{(n)}$ the contribution of n exchanged particles. The matrix element in (1.40) corresponding to a two particle exchange, say $\langle \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_3,..., \mathbf{r}_N| \exp(-\beta H_{\Lambda, N}) |\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3,..., \mathbf{r}_N\rangle$, will involve $N-2$ closed filaments $\mathbf{r}_{i,\,i}(s)$, $i = 3,..., N$ together with two open filaments $\mathbf{r}_{1,\,2}(s)$ and $\mathbf{r}_{2,\,1}(s)$. Keeping these two open filaments fixed, but performing the configuration integrals and grand-canonical sums on all the remaining closed filaments leads to the consideration of the inhomogeneous Maxwell–Boltzmann partition function $\Xi_\Lambda^{(2)(\mathrm{inhom})}$. It is the grand-partition function of a system of (closed) filaments in presence of the potential due to these two open filaments. Similarly, higher order exchange terms can be viewed as partition functions of closed filaments in presence of an external potential created by the open ones. The density of filaments $\rho^{(\mathrm{inhom})}(\mathscr{F})$ in the inhomogeneous system can be expanded in terms of the correlations $\rho(\mathscr{F})$, $\rho_T(\mathscr{F}_1, \mathscr{F}_2)$ of the homogeneous gas by standard methods. Finally, one can apply to the latter correlations all the diagrammatic techniques previously described to obtain the density expansion of the MB gas. There is however one caveat. The particle densities are given in principle by the usual relation

$$\rho_\alpha = \frac{\partial}{\partial \mu_\alpha} P(\{\mu_\gamma\}) \tag{6.64}$$

where P is the total grand-canonical pressure (6.63) including the statistics. But P^{MB} has been computed directly as function of densities that we call now $\rho_\alpha^{\mathrm{MB}}$ within the MB approximation. Then the $\rho_\alpha^{\mathrm{MB}}$ can be eliminated in favor of the true densities ρ_α by noting that both P and P^{MB} are evaluated at the same values of the chemical potentials μ_α. Hence we have the thermodynamic relation

$$\mu_\alpha = \frac{\partial}{\partial \rho_\alpha^{\mathrm{MB}}} f^{\mathrm{MB}}(\{\rho_\gamma^{\mathrm{MB}}\}) \tag{6.65}$$

with f^{MB} the free energy of the MB gas. Using (6.64) together with (6.65) enables us to express the μ_α and $\rho_\alpha^{\mathrm{MB}}$ in terms of the desired particle densities ρ_α. The final result is (Alastuey and Perez, 1996)

$$\beta P = \sum_\alpha \rho_\alpha - \frac{\kappa^3}{24\pi} \tag{6.66}$$

$$+ \pi\beta^3 \sum_{\alpha\gamma} \rho_\alpha \rho_\gamma e_\alpha^3 e_\gamma^3 \left[\frac{(\ln 2 - 1)}{6} + \left(\frac{1}{3} - \frac{3}{4} \ln 2 + \frac{1}{2} \ln 3 \right) \beta\kappa e_\alpha e_\gamma \right]$$

$$+ C_1 \beta^5 \kappa^{-1} \sum_{\alpha\gamma\delta} \rho_\alpha \rho_\gamma \rho_\delta e_\alpha^3 e_\gamma^4 e_\delta^3 + C_2 \beta^6 \kappa^{-3} \sum_{\alpha\gamma\delta\eta} \rho_\alpha \rho_\gamma \rho_\delta \rho_\eta e_\alpha^3 e_\gamma^3 e_\delta^3 e_\eta^3 \tag{6.67}$$

$$+\frac{1}{16}\beta^2\hbar^2\kappa^3\sum_\alpha \rho_\alpha \frac{e^2_\alpha}{m_\alpha} \tag{6.68}$$

$$-\frac{\pi}{\sqrt{2}}\sum_{\alpha\gamma}\rho_\alpha\rho_\gamma\left(1+\frac{3}{2}\beta\kappa e_\alpha e_\gamma\right)\left[\lambda^3_{\alpha\gamma}Q(x_{\alpha\gamma})+\frac{\sqrt{2}}{3}\beta^3 e^3_\alpha e^3_\gamma \ln(\kappa\lambda_{\alpha\gamma})\right] \tag{6.69}$$

$$+\frac{\pi}{\sqrt{2}}\sum_\alpha \frac{(-)^{2\sigma_\alpha+1}}{2\sigma_\alpha+1}\rho^2_\alpha\lambda^3_{\alpha\alpha}\left(1+\frac{3}{2}\beta\kappa e^2_\alpha\right)E(x_{\alpha\alpha}) \tag{6.70}$$

$$+O(\rho^3\ln\rho)$$

with

$$\kappa=\left(4\pi\beta\sum_\alpha e^2_\alpha\rho_\alpha\right)^{1/2}, \quad \lambda_{\alpha\gamma}=(\beta\hbar^2/m_{\alpha\gamma})^{1/2},$$

$$m_{\alpha\gamma}=m_\alpha m_\gamma/(m_\alpha+m_\gamma), \quad C_1=15.205\pm 0.001, \quad C_2=-14.733\pm 0.001$$

In (6.69), $x_{\alpha\gamma}=-\sqrt{2}\,\beta e_\alpha e_\gamma/\lambda_{\alpha\gamma}$ and $Q(x_{\alpha\gamma})$ is the quantum second order virial coefficient first introduced in (Ebeling, 1967; Ebeling, 1968)

$$Q(x_{\alpha\gamma})=\frac{1}{\sqrt{2}\,\pi\lambda^3_{\alpha\gamma}}\lim_{R\to\infty}\left\{\int_{r<R}d\mathbf{r}\Big[(2\pi\lambda^2_{\alpha\gamma})^{3/2}\langle\mathbf{r}|\exp(-\beta H_{\alpha\gamma})|\mathbf{r}\rangle\right.$$
$$\left.-1+\frac{\beta e_\alpha e_\gamma}{r}-\frac{\beta^2 e^2_\alpha e^2_\gamma}{2r^2}\Big]+\frac{2\pi}{3}\beta^3 e^3_\alpha e^3_\gamma\left(\ln\left(\frac{3\sqrt{2}\,R}{\lambda_{\alpha\gamma}}\right)+C\right)\right\} \tag{6.71}$$

while $E(x_{\alpha\alpha})$ is the exchange integral

$$E(x_{\alpha\alpha})=2\sqrt{\pi}\int d\mathbf{r}\,\langle -\mathbf{r}|\exp(-\beta H_{\alpha\alpha})|\mathbf{r}\rangle \tag{6.72}$$

In (6.71) and (6.72) $H_{\alpha\gamma}$ is the relative one-body Coulomb Hamiltonian for a particle of mass $m_{\alpha\gamma}$ submitted to the potential $e_\alpha e_\gamma/r$ and $C=0.577216...$ is the Euler–Mascheroni's constant.

The formula (6.66)–(6.70) incorporates and generalizes several earlier results. The perfect gas contribution $\sum_\alpha \rho_\alpha$ (the dominant one) has first been established rigorously in (Lebowitz and Pena, 1973), completed by (Hughes, 1985).[28] The next term is the lowest order correction to the free gas: one recognizes the familiar Debye–Hückel contribution (2.4). The quantum diffraction effects appear in the term (6.68) at the order $\rho^{5/2}$. The

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[28] Hughes studies the continuity of the free energy at vanishing density in relation to the techniques of Fefferman discussed in the next section.

term (6.69) incorporates the total contribution of bound and scattering states of the two-body Coulomb Hamiltonian.[29] The regularization of the integral in (6.71), which insures that $Q(x_{\alpha\gamma})$ is finite, is not arbitrary but comes from the structure of the bond F_q (6.61). One has here a ρ^2 contribution, the proper second order virial term, and a $\rho^{5/2}$ multiplicative correction that arises as a many-body mean field effect. Finally, the exchange term (6.70) has a similar structure.

The terms up to order $\rho^{5/2}$, including the exact ρ^2-virial contribution (6.69) are found in the work of Ebeling (Ebeling, 1967; Ebeling, 1968) and related references (Kraeft *et al.* 1986). The full formula (6.66)–(6.70), up to the diffraction term (6.68) appears in (Kraeft *et al.* 1986). These works use the method of the effective potential (or method of Morita). In this method, one associates to the quantum Coulomb gas an equivalent classical system of point particles interacting with an affective many-body interaction. In the case of the MB gas, this effective many-body potential Ψ_N is defined by interpreting the diagonal element $\langle \{\mathbf{r}_i\} | \exp(-\beta H_N) | \{\mathbf{r}_i\} \rangle$ as a classical Boltzmann factor

$$\langle \{\mathbf{r}_i\} | \exp(-\beta H_N) | \{\mathbf{r}_i\} \rangle = \prod_{i=1}^{N} \left(\frac{1}{2\pi\lambda_{\alpha_i}^2}\right)^{3/2} \exp(-\beta \Psi_N(\mathbf{r}_1, ..., \mathbf{r}_N)) \qquad (6.73)$$

One can decompose Ψ_N into a sum of two-body, three-body and higher order interactions, the two-body potential being

$$\Psi_2(\mathbf{r}_1, \mathbf{r}_2) = -\beta^{-1} \ln \left[\prod_{i=1}^{2} (2\pi\lambda_{\alpha_i}^2)^{3/2} \langle \mathbf{r}_1, \mathbf{r}_2 | \exp(-\beta H_2) | \mathbf{r}_1, \mathbf{r}_2 \rangle \right] \qquad (6.74)$$

Calculations up to order $\rho^{5/2}$ have been performed by keeping only the two-body potential (6.74), see references in (Kraeft *et al.* 1986). The long range Coulombic part of (6.74) can again be eliminated by summing the convolution chains and one can use the Abe-Meeron diagrammatics. This procedure gives the above formula for the pressure except (6.68). It turns out that one has to take the three-body interaction into account to recover the diffraction term.

One can specialize the equation of state to the one component plasma and take the classical limit:[30] these classical terms coincide with those

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[29] The $\ln(\kappa\lambda_{\alpha\gamma})$ term can be recombined with $Q(x_{\alpha\gamma})$. The splitting is introduced to have $Q(x_{\alpha\gamma})$ defined as in (Kraeft *et al.* 1986). Note also that our de Broglie length differs from that in (Kraeft *et al.* 1986) by a factor $\sqrt{2}$.

[30] This can be achieved by considering an asymmetrical two component system and letting $m_2 \to \infty$, $e_2 \to 0$, $\rho_2 \to \infty$ with $\rho_2 e_2$ finite and $\rho_2 e_2 + \rho_1 + e_1 = 0$. The one component plasma remains well behaved in the classical limit because of the spreading of the positive charge.

calculated in (Cohen and Murphy, 1969). One retrieves also the $\hbar$-correction, $\pi\beta^2 e^2 \rho^2 \hbar^2/6m$ to the classical equation of state (Pollock and Hansen, 1973). This correction has to be of order ρ^2: indeed one checks that the $\hbar^2\rho^{5/2}$ contributions coming from (6.68) and (6.69) compensate exactly. Finally high temperature series are recovered by expanding $Q(x)$ and $E(x)$ in powers of $\sqrt{\beta}$ (such expansions are derived in (Kraeft *et al.* 1986), and these series agree with the expressions obtained by the methods of (DeWitt, 1962; DeWitt, 1966; DeWitt, Schlanges, Sakakura, and Kraeft, 1995). Explicit formulae for various thermodynamic functions as well as their specialization to these particular cases can be found in (Alastuey and Perez, 1996).

The generalization of the low density equation of state to a uniformly magnetized plasma is given in (Cornu, 1997b; Cornu, 1998b).

VII. THE ATOMIC AND MOLECULAR LIMIT

A. The Electron–Proton Gas in the Saha Regime

The diagrammatic technique developed in Section V has provided a systematic low density expansion of the equation of state at fixed temperature. In particular, the lowest order term $\beta P = \sum_{\alpha=1}^{\mathcal{S}} \rho_\alpha$ in (6.66) represents a mixture of perfect Maxwell–Boltzmann gases constituted by the $\mathcal{S}$ species of fully dissociated charges: it is a free plasma state. Possible two-body bound states appear only as corrections in the second order virial coefficient. In this section, we will treat another regime where the basic constituents are now chemically bound entities behaving as ideal substances. This regime (called the Saha regime) is characterized by a joint limit where both the density and the temperature go to zero in a coupled way. The (exponentially fast) rate at which the density is reduced as $T \to 0$ determines a certain energy-entropy balance, selecting in turn the formation of some specific chemical species. Indeed low temperature favors binding over ionization, whereas low density, by increasing the available phase space per particle, favors dissociation. This limit is called the molecular (or atomic) limit. It was first formulated in precise terms by (Fefferman, 1985) and further studied by (Conlon, Lieb, and Yau, 1989; Graf and Schenker, 1995b). Equilibrium ionization phases in this context are discussed in (Macris and Martin, 1990). The Saha regime is also described in the usual language of many-body perturbation theory in (Ebeling, Kraeft, and Kremp, 1976; Kraeft *et al.* 1986).

In order to understand the issues involved in a simple setting, we consider the electron-proton (e-p) system and the possible formation of hydrogen atoms (see also (Fefferman, 1986; Martin, 1993) for general discussion and background). Let us adopt for a moment the thermodynamic view point that a chemist would take in presence of three preformed species, the electrons (e), the protons (p) and the hydrogen atoms (a) in their ground state. As a first approximation he takes into account the binding energy of each chemical species, but otherwise treats them as perfect gases of point particles. In this approximation, the grand-canonical densities are[31]

$$\rho_j = \left(\frac{m_j}{2\pi\beta\hbar^2}\right)^{3/2} \exp(-\beta(E_j - \mu_j)), \qquad j = e, p, a \tag{7.1}$$

where μ_j are the respective chemical potentials, $m_a = m_e + m_p$, $E_e = E_p = 0$ and $E_a < 0$ is the ground state energy of the hydrogen atom. The law of chemical equilibrium for the dissociation reaction $e + p \leftrightarrow a$ requires

$$\mu_a = \mu_e + \mu_p \tag{7.2}$$

and one also must have the neutrality $\rho_e = \rho_p$. Taking (7.2) into account and introducing the combinations

$$\mu = \frac{\mu_e + \mu_p}{2}, \qquad \nu = \frac{\mu_e - \mu_p}{2} \tag{7.3}$$

it is easily seen that the neutrality condition imposes the choice

$$\nu = \nu_0(\beta) = \frac{3}{4\beta} \ln \frac{m_p}{m_e} \tag{7.4}$$

and hence (7.1) becomes

$$\rho_e = \rho_p = \left(\frac{\sqrt{m_e m_p}}{2\pi\beta\hbar^2}\right)^{3/2} \exp(\beta\mu), \qquad \rho_a = \left(\frac{m_e + m_p}{2\pi\beta\hbar^2}\right)^{3/2} \exp(-\beta(E_a - 2\mu)) \tag{7.5}$$

Finally, since the species are treated as non-interacting, the pressure obeys the law of perfect gases

$$\beta P = \rho_e + \rho_p + \rho_a = \left(\frac{1+\gamma}{2}\right)\rho \tag{7.6}$$

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[31] This density $\rho_j = \rho_{\text{ideal}, j}$ as well as the densities (7.28) are those of ideal gases to which the interacting system will be eventually compared. For brevity, we drop the mention ideal here and in (7.28).

In (7.6), the pressure is expressed in terms of the total number density ρ of protons and electrons $\rho=\rho_e+\rho_p+2\rho_a$ and we have introduced the Saha coefficient for the degree of ionization

$$\gamma=\frac{\rho_e}{\rho_e+\rho_a}, \qquad 0\leqslant\gamma\leqslant 1 \tag{7.7}$$

A low density-low temperature regime can clearly be obtained by choosing μ negative and letting $\beta\to\infty$. Let us examine various cases noting from (7.5) that $\rho_a/\rho_e\sim\exp(-\beta(E_a-\mu))$.

(i) Fix $\mu<E_a$. The atomic density is exponentially small compared to that of the electrons and protons; there is full dissociation ($\gamma\to 1$) and the equation of state reduces to $\beta P=\rho$ as in the low density expansion (6.66).

(ii) Fix $\mu>E_a$ (but $\mu<E_a/2$). One obtains the opposite situation where the pure atomic phase dominates; now $\gamma\to 0$ and $\beta P=\frac{1}{2}\rho$ as $\beta\to\infty$.

(iii) At the borderline $\mu=E_a$, ρ_e and ρ_a are of the same order. More precisely, replace μ by

$$\tilde{\mu}(\beta)=E_a+\lambda\beta^{-1}+o(\beta^{-1}) \tag{7.8}$$

for some λ, $-\infty<\lambda<\infty$, i.e., approach the point $(E_a,0)$ in the (μ,T) plane along a direction having a finite slope λ. Then one obtains ionization equilibrium phases that interpolate between the fully ionized and the atomic ones. Their degree of ionization found from (7.5), (7.7) and (7.8) is

$$\gamma=\left(\left(\frac{m_e+m_p}{\sqrt{m_em_p}}\right)^{3/2}\exp(\lambda)+1\right)^{-1} \tag{7.9}$$

and they obey the equation of state (7.6). Written in terms of the pressure, the Saha coefficient reads after a short computation

$$\gamma=\left(1+\beta P\left(\frac{2\pi\beta h^2(m_e+m_p)}{m_em_p}\right)^{3/2}\exp(-\beta E_a)\right)^{-1/2} \tag{7.10}$$

This discussion makes clear that to an increase of μ corresponds an increase of the densities that favors the electron–proton binding when μ crosses the value E_a. How can we justify this picture from statistical mechanics? Consider now the exact infinite volume pressure $P(\beta,\mu_e,\mu_p)$ of the e-p system in the grand-canonical ensemble, and recall from Section I.D that it depends only on $\mu=(\mu_e+\mu_p)/2$

$$P(\beta, \mu_e, \mu_p)=P(\beta, \mu) \tag{7.11}$$

One may expect that the equation of state associated with $P(\beta, \mu)$ becomes close to (7.6) as $\beta \to \infty$ for appropriate values of μ as in cases (i)–(iii). The theorem on the atomic and molecular limit will gives a precise formulation of this assertion.

In the elementary considerations just presented, we have not taken into account, among other things, that electrons and protons can form other complexes as, for instance, hydrogen molecules. Let us examine this issue from the view point of statistical mechanics. If typical configurations of charges are indeed those of a dilute gas of hydrogen atoms (case (ii)), these configurations will be mainly formed of e-p pairs, the extension of a pair being of the order of the Bohr radius a_B, whereas two different pairs are at distance $\rho_a^{-1/3}$ ($a_B \ll \rho_a^{-1/3}$). If we choose at random in this configuration a region D of linear extension R with

$$a_B \ll R \ll \rho_a^{-1/3} \tag{7.12}$$

we will observe that this region is empty most of the time, but if it contains something it is exactly one hydrogen atom, except on rare occasions. In the grand-canonical formalism, it means that one must be able to find chemical potentials μ_e, μ_p such that for $\beta \gg 1$ and all $(N_e, N_p) \neq (0,0), (1,1)$

$$p_{00}(\beta, \mu_e, \mu_p, D) \gg p_{11}(\beta, \mu_e, \mu_p, D) \gg p_{N_e N_p}(\beta, \mu_e, \mu_p, D) \tag{7.13}$$

where

$$p_{N_e N_p}(\beta, \mu_e, \mu_p, D)=\frac{1}{\Xi_D} \exp(\beta(\mu_e N_e+\mu_p N_p)) \operatorname{Tr} \exp(-\beta H_{D, N_e N_p}) \tag{7.14}$$

is the probability to find exactly N_e electrons and N_p protons in D. Thus the condition (7.13) means indeed that if D is not void, it is more probable to find an e-p pair than anything else. The dominant term in $\operatorname{Tr} \exp(-\beta H_{D, N_e N_p})$ as $\beta \to \infty$ will be $\exp(-\beta E_{D, N_e N_p})$ where $E_{D, N_e N_p}$ is the ground state energy of $H_{D, N_e N_p}$. Hence to obtain the inequalities (7.13), one must be able to find values of μ_e and μ_p such that

$$\begin{aligned} E_{D, N_e N_p} - (\mu_e N_e+\mu_p N_p) &> E_{D,11} - (\mu_e+\mu_p) \\ &> 0 \quad \text{for all } (N_e, N_p) \neq (0,0), (1,1) \end{aligned} \tag{7.15}$$

Since ρ_a tends to zero exponentially fast as $\beta \to \infty$ we can also let the region D grow with β (but maintaining the inequalities (7.12)) so that $E_{D,\, N_e N_p}$ will differ from the bottom of the spectrum of $H_{N_e N_p}$ in infinite space

$$E_{N_e N_p} = \text{inf spectrum}(H_{N_e N_p}) \tag{7.16}$$

by a vanishingly small error. Moreover, introducing μ, ν as in (7.3)

$$\mu_e N_e + \mu_p N_p = \mu(N_e + N_p) + \nu(N_e - N_p) \tag{7.17}$$

we remark that the part μ of the chemical potential controls the total number density and ν the total charge density. We can take advantage of the fact that the infinite volume limit of the pressure will not depend on ν to make a convenient choice. As it was done in (7.4), we fix ν to ensure neutrality in the ideal gas when the lowest energy state corresponds to charged complexes. Then ν will be of order $0(\beta^{-1})$ as in the dissociated e-p system and can be dropped from (7.17) as β gets large. Therefore, in view of these remarks (that will be made mathematically more precise in Section VII.C) the relevant inequalities to be satisfied to produce the situation (7.13) as $\beta \to \infty$ are (with $E_{11} = E_a$)

$$E_{N_e N_p} - \mu(N_e + N_p) > E_a - 2\mu > 0 \quad \text{for all } (N_e, N_p) \neq (0, 0), (1, 1) \tag{7.18}$$

for some values of μ.

Let us examine some implications of (7.18). If $(N_e, N_p) = (1, 0)$ (single electron) $E_{10} = 0$ implies in (7.18)

$$E_a < \mu < 0 \tag{7.19}$$

If $(N_e, N_p) = (2, 2)$, (7.18) gives

$$\mu < \tfrac{1}{2}(E_{22} - E_a) \tag{7.20}$$

where E_{22} is the ground state energy of the hydrogen molecule. One can find μ satisfying (7.19) and (7.20) only if $E_a < \frac{1}{2}(E_{22} - E_a)$ or equivalently if $|E_{22} - 2E_a| < |E_a|$. The latter inequality means that the binding energy gained by the formation of an hydrogen molecule must be less than the binding energy of the atom itself, a well known fact. It allows the entropy to win over molecular binding at low density. However the numerical values of $(E_{22} - E_a)/2 \sim -9$ ev and of $\mu \sim -8$ ev, $k_{\mathrm{B}} T \sim 0.026$ ev under prevailing Earth conditions give an exceedingly small value of the ratio $\rho_a/\rho_{\mathrm{H}_2} \sim \exp(\beta(E_{22}-E_a-2\mu))$. Only molecular hydrogen appears on Earth, while the formation of the atomic gas discussed here can only occur in very dilute extraterrestrial medium. These considerations on molecular hydrogen do not suffice to guarantee the validity of the full set of inequalities (7.18): this necessitates a simultaneous examination of all ground state energies $E_{N_e N_p}$, a highly nontrivial problem. We shall discuss it further at the end of the next section. A geometric illustration of the inequalities (7.18) is given in Fig. 13. Notice that the binding energies of the ion H^- and the ionized molecule H_2^+ are too weak: they do not meet the inequalities analogous to (7.18), appropriate to these cases, for any value of μ.

Coming back to the e-p pressure, we may conjecture that if μ is increased just beyond $\frac{1}{2}(E_{22}-E_a)$ the chances for binding also increase, and the pressure $P(\beta, \mu)$ will become close to that a free gas of hydrogen molecules as $\beta \to \infty$. More generally, if one fixes $\mu < 0$, one expects that $P(\beta, \mu)$ approaches the pressure of free gases of some complexes that are selected at this particular value of the chemical potential.

B. The Main Theorem

With these preliminaries in mind, we are ready to formulate the main theorem about the Saha regime for electrons and an arbitrary number of nuclei with masses m_α, charges e_α, particle numbers N_α and chemical

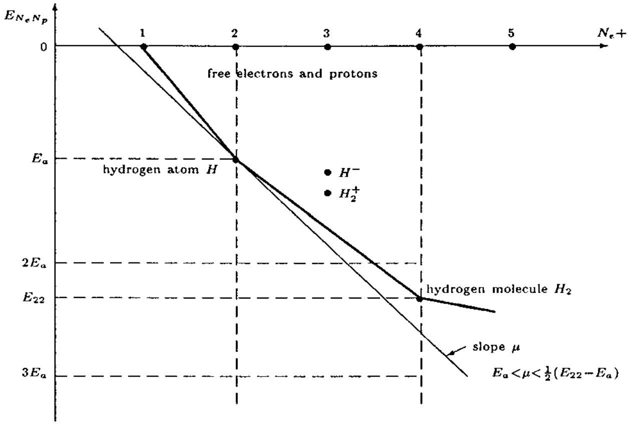

Fig. 13. The inequalities (7.18).

potentials μ_α, $\alpha = 1,..., \mathscr{S}$ ($\alpha = 1$ refers to electrons). As in Section I.D we adopt a vector notation for these. Set

$$\begin{aligned} &\underline{\mathbf{m}} = (m_1,..., m_{\mathscr{S}}), \qquad \underline{\mathbf{e}} = (e_1,..., e_{\mathscr{S}}) \\ &\underline{\mathbf{N}} = (N_1,..., N_{\mathscr{S}}), \qquad N = \sum_\alpha^{\mathscr{S}} N_\alpha, \qquad \underline{\boldsymbol{\mu}} = (\mu_1,..., \mu_{\mathscr{S}}) \end{aligned} \tag{7.21}$$

As we know (see (1.49)), the infinite volume pressure depends only on the component $\boldsymbol{\mu}$ of the chemical potential orthogonal to the charge vector. As a consequence, the kind of complexes that will occur for a certain value of the chemical potentials $\underline{\boldsymbol{\mu}}$ depends only on the value of $\boldsymbol{\mu}$. We will use this freedom to make a convenient choice of v along the proof.

The study of the molecular limit of $P(\beta, \boldsymbol{\mu})$ (i.e., $\beta \to \infty$, $\boldsymbol{\mu}$ fixed) will be carried out under the basic assumption on $\boldsymbol{\mu}$:

(A) there exists $\kappa > 0$ (κ independent of $\underline{\mathbf{N}}$) such that

$$H_{\underline{\mathbf{N}}} - \boldsymbol{\mu} \cdot \underline{\mathbf{N}} \geqslant \kappa N \qquad \text{for all } \underline{\mathbf{N}} \tag{7.22}$$

The complexes (atoms, ions, molecules) that will be formed in this limit are defined as follows. Consider the lowest energy state of the N-body Hamiltonian $H_{\underline{\mathbf{N}}}$

$$E_{\underline{\mathbf{N}}} = \inf \text{spectrum}(H_{\underline{\mathbf{N}}}) = \inf\{(\Phi, H_{\underline{\mathbf{N}}}\Phi): \Phi \in \mathscr{H}_N, \|\Phi\| = 1\} \tag{7.23}$$

and set

$$E(\boldsymbol{\mu}) = \inf_{\underline{\mathbf{N}} \neq \underline{\mathbf{0}}} (E_{\underline{\mathbf{N}}} - \boldsymbol{\mu} \cdot \underline{\mathbf{N}}) \tag{7.24}$$

A value $\underline{\mathbf{N}}_j$ for which this infimum is taken, i.e.,

$$E_{\underline{\mathbf{N}}_j} - \boldsymbol{\mu} \cdot \underline{\mathbf{N}}_j = E(\boldsymbol{\mu}) \tag{7.25}$$

is called the composition of the complex (j) having ground state energy $E_j = E_{\underline{\mathbf{N}}_j}$. Notice that (7.22) imposes the bound $N_{j,\alpha} \leqslant \kappa^{-1} E(\boldsymbol{\mu})$ for all α, so complexes are made out of a finite number of constituents, hence their number g is also finite. The complex (j), made of $N_{j,\alpha}$, $\alpha = 1,..., \mathscr{S}$, elementary constituents, has total particle number, mass and charge

$$N_j = \sum_\alpha^{\mathscr{S}} N_{j,\alpha}, \qquad m_j = \underline{\mathbf{m}} \cdot \underline{\mathbf{N}}_j, \qquad e_j = \underline{\mathbf{e}} \cdot \underline{\mathbf{N}}_j \tag{7.26}$$

Strictly speaking, $H_{\underline{\mathbf{N}}}$ has no ground state because of translation invariance. However for $N \geqslant 2$ one can decompose $H_{\underline{\mathbf{N}}} = K^{\mathrm{cm}}_{\underline{\mathbf{N}}} + H^{\mathrm{rel}}_{\underline{\mathbf{N}}}$ into the sum of the kinetic energy of the center of mass and the relative Hamiltonian, expressed in the coordinates relative to the center of mass. Since the spectrum of $K^{\mathrm{cm}}_{\underline{\mathbf{N}}}$ starts from zero, one has also $E_{\underline{\mathbf{N}}} = \inf$ spectrum$(H^{\mathrm{rel}}_{\underline{\mathbf{N}}})$. Consider now the threshold $\sigma_c(H^{\mathrm{rel}}_{\underline{\mathbf{N}}})$ of the continuous spectrum of $H^{\mathrm{rel}}_{\underline{\mathbf{N}}}$. We know from the HVZ theorem (Reed and Simon, 1979) that

$$\sigma_c(H^{\mathrm{rel}}_{\underline{\mathbf{N}}}) = \inf_{a,\, b;\; N_a + N_b = N} (E_{\underline{\mathbf{N}}_a} + E_{\underline{\mathbf{N}}_b}), \qquad N \geqslant 2 \tag{7.27}$$

where the infimum is taken over all partitions of the N particles into two clusters a and b having N_a and N_b particles, and $N_a = 1,\dots, N-1$. From the very definition of $E(\boldsymbol{\mu})$, one concludes from (7.27) that $\sigma_c(H^{\mathrm{rel}}_{\underline{\mathbf{N}}} - \boldsymbol{\mu} \cdot \underline{\mathbf{N}}) \geqslant 2E(\boldsymbol{\mu})$, $N \geqslant 2$. This means that the part of the spectrum of $H^{\mathrm{rel}}_{\underline{\mathbf{N}}} - \boldsymbol{\mu} \cdot \underline{\mathbf{N}}$ located in $[E(\boldsymbol{\mu}), 2E(\boldsymbol{\mu}))$ consists of isolated eigenvalues ($E(\boldsymbol{\mu})$ is strictly positive). In particular $E_{\underline{\mathbf{N}}_j}$ has to be an eigenvalue of $H^{\mathrm{rel}}_{\underline{\mathbf{N}}_j}$ and the corresponding eigenstate is the wave function of the bound complex (j). When $N = 1$, complexes reduce to the individual electrons or nuclei themselves with pure kinetic energy and we take then $E_{\underline{\mathbf{N}}} = 0$.

When there are charged complexes, we add to (A) the assumption

(B) if a complex has a charge $e_j \neq 0$, there is another complex having a charge of sign opposite to e_j (but not necessarily equal to $-e_j$).

insuring that an overall neutral gas can be formed.

We describe now the mixture of free gases made of these complexes. To each complex (j) one associates the density of a perfect gas of point particles

$$\rho_j(\beta, \underline{\boldsymbol{\mu}}) = \left(\frac{m_j}{2\pi\beta h^2}\right)^{3/2} \exp[-\beta(E_j - \underline{\boldsymbol{\mu}} \cdot \underline{\mathbf{N}}_j)] \tag{7.28}$$

and define the pressure of an ideal mixture of such gases by

$$\beta P_{\mathrm{ideal}}(\beta, \underline{\boldsymbol{\mu}}) = \sum_{j=1}^{g} \rho_j(\beta, \underline{\boldsymbol{\mu}}) \tag{7.29}$$

The corresponding number density of electrons and nuclei is

$$\rho_{\mathrm{ideal}}(\beta, \underline{\boldsymbol{\mu}}) = \sum_{\alpha=1}^{\mathscr{S}} \frac{\partial}{\partial \mu_\alpha} P_{\mathrm{ideal}}(\beta, \underline{\boldsymbol{\mu}}) = \sum_{j=1}^{g} N_j \rho_j(\beta, \underline{\boldsymbol{\mu}}) \tag{7.30}$$

If some complexes are charged, $P_{\text{ideal}}(\beta, \underline{\boldsymbol{\mu}})$ for a general $\underline{\boldsymbol{\mu}}$ may belong to a non-neutral ensemble. Then, under assumption (B), the neutrality $\sum_j e_j \rho_j = 0$ is implemented by setting

$$P_{\text{ideal, neutral}}(\beta, \underline{\boldsymbol{\mu}}) = \inf_{\nu} P_{\text{ideal}}(\beta, \underline{\boldsymbol{\mu}} + \nu \underline{\mathbf{e}}) \tag{7.31}$$

Then $P_{\text{ideal, neutral}}(\beta, \underline{\boldsymbol{\mu}}) = P_{\text{ideal, neutral}}(\beta, \boldsymbol{\mu})$ verifies (1.49), and one can formulate the theorem on the molecular limit as

Theorem. Let $\boldsymbol{\mu}$ be a chemical potential satisfying the condition (A) and determining complexes (j), $j = 1,..., g$, as described above, fulfilling the condition (B). Then there exists $\varepsilon > 0$ such that

$$P(\beta, \tilde{\boldsymbol{\mu}}) = P_{\text{ideal, neutral}}(\beta, \tilde{\boldsymbol{\mu}})(1 + O(\exp(-\beta\varepsilon))) \tag{7.32}$$

as $\beta \to \infty$ and $\tilde{\boldsymbol{\mu}} \to \boldsymbol{\mu}$.

The theorem deserves several comments that will be again illustrated in the e-p system. One should first appreciate that all the residual effects due to thermal excitations and interactions between complexes when the temperature and the densities are not strictly equal to zero are controlled by the $O(\exp(-\beta\varepsilon))$ correction. The issue of the theorem is precisely about obtaining this control.

Concerning the assumption (A), it is a difficult task to find what are the complexes associated with a chemical potential $\boldsymbol{\mu}$ and to verify (7.22). Conversely, if we ask for the occurrence of a certain chemical species, it is still beyond the present possibilities to rigorously determine the range of $\boldsymbol{\mu}$ (if any) allowing for the formation of this molecule. Suppose that we ask for the formation of hydrogen atoms in the e-p system. This means that there should be an interval $\mu \in (\mu_1, \mu_2)$ such that (A) holds and $\inf_{(N_e, N_p) \neq (0,0)}(E_{N_e N_p} - \mu(N_e + N_p))$ is taken at $(N_e, N_p) = (1, 1)$ with $E(\mu) = E_a - 2\mu$. This is equivalent to the fact that the inequalities (7.18) hold when $\mu \in (\mu_1, \mu_2)$ (if (7.18) is true for such a μ, one can pick $\kappa > 0$ small enough so that the same inequalities are true for $\mu + \kappa$; then κ provides the constant in the lower bound (7.22)). A little bit of thinking reveals that the validity of the inequalities (7.18) for a range of μ (μ slightly above E_a) is equivalent in turn with the following statement about the stability of matter: there exists a constant B with $0 < B < |E_a|$ such that

$$H_{N_e N_p} \geqslant -B(N_e + N_p - 1) \qquad \text{for all } (N_e, N_p) \neq (0, 0), (1, 1) \tag{7.33}$$

The point in (7.33) is that the constant B can be chosen strictly less than $|E_a|$ for all cases except of course for the hydrogen atom itself. Therefore a complete proof of the existence of the atomic phase relies on exhibiting a sufficiently small stability constant. Although (7.33) must hold on experimental and numerical grounds, a rigorous proof has not yet been provided (see (Fefferman, 1986) for a more detailed discussion).

Taking from now on (7.33) as a working hypothesis, we recover easily the previous cases (i)–(iii) when applying the theorem to the e-p system. If μ is slightly above E_a, there is a single complex, the hydrogen atom (a) with $E(\mu)=E_a-2\mu$ (case (ii)). If $\mu=E_a$ we have three complexes (e, p, a) and $E(\mu)=|E_a|$ (case (iii)). If $\mu<E_a$, the complexes are (e, p) and $E(\mu)=|\mu|$ (case (i)). When there are charged complexes, the minimizer ν of $P_{\text{ideal}}(\beta, \boldsymbol{\mu}+\nu\underline{\mathbf{e}})$ has the value (7.4) so that the result of the theorem is precisely the equation of state (7.6) up to an exponentially small correction.

For arbitrary nuclei, the theorem describes generically similar situations involving more complicated atoms, ions and molecules. If $\boldsymbol{\mu}$ selects a single complex, we have a free gas of that chemical species. If $\boldsymbol{\mu}$ selects several complexes, we can have coexisting free gases as $T\to 0$, generalizing the situation (iii) of the Section VII.A. As a corollary of the theorem, we can specify the relative proportion of these gases by taking $\tilde{\boldsymbol{\mu}}$ a function of the temperature that approaches $\boldsymbol{\mu}$ linearly as $T\to 0$ (as in (7.8))

$$\tilde{\boldsymbol{\mu}}(\beta)=\boldsymbol{\mu}+\boldsymbol{\lambda}\beta^{-1}+o(\beta^{-1}) \tag{7.34}$$

The densities of the gases will have weights proportional to $\exp(\boldsymbol{\lambda}\cdot\underline{\mathbf{N}}_j)$, leading then to general Saha formulae.

Although the determination of the kind of complexes occurring for a given value of $\boldsymbol{\mu}$ remains unsolved, it is pleasing to see how the thermodynamics of ideal substances emerges in principle from the basic statistical mechanics of electrons and nuclei in the molecular limit.

C. Elements of Proof

The theorem was first proven (Fefferman, 1985) for the e-p system under the assumption (7.33) (with a weaker control $O(\beta^{-1})$ of the error term). All the main ideas and subsequent developments summarized here have their roots in this work.

The general strategy of the proof does not rely on low density expansions, but on an analysis of typical equilibrium configurations of dilute gases of atoms and molecules. It proceeds along the following qualitative ideas. Let $\boldsymbol{\mu}$ be fixed and satisfy the condition (7.22), and take β very large. Then, in such configurations, if we look into a region of linear extension R in the range (7.12), according to the same discussion as that following

(7.12), this region is empty with high probability, but if it contains something, this will essentially be one of the complexes determined by $\boldsymbol{\mu}$. The idea is now to decompose the total domain $\Lambda = \bigcup_r D_r$ into subdomains D_r of diameter R and to let R grow with β in a suitable way. One has to solve the two following problems.

Problem 1. Determine the size of D_r such that the partition function $\Xi_{D_r}(\beta, \underline{\boldsymbol{\mu}})$ of a single subdomain is that of a system having at most complexes of the type (j), $j = 1,..., g$, in D_r.

Problem 2. Show that the residual interaction between the different regions D_r is negligible as $\beta \to \infty$ so that the total partition function $\Xi_\Lambda(\beta, \underline{\boldsymbol{\mu}}) \simeq \prod_r \Xi_{D_r}(\beta, \underline{\boldsymbol{\mu}})$ is close to that of independent subdomains D_r.

We make the preliminary decision (valid throughout the whole proof) to choose $v = v_0(\beta)$ as the minimizer of (7.31) insuring the neutrality of the ideal gas. This is equivalent to the pseudo-neutrality condition met earlier on several occasions. If some complex is not neutral and the condition (B) holds, $v_0(\beta)$ exists, is unique and $v_0(\beta) = \mathrm{O}(\beta^{-1})$ as can be checked from the explicit formulae (7.29) and (7.30) (see (7.4) in the e-p system). If all complexes are neutral one takes $v = 0$. Thus in the sequel we keep in mind that

$$\underline{\boldsymbol{\mu}} = \boldsymbol{\mu} + \mathrm{O}(\beta^{-1})\,\underline{\mathbf{e}} \tag{7.35}$$

1. Towards a Solution of Problem 1. We envisage now problem 1, following mainly (Conlon *et al.* 1989). we write the grand-canonical partition function for a finite region $D \subset \mathbb{R}^3$ of volume $|D|$ as a sum on all particle numbers

$$\Xi_D(\beta, \underline{\boldsymbol{\mu}}) = 1 + \sum_{j=1}^{g} \Xi_D(\beta, \underline{\boldsymbol{\mu}}, \underline{\mathbf{N}}_j) + \sum_{\underline{\mathbf{N}} \neq \underline{\mathbf{N}}_j} \Xi_D(\beta, \underline{\boldsymbol{\mu}}, \underline{\mathbf{N}}) \tag{7.36}$$

where we have singled out the contribution of the g complexes that correspond to the chosen value of $\boldsymbol{\mu}$ and

$$\begin{aligned} \Xi_D(\beta, \underline{\boldsymbol{\mu}}, \underline{\mathbf{N}}) &= \mathrm{Tr}_D \exp(-\beta(H_{D, \underline{\mathbf{N}}} - \underline{\boldsymbol{\mu}} \cdot \underline{\mathbf{N}})) \\ &= \mathrm{Tr}_D \exp(-\beta K^{\mathrm{cm}}_{D, \underline{\mathbf{N}}})\, \mathrm{Tr}_D \exp(-\beta(H^{\mathrm{rel}}_{D, \underline{\mathbf{N}}} - \underline{\boldsymbol{\mu}} \cdot \underline{\mathbf{N}})) \end{aligned} \tag{7.37}$$

In (7.37), Tr_D means that the trace is taken on states having the Dirichlet conditions appropriate to the finite volume Hamiltonians H_D as well as the appropriate particle statistics. For R large enough, one expects that the center of mass contribution is close to that of a free particle in space, and that the finite volume ground state energy $E_{D,\,j}$ of the complex j is close to its value E_j in infinite space. Indeed one can establish

$$\operatorname{Tr}_D \exp(-\beta K^{\mathrm{cm}}_{D,\,\underline{\mathbf{N}}_j}) = \left(\frac{m_j}{2\pi\beta\hbar^2}\right)^{3/2} |D| \left(1 + \mathrm{O}\left(\frac{1}{R}\right)\right) \tag{7.38}$$

and

$$E_{D,\,j} = E_j + \mathrm{O}\left(\frac{1}{R^2}\right) \tag{7.39}$$

Now let

$$|D| = |D_\beta| \simeq e^{c\beta}, \qquad c > 0 \tag{7.40}$$

grow exponentially fast as the temperature tends to zero, and consider the contribution of the ground state of $H^{\mathrm{rel}}_{D,\,\underline{\mathbf{N}}_j}$ to the partition function (7.37) for $\underline{\mathbf{N}} = \underline{\mathbf{N}}_j$. Taking (7.38), (7.39) and (7.40) into account, this contribution is

$$\begin{aligned} &\left(\frac{m_j}{2\pi\beta\hbar^2}\right)^{3/2} e^{-\beta(E_j - \underline{\boldsymbol{\mu}}\cdot\underline{\mathbf{N}}_j)}\, |D_\beta|\, (1 + \mathrm{O}(e^{-(c/3)\,\beta})) \\ &\qquad = \rho_j(\beta, \underline{\boldsymbol{\mu}})\, |D_\beta|\, (1 + \mathrm{O}(e^{-(c/3)\,\beta})) \end{aligned} \tag{7.41}$$

By (7.25) and (7.35), the density of the ideal gas $\rho_j(\beta, \underline{\boldsymbol{\mu}})$ (7.28) decreases as $\beta^{-3/2} e^{-\beta E(\boldsymbol{\mu})}$, $E(\boldsymbol{\mu}) > 0$; thus one can choose $c > 0$ small enough so that (7.41) is still exponentially small for β large.

We like to show that, under the condition (7.22), all the other terms in the sum (7.36) are negligible compared to (7.41), provided that the rate of growth of $|D_\beta|$ is suitably chosen. As $|D| \to \infty$, part of the spectrum of $H^{\mathrm{rel}}_{D,\,\underline{\mathbf{N}}}$ becomes continuous, corresponding to the scattering states of all the sub-complexes belonging to $H^{\mathrm{rel}}_{D,\,\underline{\mathbf{N}}}$. The basic idea is to ensure the convergence of the traces by the pure kinetic energy: one will dispense with the full Hamiltonian with the help of (7.22) and the ensuing gap property. Then the strict positivity of the constant κ in (7.22) and of the gap will be used to control the volume dependence of these traces. For this one borrows a small fraction of the kinetic energy $K_{\underline{\mathbf{N}}}$ writing

$$H_{\underline{\mathbf{N}}} = \eta K_{\underline{\mathbf{N}}} + (1 - \eta)\, K_{\underline{\mathbf{N}}} + V_{\underline{\mathbf{N}}}, \qquad \eta > 0 \tag{7.42}$$

where $K_{\underline{\mathbf{N}}} = -\sum_{i=1}^{N} (\hbar^2 \Delta_i / 2m_i)$ and $V_{\underline{\mathbf{N}}}$ is the total Coulomb interaction. Clearly the Hamiltonians $(1-\eta) K_{\underline{\mathbf{N}}} + V_{\underline{\mathbf{N}}}$ and $(1-\eta)^{-1} (K_{\underline{\mathbf{N}}} + V_{\underline{\mathbf{N}}}) = (1-\eta)^{-1} H_{\underline{\mathbf{N}}}$ are related by the scaling transformation $x_i \to (1-\eta) x_i$. Hence they are unitarily equivalent. This implies, using (7.22) and (7.35)

$$\begin{aligned}(1-\eta) K_{\underline{\mathbf{N}}} &+ V_{\underline{\mathbf{N}}} - \underline{\boldsymbol{\mu}} \cdot \underline{\mathbf{N}} \\ &\geqslant (1-\eta)^{-1} \inf \operatorname{spectrum}(H_{\underline{\mathbf{N}}} - \underline{\boldsymbol{\mu}} \cdot \underline{\mathbf{N}}) + (1-\eta)^{-1} \eta \underline{\boldsymbol{\mu}} \cdot \underline{\mathbf{N}} + \mathrm{O}(\beta^{-1}) N \\ &\geqslant (1-\eta)^{-1} (\kappa - \eta \max_i |\mu_i|) N + \mathrm{O}(\beta^{-1}) N \equiv c_1 N \end{aligned} \tag{7.43}$$

Thus

$$H_{\underline{\mathbf{N}}} - \underline{\boldsymbol{\mu}} \cdot \underline{\mathbf{N}} \geqslant \eta K_{\underline{\mathbf{N}}} + c_1 N \tag{7.44}$$

where $c_1 > 0$ provided that η is small enough and β is large enough. The same inequality holds when $H_{\underline{\mathbf{N}}}$ is replaced by $H_{D, \underline{\mathbf{N}}}$ since Dirichlet boundary conditions increase the kinetic energy; hence one concludes that

$$\begin{aligned}\Xi_D(\beta, \underline{\boldsymbol{\mu}}, \underline{\mathbf{N}}) &\leqslant \exp(-\beta c_1 N) \operatorname{Tr}_D e^{-\beta \eta K_{\underline{\mathbf{N}}}} \\ &\leqslant |D|^N \prod_{i=1}^{N} \left(\frac{m_i}{2\pi \eta \beta \hbar^2} \right)^{3/2} e^{-\beta c_1 N} \end{aligned} \tag{7.45}$$

If now $|D| = |D_\beta|$ grows at the rate $e^{c\beta}$ with $0 < c < c_1$, $\Xi_{D_\beta}(\beta, \underline{\boldsymbol{\mu}}, \underline{\mathbf{N}})$ is bounded by $e^{-c_2 \beta N}$ for some $c_2 > 0$. Thus by choosing N_0 large, one can make the exponential decay of the whole sum of terms with $N \geqslant N_0$ in (7.36) fast enough to have

$$\sum_{\underline{\mathbf{N}},\, N \geqslant N_0} \Xi_{D_\beta}(\beta, \underline{\boldsymbol{\mu}}, \underline{\mathbf{N}}) = \rho_j(\beta, \underline{\boldsymbol{\mu}}) \, |D_\beta| \, \mathrm{O}(e^{-\beta\varepsilon}), \qquad \varepsilon > 0 \tag{7.46}$$

For the remaining terms, i.e., the terms with $\underline{\mathbf{N}} \neq \underline{\mathbf{N}}_j$, $N < N_0$ and the contribution of the excited states to $\Xi_D(\beta, \underline{\boldsymbol{\mu}}, \underline{\mathbf{N}}_j)$, one uses essentially the fact that $E(\underline{\boldsymbol{\mu}})$ is separated from the rest of the spectrum by a gap, according to the discussion following (7.27). On the subspace orthogonal to the ground states of $H^{\mathrm{rel}}_{\underline{\mathbf{N}}_j} - \underline{\boldsymbol{\mu}} \cdot \underline{\mathbf{N}}_j$ one has, arguing as in (7.43)

$$\begin{aligned}(1-\eta) K_{\underline{\mathbf{N}}} &+ V_{\underline{\mathbf{N}}} - \underline{\boldsymbol{\mu}} \cdot \underline{\mathbf{N}} \\ &\geqslant (1-\eta)^{-1} (E(\underline{\boldsymbol{\mu}}) + 2\delta) + (1-\eta)^{-1} \eta \underline{\boldsymbol{\mu}} \cdot \underline{\mathbf{N}} + \mathrm{O}(\beta^{-1}) N \\ &\geqslant (1-\eta)^{-1} (E(\underline{\boldsymbol{\mu}}) + 2\delta - \eta \max_i |\mu_i| N) + \mathrm{O}(\beta^{-1}) N \end{aligned} \tag{7.47}$$

for some $\delta > 0$. Since now $N < N_0$, one can choose η sufficiently small and β sufficiently large to have on this subspace

$$H_{\underline{\mathbf{N}}} - \underline{\boldsymbol{\mu}} \cdot \underline{\mathbf{N}} \geqslant \eta K_{\underline{\mathbf{N}}} + E(\boldsymbol{\mu}) + \delta, \qquad \delta > 0, \qquad N < N_0 \tag{7.48}$$

Hence for $\underline{\mathbf{N}} \neq \underline{\mathbf{N}}_j$, $N < N_0$, one finds as in (7.45)

$$\begin{aligned} \Xi_D(\beta, \underline{\boldsymbol{\mu}}, \underline{\mathbf{N}}) &\leqslant e^{-\beta(E(\boldsymbol{\mu}) + \delta)} \operatorname{Tr}_D e^{-\beta\eta K_{\underline{\mathbf{N}}}} \\ &\leqslant |D|^N \prod_{i=1}^{N} \left(\frac{m_i}{2\pi\eta\beta\hbar^2}\right)^{3/2} e^{-\beta E(\boldsymbol{\mu})} e^{-\beta\delta} \end{aligned} \tag{7.49}$$

Since $|D_\beta|^N$ grows at most as $e^{c\beta N_0}$ we can again have

$$\Xi_{D_\beta}(\beta, \underline{\boldsymbol{\mu}}, \underline{\mathbf{N}}) = \rho_j(\beta, \underline{\boldsymbol{\mu}})\, |D_\beta|\, \mathrm{O}(e^{-\beta\varepsilon}), \quad \underline{\mathbf{N}} \neq \underline{\mathbf{N}}_j, \quad N < N_0, \quad \varepsilon > 0 \tag{7.50}$$

by taking c small. Notice that a volumes factor $|D_\beta|$ corresponding to the free motion of the overall center of mass has been explicitly maintained in the estimates (7.46) and (7.50) (at the expense of a possibly smaller constant ε). Finally one deals with the excited states of $H^{\mathrm{rel}}_{\underline{\mathbf{N}}_j} - \boldsymbol{\mu} \cdot \underline{\mathbf{N}}_j$ in the same way. Combining this with (7.41), (7.46) and (7.50) in the grand canonical sum (7.36), one obtains

$$\Xi_{D_\beta}(\beta, \underline{\boldsymbol{\mu}}) = 1 + \sum_{j=1}^{g} \rho_j(\beta, \underline{\boldsymbol{\mu}})\, |D_\beta|\, (1 + \mathrm{O}(e^{-\varepsilon\beta})) \tag{7.51}$$

Since the second term in the right hand side is exponentially small as $\beta \to \infty$ (see the comment after (7.41)) one has also

$$\ln \Xi_{D_\beta}(\beta, \underline{\boldsymbol{\mu}}) = \sum_{j=1}^{g} \rho_j(\beta, \underline{\boldsymbol{\mu}})\, |D_\beta|\, (1 + \mathrm{O}(e^{-\varepsilon\beta})) \tag{7.52}$$

Taking into account the definition (7.29) together with our choice of v, this says that the pressure $P_{D_\beta}(\beta, \underline{\boldsymbol{\mu}})$ in D_β is given by

$$\beta P_{D_\beta}(\beta, \underline{\boldsymbol{\mu}}) = \frac{1}{|D_\beta|} \ln \Xi_{D_\beta}(\beta, \underline{\boldsymbol{\mu}}) = \beta P_{\mathrm{ideal}}(\beta, \underline{\boldsymbol{\mu}})(1 + \mathrm{O}(e^{-\varepsilon\beta})) \tag{7.53}$$

This solves problem 1: in a volume $|D_\beta| \simeq e^{c\beta}$ with $c > 0$ sufficiently small (depending only on $\boldsymbol{\mu}$), the pressure is exclusively due to the non-interacting complexes (j), $j = 1,..., g$. However this does not prove the theorem yet. In (7.53), D_β is constrained by the growth condition (7.40) and not an independent thermodynamic variable as it should be in the grand canonical ensemble. One needs to solve problem 2.

2. Towards a Solution of Problem 2. Problem 2 is technically considerably more sophisticated, so let us give first some very heuristic ideas. Decompose $\mathbb{R}^3 = \bigcup_r D_r$ into a disjoint union of domains D_r with characteristic functions χ_{D_r}, $\chi_{D_r}(x) = 1$ if x is in D_r and $\chi_{D_r}(x) = 0$ otherwise. One wants to show that the interactions between the different domains D_r become negligible as $\beta \to \infty$. To this end, define an uncorrelated Hamiltonian by

$$H_\Lambda^{\text{uncor}} = H_\Lambda - U^{\text{cor}} \tag{7.54}$$

where U^{cor} is the potential energy between the different domains

$$U^{\text{cor}} = \sum_{i<j} e_{\alpha_i} e_{\alpha_j} V^{\text{cor}}(x_i, x_j) \tag{7.55}$$

$$V_{\text{cor}}(x_1, x_2) = \frac{1 - \sum_r \chi_{D_r(x_1)} \chi_{D_r}(x_2)}{|x_1 - x_2|} \tag{7.56}$$

U^{cor} (as well as H_Λ^{uncor}) will be an effective temperature dependent energy via the condition $|D_r| \simeq e^{c\beta}$ determined in problem 1. Note that if $|x_1 - x_2| < R$ and both x_1 and x_2 belong to the same subdomain, then $V^{\text{cor}}(x_1, x_2) = 0$; also $V^{\text{cor}}(x_1, x_2)$ is Coulombic at large distances. This resembles the properties of a regularized Coulomb interaction. Suppose that we are able to define the uncorrelated Hamiltonian in a less crude way than in (7.54) and (7.56) with the effect of replacing (7.56) by a smooth positive definite regularized potential, finite everywhere for $|x_1 - x_2| < R$ and asymptotically Coulombic. A possible candidate is

$$V_{\text{reg}}^{\text{cor}}(x_1, x_2) = \int dy_1 \int dy_2 \, \frac{\phi_R(y_1)\, \phi_R(y_2)}{|x_1 - y_1 - x_2 + y_2|} \tag{7.57}$$

where $\phi_R(y) = R^{-3} \phi(y/R)$ with $\phi(y)$ a smooth function, $(\phi(y) = 0,\ |y| \geqslant 1,$ $\int dy\, \phi(y) = 1)$ representing a charge density supported in a region of extension R with total charge equal to 1. Other candidates closer to the form (7.56) are

$$V_{\text{reg}}^{\text{cor}}(x_1, x_2) = \frac{1 - h((x_1 - x_2)/R)}{|x_1 - x_2|} \tag{7.58}$$

with $h(x)$ a smooth short range function, $h(0)=1$, and $(1-h(x))/|x|$ positive definite. Then we can use the basic positivity argument already introduced in Section I.B

$$\begin{aligned} U^{\mathrm{cor}}_{\mathrm{reg}} &= \tfrac{1}{2}\sum_{ij}^{N} e_{\alpha_i} e_{\alpha_j} V^{\mathrm{cor}}_{\mathrm{reg}}(x_i, x_j) - \tfrac{1}{2} V^{\mathrm{cor}}_{\mathrm{reg}}(0) \sum_{i}^{N} e^2_{\alpha_i} \\ &\geqslant -\tfrac{1}{2} V^{\mathrm{cor}}_{\mathrm{reg}}(0) \sum_{i=1}^{N} e^2_{\alpha_i} \end{aligned} \tag{7.59}$$

because of the positive definiteness of $V^{\mathrm{cor}}_{\mathrm{reg}}(x_1, x_2)$. Note that by scaling, in both forms (7.57) and (7.58), one has $V^{\mathrm{cor}}_{\mathrm{reg}}(0) = \mathrm{O}(1/R)$. Therefore if one can find such a regularized correlation energy, one will have (being still very sketchy) that $H^{\mathrm{uncor}}_{\Lambda}$ provides a lower bound to the full Hamiltonian

$$H_{\Lambda} - \underline{\boldsymbol{\mu}} \cdot \underline{\mathbf{N}} = H^{\mathrm{uncor}}_{\Lambda} + U^{\mathrm{cor}}_{\mathrm{reg}} - \underline{\boldsymbol{\mu}} \cdot \underline{\mathbf{N}} \geqslant H^{\mathrm{uncor}}_{\Lambda} - (1 + \mathrm{O}(R^{-1}))\, \underline{\boldsymbol{\mu}} \cdot \underline{\mathbf{N}} \tag{7.60}$$

Thus, up to a small correction to the chemical potential, one finds that the partition function is dominated by that of the uncorrelated domains

$$\Xi_{\Lambda}(\beta, \underline{\boldsymbol{\mu}}) \leqslant \prod_{D_r \cap \Lambda \neq \varnothing} \Xi_{D_r}(\beta, \underline{\boldsymbol{\mu}}(1 + \mathrm{O}(R^{-1}))) \tag{7.61}$$

We set now $|D_r| = |D_{r,\beta}| \simeq e^{c\beta}$, β sufficiently large, and apply to each of the D_r the result (7.52) of problem 1. Taking the logarithm of (7.61) and absorbing the error in the chemical potential in the $\mathrm{O}(e^{-\varepsilon\beta})$ correction, one obtains in the thermodynamic limit

$$\begin{aligned} \beta P(\beta, \underline{\boldsymbol{\mu}}) &\leqslant \lim_{|\Lambda| \to \infty} \left[\frac{1}{|\Lambda|} \sum_{D_{r,\beta} \cap \Lambda \neq \varnothing} |D_{r,\beta}| \right] \beta P_{\mathrm{ideal}}(\beta, \underline{\boldsymbol{\mu}})(1 + \mathrm{O}(e^{-\varepsilon\beta})) \\ &= \beta P_{\mathrm{ideal}}(\beta, \underline{\boldsymbol{\mu}})(1 + \mathrm{O}(e^{-\varepsilon\beta})) \end{aligned} \tag{7.62}$$

The technically most elaborate parts of the works (Fefferman, 1985; Conlon *et al.* 1989; Graf and Schenker, 1995b) consists in constructing an uncorrelated Hamiltonian having the requested positivity and smoothness properties, and comparing it with the true Hamiltonian H_{Λ}. In its main lines the construction of (Conlon *et al.* 1989; Graf and Schenker, 1995b) goes as follows.

The decomposition $\mathbb{R}^3 = \bigcup_r D_r$ is realized with regions D_r that are translates and dilations (with the scale parameter R) of a fundamental domain D_0. Let $\mathscr{F}_{D_r}$ be the Fock space for a Coulomb system localized in D_r, having Hamiltonian H_{D_r} with Dirichlet boundary conditions on ∂D_r.

The most obvious way to define states of independent Coulomb systems, each of them confined in a region D_r, is to introduce the product space $\mathscr{F}_{\Lambda}^{\text{uncor}} = \prod^{\otimes}_{D_r \cap \Lambda \neq \varnothing} \mathscr{F}_{D_r}$ and the Hamiltonian $\sum_{D_r \cap \Lambda \neq \varnothing} H_{D_r}$ on it. One wants to compare this obviously strictly uncorrelated Hamiltonian with the true H_Λ acting on $\mathscr{F}_\Lambda$ when the scale parameter $R \to \infty$. For this, one introduces a partition of the unity on $\mathbb{R}^3$ of the form $\sum_r \chi^2_{r,R}(x) = 1$ for all $x \in \mathbb{R}^3$ where $\chi_{r,R}$ are suitably chosen smooth functions essentially supported in the region D_r of linear size R. With the help of this partition, one defines an isometry $J: \mathscr{F}_\Lambda \to \mathscr{F}_{\Lambda}^{\text{uncor}}$ which maps the states of the system onto the uncorrelated ones. Then one compares the image $J^{-1}(\sum_{D_r \cap \Lambda \neq \varnothing} H_{D_r})\, J$ of the strictly uncorrelated Hamiltonian with H_Λ on $\mathscr{F}_\Lambda$. The calculation gives

$$H_\Lambda - J^{-1}\left(\sum_{D_r \cap \Lambda \neq \varnothing} H_{D_r}\right) J = U^{\text{cor}}_{\text{reg}} + O\left(\frac{1}{R^2}\right) \tag{7.63}$$

where $U^{\text{cor}}_{\text{reg}}$ has the form (7.55) and (7.58), and

$$h(x) = \int dy\, \chi^2(x+y)\, \chi^2(y) \tag{7.64}$$

is a smooth function localized in the neighborhood of D_0: (7.63) is a more precise version of (7.54). The $O(1/R^2)$ term is the price of the increase in kinetic energy paid for the additional Dirichlet conditions imposed at the boundary of each D_r in the strictly uncorrelated Hamiltonian $\sum_r H_{D_r}$. This price can be made small as $R \to \infty$ because of the differentiability of the localization functions $\chi_{r,R}$.

The main issue is now the lower bound (7.59), i.e., to have $V^{\text{cor}}_{\text{reg}}(x_1, x_2)$ positive definite. In (Conlon *et al.* 1989), the regions D_r are cubes, and this positivity is obtained by replacing the Coulomb potential in $\sum_{D_r \cap \Lambda \neq \varnothing} H_{D_r}$ by a Debye potential $e^{-\varepsilon |x|}/|x|$ with small ε ($\varepsilon \simeq e^{-c\beta}$). Then it turns out that

$$V^{\text{cor}}_{\text{reg}}(x_1, x_2) = \frac{1}{|x_1 - x_2|}\left(1 - \frac{h((x_1 - x_2)/R)}{h(0)}\, e^{-\varepsilon |x_1 - x_2|}\right)$$

is similar to $V_{\infty,\lambda}$ (1.8). Its Fourier transform can be shown to be positive for ε and R in appropriate ranges by using properties of $h(x)$ (7.64), and the arguments (7.59)–(7.62) can eventually be cast in a rigorous form. However, to complete the proof, one has to show that the assumption (A) in the main theorem as well as the results obtained in problem 1 are stable when the Coulomb potential is approximated by the Debye potential. In particular, if (A) holds with a constant κ, then one has also for the Debye Hamiltonian $H^{\varepsilon}_{\underline{\mathbf{N}}}$

$$H^{\varepsilon}_{\underline{\mathbf{N}}} - \boldsymbol{\mu} \cdot \underline{\mathbf{N}} \geqslant \kappa(\varepsilon)\, N \qquad \text{with} \quad \kappa(\varepsilon) \to \kappa, \quad \varepsilon \to 0 \tag{7.65}$$

This theorem is proven in (Conlon *et al.* 1989) with the same localization techniques.

In (Graf and Schenker, 1995b), the decomposition $\mathbb{R}^3 = \bigcup_r D_r$ is realized with simplices. Then the stability (7.59) follows remarkably from the geometrical properties of a simplex. Namely for the spherical average $\bar{h}(|x|)$ of $h(x)$ (7.64) (here $\chi = \chi_{D_0}$ is the characteristic function of a simplex), the function $(\bar{h}(0) - \bar{h}(|x|))/|x|$ has a positive Fourier transform.

The original proof (Fefferman, 1985) uses certain coverings of $\mathbb{R}^3$ (called Swiss cheese) made of small cubes and large balls of different radii, and a positive definite potential of the form (7.57). The delicate point is to estimate the difference $V^{\text{error}} = V^{\text{cor}} - V^{\text{cor}}_{\text{reg}}$ between (7.56) and (7.57). V^{error} still contains a local singularity as well as non-positive definite Coulomb energy terms. By averaging on the different radii of the balls, Fefferman shows that these dangerous contributions in V^{error} are majorized by a Coulomb potential $O(\beta^{-1})/|x|$ with a small amplitude, and that these dangerous terms) become eventually negligible. Then the stability (7.59) follows from the positive definiteness of $V^{\text{cor}}_{\text{reg}}$ (7.57).

In all cases the proofs involve fixing a number of important details not mentioned here.

Finally, (7.62) must be completed by the converse inequality; the job is fortunately easier and relies on an application of the variational principle. We refer to the original papers for this final step.

VIII. CONVERGENT EXPANSIONS

In previous sections we have alluded to the Mayer expansion and results on the convergence of Mayer expansions. This is an old subject reviewed in numerous places including (Brydges, 1984) but since that review some beautiful new combinatoric formulas have been discovered. The main objective of this summary is to update (Brydges, 1984) to bring these to the attention of our readers, together with some applications and ramifications. This is done in Sections VIII.A, VIII.B.

Related ideas convert the considerations of Section II.G into convergent expansions and thereby prove there is screening. We outline these arguments in Sections VIII.C, VIII.D, VIII.E. This updates an older review (Brydges and Federbush, 1981).

We are accustomed to expansions in theoretical physics where the terms are labeled by connected graphs. It is usually the case that the number of connected graphs at order N grows more rapidly than $N!$ so that such expansions appear to be divergent at least until cancellations between graphs have been taken into account. The older review (Brydges, 1984) was centered on rigorous bounds that say that the sum over all connected graphs at order N is actually smaller than the sum over just the least connected graphs, i.e., tree graphs. The new part of this review is Theorem VIII.2 which makes the relation between all graphs and tree graphs much clearer.

A. Tree Graph Formulas and the Mayer Expansion

We begin with a little review of the theory of activity expansions (Ruelle, 1969; Hansen and McDonald, 1976; Mayer and Mayer, 1977). Suppose N particles labeled $1, 2,..., N$ have two-body potentials V_{ij}. The total potential of a subset X of these particles is

$$U_X = \sum_{ij \in X} V_{ij} \tag{8.1}$$

where $ij = ji$ is an unordered pair of distinct particles and $ij \in X$ means $i, j \in X$. Consider the formulas

$$\begin{aligned} e^{-U_X} &= \sum_{G} \prod_{ij \in G} (e^{-V_{ij}} - 1) \\ (e^{-U_X})_c &= \sum_{G \text{ connected}} \prod_{ij \in G} (e^{-V_{ij}} - 1) \end{aligned} \tag{8.2}$$

In the first the sum is over all graphs G, connected or disconnected, on vertices in X. It is an immediate consequence of expanding the product over ij of $\exp(-V_{ij}) - 1 + 1$, remembering that a graph on X is, by definition, an arbitrary subset of $\{ij : ij \in X\}$. The second formula is the usual way to define the connected part $\exp(-U_X)_c$, but there is another equivalent definition, namely the connected part is the (unique) recursive solution of

$$\begin{aligned} e^{-U_X} &= \sum_{M \geqslant 1} \frac{1}{M!} \sum_{\substack{X_1,..., X_M \\ \cup X_j = X}} \prod_{j=1}^{M} (e^{-U_{X_j}})_c \qquad \text{if} \quad |X| > 1 \\ (e^{-U_X})_c &= 1 \qquad \text{if} \quad |X| = 1 \end{aligned} \tag{8.3}$$

where $X_1,..., X_M$ are disjoint. The equivalence of the two definitions is not a hard exercise and is the main step in obtaining the Mayer expansion, which is

Theorem VIII.1. Let $U_N = U_{\{1,..., N\}}$ where $V_{ij} = V(\mathbf{r}_i, \mathbf{r}_j)$ is the pair interaction between particles in a grand canonical ensemble Ξ. Then

$$\ln \Xi \sim \sum_{N \geqslant 1} \frac{1}{N!} \int \prod_{j=1}^{N} d\mathscr{E}_j \, z(\mathscr{E}_j)(e^{-\beta U_N})_c \tag{8.4}$$

The proof that this formal expansion results from (8.3) is in most textbooks in statistical mechanics. The classical proofs that this expansion is convergent for small activity were given in (Groeneveld, 1962; Penrose, 1963; Ruelle, 1963). Our line development begins with (Penrose, 1967) who showed that when the interactions are repulsive the sum over *all* connected graphs at order N is dominated by the sum over tree graphs at the same order. By Cayley's theorem the number of tree graphs on N vertices is N^{N-2} which is comparable to $N!$. The convergence of the Mayer expansion at small activity will be seen to be an immediate consequence.

Notation. We consider the class $\mathscr{F}$ of graphs called forests: A graph G is a forest if it has no closed loops or equivalently if each connected component of G is a tree graph. A single isolated vertex which is not in any bond is considered to be an empty tree graph. The empty graph which has no lines, so that every vertex is isolated, is therefore a forest. A forest G has the property that for any pair of vertices ij, either there is a unique path that joins i to j consisting of bonds in G or there is no path at all. To every bond $ij \in \{1, 2,..., N\}$ is associated a non-negative parameter s_{ij}. The vector whose components are all these parameters is denoted by $\mathbf{s}$ and $\mathbb{1}$ is the vector where each $s_{ij} = 1$. Let G be a forest. For each bond ij we set

$$\sigma_{ij}(G, \mathbf{s}) = \begin{cases} \inf\{s_b : b \in \text{path in } G \text{ joining } i \text{ and } j\} \\ 0 \text{ if no path} \end{cases} \tag{8.5}$$

Thus if ij belongs to the forest G then $\sigma_{ij} = s_{ij}$. Also, $\sigma_{ij}(G, \mathbf{s})$ depends only on the s_{ij} parameters assigned to bonds in G. We let $\boldsymbol{\sigma}(G, \mathbf{s})$ denote the vector whose components are $\sigma_{ij}(G, \mathbf{s})$. We set $\partial^G = \prod_{b \in G} \partial/\partial s_b$. The symbol $\int^t d^G s$ means that for each $b \in G$ s_b is integrated over the interval $[0, t]$. We write $f \circ \boldsymbol{\sigma}(G, \mathbf{s}) = f(\boldsymbol{\sigma}(G, \mathbf{s}))$ so that the notation $(\partial^G F) \circ \boldsymbol{\sigma}(G, \mathbf{s})$ will mean: first do the derivatives with respect to s_b with $b \in G$ and then evaluate at $\boldsymbol{\sigma}(G, \mathbf{s})$.

The following theorem is a type of fundamental theorem of calculus. It reached this simple form through the series of papers (Glimm, Jaffe, and Spencer, 1974; Brydges and Federbush, 1978; Battle and Federbush, 1984; Brydges and Kennedy, 1987; Abdesselam and Rivasseau, 1995).

Theorem VIII.2. Let $F(\mathbf{s})$ be any continuously differentiable function of parameters s_{ij} where $ij = ji$ and $i \neq j \in \{1, 2,..., N\}$ and $N \geqslant 2$. Let $t \geqslant 0$. Then

$$F(t\mathbb{1}) = \sum_{G \in \mathscr{F}} \int^{t} d^{G}s (\partial^{G} F) \circ \boldsymbol{\sigma}(G, \mathbf{s}) \tag{8.6}$$

where

$$\int^{t} d^{G}s (\partial^{G} F) \circ \boldsymbol{\sigma}(G, \mathbf{s}) = F(0\mathbb{1})$$

when G is the empty forest.

Note that the theorem is valid when $t = 0$ because all terms in the sum over G vanish except when G is the empty forest and in this case the right hand side is $F(0\mathbb{1})$, by definition. Also, if $N = 2$, the theorem reduces to $F(t) = F(0) + \int^{t} \partial_{12} F(s_{12}) \, ds_{12}$, which is the fundamental theorem of calculus. A proof of this theorem is given in Section VIII.F.

To study the Gibbs factor $\exp(-\beta \sum V_{ij})$ by this theorem we introduce parameters s_{ij} in such a way that the Gibbs factor is the value of

$$F(\mathbf{s}) = e^{-\beta U_N(\mathbf{s})} = \exp\left(-\beta \sum_{ij} V_{ij}(s_{ij})\right) \tag{8.7}$$

when $\mathbf{s} = \mathbb{1}$. We choose $V_{ij}(s_{ij})$ to vanish at $s_{ij} = 0$ so that $\mathbf{s} = 0$ corresponds to all interactions being switched off. We will call such a choice of dependence on s_{ij} an interpolation.

Assume we have such an interpolation. Given a forest G on vertices $\{1, 2,..., N\}$, we can decompose it into connected components. These connected components are subgraphs, trees, on subsets of vertices $X_1,..., X_M$. Thus G determines a partition of the set of vertices into "clusters" $X_1,..., X_M$. Vertices label particles and from the definition of $\boldsymbol{\sigma} \equiv \boldsymbol{\sigma}(G, \mathbf{s})$ there are no interactions in $U_N(\boldsymbol{\sigma})$ between particles in different trees so that $(\partial^{G} F) \circ \boldsymbol{\sigma}$ factors across the partition $X_1,..., X_M$. By comparing the definition of connected part (8.3) with the result of the theorem one obtains

Theorem VIII.3. For $N \geqslant 2$

$$(e^{-\beta U_N})_c = \sum_T \int^1 d^T s (\partial^T e^{-\beta U_N}) \circ \boldsymbol{\sigma}(T, \mathbf{s}) \tag{8.8}$$

where T is summed over all connected trees T on N vertices.

Tree Graph Domination: Suppose that the potential is repulsive, $V_{ij} \geqslant 0$. Then let $V_{ij}(s_{ij}) = s_{ij} V_{ij}$ or indeed any other interpolation with $V'_{ij}(s) \geqslant 0$. By

$$U_N(\boldsymbol{\sigma}(T, \mathbf{s})) \geqslant \sum_{ij \in T} V_{ij}(\sigma_{ij}(T, \mathbf{s})) = \sum_{ij \in T} V_{ij}(s_{ij}) \tag{8.9}$$

and Theorem VIII.3

$$|(e^{-\beta U_N})_c| \leqslant \sum_T \int^1 d^T s \prod_{ij \in T} \beta V'_{ij}(s_{ij})\, e^{-\beta V_{ij}(s_{ij})} = \sum_T \prod_{ij \in T} (1 - e^{-\beta V_{ij}}) \tag{8.10}$$

which says that the connected part—the sum over all connected graphs—is dominated by the sum just over tree graphs, which is the remarkable result (Penrose, 1967).

However there are also tree graph domination results when the interaction is not purely repulsive. $\boldsymbol{\sigma}(G, \mathbf{s})$ has the following unobvious property to be proved in Section VIII.F.

Theorem VIII.4. If

$$\sum_{ij} V_{ij} \geqslant -BN \tag{8.11}$$

then

$$\sum_{ij} \sigma_{ij}(G, \mathbf{s})\, V_{ij} \geqslant -BN \tag{8.12}$$

The theorem remains valid when self-energies $1/2 \sum_{ii} V_{ii}$ are added to both left hand sides.

When (8.11) holds, Theorems VIII.3 and VIII.4 imply

$$|(e^{-\beta U_N})_c| \leqslant e^{\beta BN} \sum_T \prod_{ij \in T} \beta\, |V_{ij}| \tag{8.13}$$

Tree Graph Limit: Consider the limit

$$z \to \infty, \qquad \beta \to 0 \qquad \text{with } z\beta \text{ fixed} \tag{8.14}$$

By Theorems VIII.1 and VIII.3 the leading terms are

$$\ln \Xi \sim \sum_N \frac{1}{N!} \sum_T \int \prod_{k=1}^{N} z(\mathscr{E}_k)\, d\mathscr{E}_k \prod_{ij \in T} (-\beta V(\mathscr{E}_i, \mathscr{E}_j)) \tag{8.15}$$

where T is summed over all connected trees T on N vertices. There are $N-1$ lines in a connected tree graph on N vertices so every term in the sum is $O(z^N \beta^{N-1}) = O(z)$. The estimates in Section VIII.B show that the Mayer expansion converges uniformly [after dividing out an overall factor of $z \times$ volume] as this tree graph limit is taken so the limit can be taken under the sum over N. This series can even be summed exactly. It is identical with the series in powers of z for

$$\tfrac{1}{2} \int h(\mathscr{E})\, V^{-1} h(\mathscr{E})\, d\mathscr{E} + \int z(\mathscr{E})\, d\mathscr{E}\, e^{-\beta h(\mathscr{E})} \tag{8.16}$$

evaluated at the h that makes it stationary. V^{-1} is the operator inverse of of the operator whose kernel is V. This is the well known folk theorem that Feynman tree graphs sum to the classical action.

More general interpolations besides $s_{ij} V_{ij}$ are actually useful because sometimes one has interactions which are really the sum of several interactions at different scales and then it is useful to use more complicated interpolations that turn them off one after the other. Since there will be examples of this in the next section we also record a more general stability result.

Theorem VIII.5. If the interpolation satisfies

$$\sum_{ij} V'_{ij}(t) \geqslant -B(t)\, N \tag{8.17}$$

then

$$U_N(\boldsymbol{\sigma}(G, \mathbf{s})) \geqslant -2 \sum_{ij \in T} \int_0^{s_{ij}} B(s)\, ds \tag{8.18}$$

Tree Graph Domination (8.13) now becomes

$$|(e^{-\beta U_N})_c| \leqslant \sum_T \int^1 d^T s \prod_{ij \in T} \beta\, |V'_{ij}(s_{ij})|\, e^{2\beta \int_0^{s_{ij}} B(s)\, ds} \tag{8.19}$$

B. Convergence of Mayer Expansions

We demonstrate some uses of tree graph domination by giving estimates on the radius of convergence for the Mayer expansion for a variety of systems including ones discussed earlier in this review.

We will use the following two principles: A tree graph on N vertices whose lines represent factors $f(\mathbf{r}-\mathbf{r}')$ contributes exactly

$$\left(\int f(\mathbf{r})\,d\mathbf{r}\right)^{N-1} \times \text{Volume} \tag{8.20}$$

because tree graphs, being connected, have $N-1$ lines. The integrals over vertices can be evaluated in order starting with ones on lines that are outermost branches (Trim the tree!). Furthermore the number of tree graphs at order N is N^{N-2} (Cayley's theorem).

1. Repulsive Potentials. As an instructive exercise we recover the result in (Penrose, 1967). Consider for simplicity one species. By tree graph domination (8.10) the Mayer expansion is bounded by

$$\begin{aligned}
&\sum_N \frac{1}{N!}\int |(e^{-\beta U_N})_c\, z^N|\, d^N\mathbf{r}\\
&\quad \leqslant \sum_N \frac{1}{N!}\sum_T \left(|z|\int (1-e^{-\beta V(\mathbf{r})})\,d\mathbf{r}\right)^{N-1} |z|\,|\Lambda|\\
&\quad = \sum_N \frac{N^{N-2}}{N!}\left(|z|\int (1-e^{-\beta V(\mathbf{r})})\,d\mathbf{r}\right)^{N-1} |z|\,|\Lambda|\\
&\quad = \sum_N \frac{N^{N-2}}{N!}\,Q^{N-1}\,|z|\,|\Lambda|
\end{aligned} \tag{8.21}$$

which is convergent provided

$$Q := |z|\int d\mathbf{r}(1-e^{-\beta V(\mathbf{r})}) < e^{-1} \tag{8.22}$$

This estimate is also used in the next two examples

2. Debye Spheres. In Section II.D we encountered conditions (2.44). The system consisted of charged particles interacting either by two body potentials

$$V_{L,\lambda}(\mathbf{r}) = |\mathbf{r}|^{-1}\,(e^{-|\mathbf{r}|/L} - e^{-|\mathbf{r}|/\lambda}) \tag{8.23}$$

or by the Yukawa potential $V_L(\mathbf{r})$ and hard cores of radius λ. First we consider two species interacting by (8.23). Suppose we can find an interpolation as in Theorem VIII.5, then we can repeat the argument given above for repulsive potentials, but now using the tree graph domination (8.19) instead and find convergence when

$$Q := 2\,|z| \int_0^1 ds \int d\mathbf{r}\,|\beta V'(\mathbf{r}, s)| \exp\left(2\beta \int_0^s B(s')\,ds'\right) < e^{-1} \tag{8.24}$$

The factor 2 is there because there are two species.

The interpolation is chosen to be $V(\mathbf{r}, t) = V_{L,\ell(t)}(\mathbf{r})$ where $\ell(t)$ is a length scale which decreases from L when $t=0$ to λ when $t=1$. Then we show below that

$$V'(\mathbf{r}, t) = -\frac{\partial}{\partial t}\frac{e^{-|\mathbf{r}|/\ell(t)}}{|\mathbf{r}|} \tag{8.25}$$

obeys a stability estimate (8.17) with

$$B(t) = \frac{\partial}{\partial t}\frac{1}{2\ell(t)} \tag{8.26}$$

Also

$$\int |V'(\mathbf{r}, s)|\,d\mathbf{r} = -\frac{\partial}{\partial s}\int \frac{e^{-|\mathbf{r}|/\ell(s)}}{|\mathbf{r}|}\,d\mathbf{r} = -\frac{\partial}{\partial s}\,4\pi\ell(s)^2 \tag{8.27}$$

because $|V'(\mathbf{r}, s)| = V'(\mathbf{r}, s)$. Therefore (8.24) reads

$$\begin{aligned} Q &= -2\,|z|\,\beta \int_0^1 ds\,\frac{\partial}{\partial s}\,4\pi\ell(s)^2 \exp\left(\beta \int_0^s \frac{\partial}{\partial s'}\frac{1}{\ell(s')}\,ds'\right) \\ &= 16\pi\,|z|\,\beta \int_\lambda^L d\ell\;\ell \exp\left(\frac{\beta}{\ell} - \frac{\beta}{L}\right) < e^{-1} \end{aligned} \tag{8.28}$$

When $\lambda < \beta < L$ we break up the range of the $d\ell$ integration into $[\lambda, \beta]$ and $[\beta, L]$ and find that this criterion is satisfied if

$$|z|\,\beta L^2 \ll 1, \qquad |z|\,\beta^3 e^{\beta/\lambda} \ll 1 \tag{8.29}$$

which is the condition (2.44). The Ruelle estimate (2.43) is not as good because it does not distinguish the length scales and essentially associates the bad stability factor $\exp(\beta/\lambda)$ to all scales. In the Debye–Hückel limit $Q = O(L^2 l_D^{-2})$ is determined by the first criterion because $|z|\ \beta^3 e^{\beta/\lambda} \to 0$. By this remark and (8.21) estimate (2.46) follows. Results related to (2.44) were given in (Göpfert and Mark, 1981; Imbrie, 1983b; Brydges and Kennedy, 1987).

To obtain the stability estimate (8.26), note that by the argument given near (1.12) the stability constant $B(\ell)$ for $V_{L,\ell}$ is half the self-energy, which can be calculated using the Fourier transform to be

$$B = \left(\frac{1}{2\ell} - \frac{1}{2L}\right) \tag{8.30}$$

Now take L in (8.30) equal to $\ell + d\ell$.

It is not a hard exercise to rework this calculation for two dimensions. One recovers a result of (Benfatto, 1985) that if $\beta < 2$ [4π using the units in (Benfatto, 1985)] that the Mayer expansion is convergent for $|z|$ small uniformly in the short distance cutoff λ. In other words for β smaller than the first threshold the Mayer expansion converges for the two dimensional Yukawa gas without any cutoff. This is notable because this interaction is singular at $\mathbf{r} = 0$ and is not stable in the Ruelle sense. The reader will find this exercise done in (Brydges and Kennedy, 1987).

The Yukawa gas with hard core is convergent under the conditions (Brydges and Kennedy, 1987), see also (Imbrie, 1983b),

$$|z|\ \lambda^3 \ll 1; \qquad |z|\ \beta L^2 \ll 1; \qquad |z|\ \beta^3 e^{\beta/\lambda} \ll 1 \tag{8.31}$$

Briefly, this is derived by combining the hard core example with the Yukawa by letting s vary over $[0, 2]$ so that $V(\mathbf{r}, s)$ has no interactions at $\mathbf{s} = 0$ and has the complete interaction when $s = 2\mathbb{1}$. For $s \in [0, 1]$ we choose V' as in the repulsive example and for $s \in [1, 2]$ we have V' given by (8.25) with $\ell(s) = L$ at $s = 1$ and $\ell(s) = 0$ at $s = 2$. The main point is that the hard core is already there when the Yukawa is turned on so that $2B(s)$ for s corresponding to $\ell(s) \approx 0$ is the stability constant including the hard cores, which prevents a divergence.

Tree graph formulas were applied iteratively by (Göpfert and Mack, 1981) to expand successive scales in the interaction in a renormalization group analysis. They showed how to adapt stability estimates to scales and particular clusters of particles. They were motivated to look for better estimates on the convergence of Mayer expansions in order to prove confinement at all parameters for three dimensional Euclidean lattice quantum electromagnetism by exploiting a connection with screening. The iterated tree graph formulas of Göpfert and Mack were then simplified (Brydges and Kennedy, 1987) by passing to a limit in which the scales are replaced by a continuous parameter (the t in Theorem VIII.2). This was partly motivated by the study of renormalization (Polchinski, 1984). (Abdesselam and Rivasseau, 1995) then found Theorem VIII.2 as a corollary of the results in (Brydges and Kennedy, 1987).

The ideas in (Göpfert and Mack, 1981) were independently developed by Gallavotti and Nicolo and applied by Benfatto to the two dimensional Yukawa gas (Gallavotti, 1985; Gallavotti and Nicolo, 1985a; Benfatto, 1985; Gallavotti and Nicolo, 1986). Note that the trees in these papers express the hierarchical structure of the clusters on different scales and should not be confused with our trees which are Feynman or Mayer graphs.

3. The Mayer Expansion for a Polymer Gas. This application is technical and should be omitted on first reading. It will be used later in this chapter. Consider the grand canonical partition function

$$Z(\Lambda)=\sum_{N}\frac{1}{N!}\sum_{\substack{X_1,\ldots,X_N\subset\Lambda\\ \bigcup X_j=\Lambda}}\prod_{j}A(X_j) \tag{8.32}$$

where Λ is a finite set. In applications to lattice models Λ is all lattice points in a big box. A typical element of Λ is denoted by η. Swimming around in this big box are the "polymers" $X_1,\ldots,X_N$, which are disjoint subsets of Λ. For lattice models they are often nearest neighbor connected but instead of making this assumption we assume that the activity $A(X)$ of polymer X obeys a bound of the form

$$|A(X)|<a^{|X|}\sum_{G}\prod_{\eta\eta'\in G}w(\eta,\eta') \tag{8.33}$$

where $|X|$ is the number of elements η in X, G is summed over all tree graphs on X. For example when Λ is a box in a lattice, we could take $w(\eta,\eta')$ to vanish whenever η,η' are not nearest neighbors and to be one otherwise. In this case $A(X)=0$ unless X is connected.

Now we show that the Mayer expansion is convergent when

$$Q:=a\sum_{\eta'}(\delta_{\eta,\eta'}+w(\eta,\eta'))<e^{-1} \tag{8.34}$$

where $\delta_{\eta,\eta'}$ is the Kronecker delta function on the elements of the set Λ. Suppose there is a notion of distance between elements in Λ and $w(\eta,\eta')$

decays exponentially as $\operatorname{dist}(\eta, \eta') \to \infty$. If $eQ < 1$ then correlations obtained by differentiating in $Z(\Lambda)$ with respect to external fields ψ with $A(X) = A(X, \psi)$ decay exponentially.

For example η could be a point in a lattice in $\mathbb{R}^3$ which actually represents a unit box centered on η so that X represents a union of these boxes. If $A(X, \psi)$ is independent of variations of $\psi(\mathbf{r})$ at points $\mathbf{r}$ outside X then

$$\frac{\delta^2}{\delta\psi(\mathbf{r})\, \delta\psi(\mathbf{r}')} \ln Z(\Lambda) \tag{8.35}$$

and higher variational derivatives will decay exponentially, uniformly in the size of Λ as the points $\mathbf{r}, \mathbf{r}'$ are separated.

We drop the constraint that polymers are disjoint from the sum in (8.32) and impose it instead by a hard core Gibbs factor $\exp(-U_N)$. Let

$$J(X_1,..., X_N) = A(X_1) \cdots A(X_N)(e^{-U_N(X_1,..., X_N)})_c \tag{8.36}$$

In the Mayer expansion

$$\sum_{N \geqslant 1} \frac{1}{N!} \sum_{X_1,..., X_N \subset \Lambda} J(X_1,..., X_N) \tag{8.37}$$

we write

$$\sum_{X_i} = \sum \frac{1}{n_i!} \sum_{\eta_1,..., \eta_{n_i}} \cdots \tag{8.38}$$

Then we set $M = \sum_i n_i$ and note that $M!/(\prod n_i!)$ is the number of ways to partition $\{1,..., M\}$ into subsets $\gamma_1,..., \gamma_N$. Therefore (8.37) is the same as

$$\sum_{M \geqslant 1} \frac{1}{M!} \sum_{N \geqslant 1} \frac{1}{N!} \sum_{\gamma_1,..., \gamma_N} \sum_{\eta_1,..., \eta_M} J(X_1,..., X_N)$$
$$X_i = \{\eta_j : j \in \gamma_i\} \tag{8.39}$$

with the constraint on the sum over $\eta_1,..., \eta_M$ that η_j with j in the same partition are distinct. We substitute in the tree graph domination bound (8.10)

$$\begin{aligned} |(e^{-U_N(X_1,..., X_N)})_c| &\leqslant \sum_T \prod_{ij \in T} |e^{-V(X_i, X_j)} - 1| \\ &\leqslant \sum_T \prod_{ij \in T} \sum_{\eta \in X_i,\, \eta' \in X_j} |e^{-V(\eta, \eta')} - 1| \end{aligned} \tag{8.40}$$

and (8.33). Note that the hard core interaction $V(\eta, \eta')$ means that $\exp(-V(\eta, \eta'))-1$ is $-\delta_{\eta, \eta'}$. The trees with w bonds and the tree with $\delta_{\eta, \eta'}$ bonds link into one connected tree G on $\{1,..., M\}$ and the respective sums are equivalent to a sum over all possible connected trees on $\{1,..., M\}$. The partition $\{\gamma_1,..., \gamma_N\}$ determines uniquely which bonds in this tree are V bonds and which are w bonds. Indeed the sum over partitions, including the $1/N!$ is equivalent[32] to summing over the choice w bond or V bond for each bond in the tree. Therefore the sum over partitions is the same as assigning to each bond ij

$$\delta_{\eta_i, \eta_j} + w(\eta_i, \eta_j) \tag{8.41}$$

Therefore the expansion (8.39) is bounded by

$$\leqslant \sum_{M \geqslant 1} \frac{a^M}{M!} \sum_{\eta_1,..., \eta_M} \sum_G \prod_{ij \in G} (\delta_{\eta_i, \eta_j} + w(\eta_i, \eta_j)) \tag{8.42}$$

dropping the constraints on the distinctness of $\eta_1,..., \eta_M$. As above, (8.20)–(8.22), this is convergent if (8.34) holds.

The additional claim we made concerning exponential decay of correlations is an immediate consequence: suppose we perform variational derivatives such as

$$\frac{\delta}{\delta\psi(\eta_a)} \frac{\delta}{\delta\psi(\eta_b)}$$

on $\ln Z$ where ψ is an external field that enters through dependence $A(X) = A(X, \psi)$. Then all terms in the Mayer expansion (8.37) vanish except those where the union of the sets X_j contains both points η_a, η_b, because $\delta A(X, \psi)/(\delta\psi(\eta)) = 0$ when $\eta \notin X$. When η_a, η_b are far apart the surviving terms are exponentially small since they are connected graphs with exponentially decaying propagators. This argument that is being made term by term in the Mayer expansion is valid when all the terms are summed because we established that the expansion is convergent, provided the convergence has some uniformity in ψ.

C. Gaussian Integrals and Truncated Expectations

In this section, following (Brydges, 1984; Brydges and Kennedy, 1987) we derive tree graph formulas for truncated Gaussian expectations. The

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[32] This idea appeared in (Abdesselam and Rivasseau, 1995) and (Göpfert and Mack, 1981).

point of the formulas is that all the loops in the associated Feynman diagrams are resummed back into a positive Gaussian measure, leaving only tree diagrams, which 'carry the connectedness information.

Truncated expectations for arbitrary observables will be defined later in (8.60) but for products of polynomials they can equivalently be defined by applying Wick's theorem and then discarding all but the connected graphs.

Suppose $\langle\ \rangle$ is a Gaussian average over variables ϕ_i, $i=1,..., N$.

$$\begin{aligned} \langle P\rangle &= Z^{-1}\int Pe^{-1/2\sum_{i,j}\phi_i A_{ij}\phi_j}\prod_i d\phi_i \\ \langle\phi_i\phi_j\rangle &= A^{-1}_{ij}\equiv C_{ij} \end{aligned} \tag{8.43}$$

A is a matrix with positive eigenvalues. Suppose $P_i=P_i(\phi_i)$ are polynomials each of which depends only on one of the variables, then by Wick's theorem

$$\left\langle\prod_l P_l\right\rangle = e^{1/2\sum_{i,j}\Delta_{ij}}\prod_l P_l|_{\phi=0} \tag{8.44}$$

where the exponential is defined by power series and

$$\Delta_{ij}=C_{ij}\frac{\partial}{\partial\phi_i}\frac{\partial}{\partial\phi_j} \tag{8.45}$$

We apply Theorem VIII.2 with

$$F(\mathbf{s})=\exp\left(\frac{1}{2}\sum_{i,j}s_{ij}\,\Delta_{ij}\right)P \tag{8.46}$$

with $P=\prod_l P_l$ and the conventions $s_{ij}=s_{ji}$ and $s_{ii}=1$. The right hand side of Theorem VIII.2 will then contain

$$\exp\left(\frac{1}{2}\sum_{i,j}\sigma_{ij}(G,\mathbf{s})\,\Delta_{ij}\right)\Delta^G P|_{\phi=0} \tag{8.47}$$

where $\Delta^G=\prod_{ij\in G}\Delta_{ij}$. This is a new Gaussian expectation $\langle\ \rangle^{G,\mathbf{s}}$ characterized by

$$\langle\phi_i\phi_j\rangle^{G,\mathbf{s}}=\sigma_{ij}(G,\mathbf{s})\;C_{i,j} \tag{8.48}$$

The key point is that it truly is a Gaussian expectation: we shall show below that $C_{ij}\sigma_{ij}$ has positive eigenvalues, so that it has an inverse which defines the expectation $\langle \phi_i \phi_j \rangle^{G,\mathbf{s}}$ in parallel to (8.43). We define

$$\langle P \rangle^{G} := \int^{1} d^{G}s \langle P \rangle^{G,\mathbf{s}} \tag{8.49}$$

and conclude from Theorem VIII.2 that

$$\left\langle \prod_i P_i \right\rangle = \sum_G \left\langle \mathbb{\Delta}^{G} \prod_i P_i \right\rangle^{G} \tag{8.50}$$

where G is summed over all forests.

Notice that the previous equations contained exponentials of $\mathbb{\Delta}$ which only make immediate sense on polynomials, but now that we have got rid of these we can use this formula when the P_i are arbitrary smooth functions.

By the discussion above Theorem VIII.3 there is a factorization $\langle\ \rangle^{G} = \prod_{T \subset G} \langle\ \rangle^{T}$ where T runs over trees in the forest G. Therefore by definition of the truncated expectation[33] $\langle\ \rangle_T$ given in (8.60) we obtain

$$\left\langle \prod_{i=1}^{N} P_i \right\rangle_T = \sum_G \left\langle \mathbb{\Delta}^{G} \prod_i P_i \right\rangle^{G} \tag{8.51}$$

where G runs only over connected trees on N vertices. This argument easily generalizes to allow each P_i to depend on more variables ϕ_x, $x \in X_i$. This formula expresses a truncated Gaussian expectation as a sum only over tree graphs. The loops that would appear in a standard application of Wick's theorem are resummed into the expectation $\langle - \rangle^{G}$ defined in terms of the Gaussian expectation with the altered propagator $C_{ij}\sigma_{ij}$.

To see that the matrix $C_{ij}\sigma_{ij}$ has positive eigenvalues: since A_{ij} has positive eigenvalues, C_{ij} has positive eigenvalues which is equivalent to

$$\sum_{i,j} \eta_i C_{ij} \eta_j \geqslant \lambda_{\min} \sum_j \eta_j^2 \tag{8.52}$$

By Theorem VIII.4 with $V_{ij} = \eta_i [C_{i,j} - \lambda_{\min} \delta_{ij}] \eta_j$, $B = 0$ and self energies included,

$$\sum_{i,j} \eta_i C_{ij} \sigma_{ij} \eta_j \geqslant \lambda_{\min} \sum_j \eta_j^2 \tag{8.53}$$

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[33] A superscript T refers to a tree graph and a subscript T means the expectation is truncated. We apologize for the notational collision.

which implies that the matrix $A(\boldsymbol{\sigma})^{-1} = C_{ij}\sigma_{ij}$ has positive eigenvalues. We define the expectation $\langle\ \rangle^{G, \mathbf{s}}$ by replacing the matrix A by $A(\boldsymbol{\sigma})$ in (8.43).

D. Polymer Representations and Exponential Decay

In this section we describe how to obtain a convergent expansion for the logarithm of functional integrals of the form

$$\langle Z(\Lambda)\, e^{i \int \phi f} \rangle = \int d\mu(\phi)\, Z(\Lambda, \phi)\, e^{i \int \phi f} \tag{8.54}$$

where $d\mu$ is a Gaussian measure with a propagator [covariance] $C(\mathbf{r}, \mathbf{r}')$ that has both infrared and ultraviolet cutoffs so that it is smooth on the diagonal and has exponential decay as $\mathbf{r} - \mathbf{r}' \to \infty$. The Λ in the functional $Z(\Lambda, \phi)$ means that variational derivatives at points outside Λ vanish:

$$Z_1(\Lambda, \phi; f) \equiv \frac{\partial}{\partial\alpha} Z(X, \phi + \alpha f)|_{\alpha=0} = 0 \tag{8.55}$$

if $f = 0$ in Λ and the same is true for all higher derivatives.

Functionals such as

$$Z(\Lambda, \phi) = \exp\left(z \int_\Lambda \cos\phi(\mathbf{r})\, d\mathbf{r}\right) \tag{8.56}$$

factorize, for X_1, X_2 disjoint,

$$Z(X_1 \cup X_2, \phi) = Z(X_1, \phi)\, Z(X_2, \phi) \tag{8.57}$$

but we will work with a less restrictive property, which is that $Z(\Lambda, \phi)$ has a polymer representation

$$Z(\Lambda, \phi) = \sum_N \frac{1}{N!} \sum_{\substack{X_1, \dots, X_N \subset \Lambda \\ \bigcup X_j = \Lambda}} \prod_j K(X_j, \phi) \tag{8.58}$$

where the interiors of the sets $X_1, \dots, X_N$ are disjoint. In other words $Z(\Lambda, \phi)$ is at least a sum over contributions that factorize. This type of representation is not useful if the sets X_j are very complex so we insist that all sets are finite unions of unit cubes in $\mathbb{R}^3$, centered on points with integral coordinates.

Recall the well known combinatoric miracle that when the partition function has a graphical expansion, the logarithm has the same expansion except that only the connected graphs appear. This comes about as a result of the following easily verified relation (cumulant expansion) between expectations and exponentials

$$\langle e^F \rangle = \exp\left(\sum_{N \geqslant 1} \frac{1}{N!} \langle F^N \rangle_T \right) \tag{8.59}$$

where the truncated expectation $\langle F_1 \cdots F_N \rangle_T$ is recursively defined by solving

$$\begin{aligned} \langle F_1 \cdots F_N \rangle &= \sum_{\pi} \prod_{\gamma \in \pi} \langle F^\gamma \rangle_T \qquad \text{if} \quad N > 1 \\ \langle F_1 \rangle_T &= \langle F_1 \rangle \end{aligned} \tag{8.60}$$

where π is summed over all partitions of $\{1, 2,..., N\}$ and $F^\gamma = \prod_{j \in \gamma} F_j$. For the case (8.56) the expansion for the logarithm of (8.54) based on these relations is convergent at small z, essentially because the cosine has the special property that it and all of its derivatives are bounded uniformly in ϕ.[34] The next steps can be viewed as a reduction of more general functionals such as $\exp(-\lambda \int \phi^4)$ to this bounded case.

Relations similar to (8.59), (8.60) hold for the polymer representation (8.58). This is plausible once one realizes that the polymer representation is an exponential in a different commutative product $\circ$ defined by

$$A \circ B(X) = \sum_{Y \subset X} A(Y)\, B(X \setminus Y) \tag{8.61}$$

As always Y, X are finite unions unit cubes. Y, X are permitted to be the empty set. We do not distinguish between open and closed cubes, that is we identify two cubes if they have the same interior and regard them as disjoint if their interiors are disjoint. Define

$$\mathscr{E}xp(K) = \mathscr{I} + K + \frac{1}{2!} K \circ K + \cdots \tag{8.62}$$

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[34] By reversing the Sine–Gordon transformation the expansion becomes the Mayer expansion for ± 1 charges interacting by two body potential $C(\mathbf{r}, \mathbf{r}')$.

$\mathscr{I}(X)=0$ unless X is the empty set, in which case it is one. $\mathscr{I}$ is the identity for this product. We only define $\mathscr{E}xp(K)$ for functionals K that vanish when applied to the empty set. It is easy to verify that

$$\mathscr{E}xp(K)(X,\phi)=\begin{cases}\displaystyle\sum_{N\geqslant 0}\frac{1}{N!}\sum_{\substack{X_1,\dots,X_N\subset X\\ \cup X_j=X}}\prod_j K(X_j,\phi)\\ 1 \qquad \text{if} \quad X=\varnothing\end{cases} \tag{8.63}$$

Thus $Z(\Lambda,\phi)=\mathscr{E}xp(K)(\Lambda,\phi)$. Furthermore $\mathscr{E}xp(A+B)=\mathscr{E}xp(A)\circ\mathscr{E}xp(B)$. As an example, consider the function $\square(X)$ that equals one if X is a cube and vanishes in all other cases. Then by (8.63), for any set X,

$$\mathscr{E}xp(\square)(X)=1 \tag{8.64}$$

Returning to our functional integral (8.54), let us define

$$K_T(X)=\sum_{N\geqslant 1}\frac{1}{N!}\langle K^{\circ N}(X)\rangle_T, \qquad =0 \text{ if } X=\varnothing \tag{8.65}$$

More explicitly

$$\langle K^{\circ N}(X)\rangle_T=\langle K\circ\cdots\circ K(X)\rangle_T=\sum_{\substack{X_1,\dots,X_N\subset X\\ \cup X_j=X}}\left\langle\prod_j K(X_j)\right\rangle_T \tag{8.66}$$

where the truncated expectation $\langle\ \rangle_T$ is defined as above. Then K_T is the logarithm in the sense

$$\langle\mathscr{E}xp(K)(X)\rangle=\mathscr{E}xp(K_T)(X) \tag{8.67}$$

which is the $\circ$ equivalent of (8.59). However these series are terminating after a finite number of terms that depends on the set X because there are at most a finite number of partitions of any given X. As an extreme example, if $X=\Delta$ is a single cube, then there are no partitions of X into proper subsets so only the $N=1$ term in (8.65) survives and accordingly $K_T(\Delta)=\langle K(\Delta)\rangle$.

This analysis is unaffected by the external field term $\exp(\int\phi f)$ in the partition function (8.32) because it can be absorbed into the polymer activities K. From the definition of $\mathscr{E}xp$

$$\mathscr{E}xp(K(\phi))(\Lambda)\,e^{\int_\Lambda\phi f}=\mathscr{E}xp(K(\phi,f))(\Lambda), \qquad K(X,\phi,f):=K(X,\phi)\,e^{\int_X\phi f} \tag{8.68}$$

We want an expansion for the standard logarithm of the partition function. Comparing the definition of $\mathscr{E}xp$ in (8.63) with the polymer gas partition function (8.32), we see that the standard logarithm is given by the Mayer expansion described in Section VIII.B.3, provided we can weaken the constraint $\bigcup X_j = X$ that occurs in $\mathscr{E}xp(K_T)(X)$ to $\bigcup X_j \subset X$. There is a simple way to achieve this: for any function of sets $\tilde{A}(X)$ declare that $\tilde{A}$ is normalized if $\tilde{A}(X) = 1$ whenever X is a unit box Δ, then

$$\begin{aligned}\mathscr{E}xp(\tilde{A})(X) &= \mathscr{E}xp(\Box) \circ \mathscr{E}xp(\tilde{A} - \Box)(X) \\ &= \sum_N \frac{1}{N!} \sum_{X_1, \ldots, X_N \subset X} \mathscr{E}xp(\Box)\Big(X \backslash \bigcup X_j\Big) \prod_j A(X_j) \\ &= \sum_N \frac{1}{N!} \sum_{X_1, \ldots, X_N \subset X} \prod_j A(X_j), \qquad A := \tilde{A} - \Box \end{aligned} \tag{8.69}$$

The constraint $\bigcup X_j = X$ has been lifted because by (8.64) $\mathscr{E}xp(\Box) = 1$ on $X \backslash \bigcup X_j$. If $\tilde{A}$ is

$$\tilde{A}(X) = K_T(X) \Big/ \prod_{\Delta \subset X} K_T(\Delta) \tag{8.70}$$

where / has its usual division meaning, then it is normalized. Also, by the same principle as was used in (8.68)

$$\mathscr{E}xp(K_T)(X) = \Big(\prod_{\Delta \subset X} K_T(\Delta)\Big) \mathscr{E}xp(\tilde{A})(X) \tag{8.71}$$

so

$$\mathscr{E}xp(K_T)(X) = \Big(\prod_{\Delta \subset X} K_T(\Delta)\Big) \sum_N \frac{1}{N!} \sum_{X_1, \ldots, X_N \subset X} \prod_j A(X_j) \tag{8.72}$$

In Section VIII.B.3 we gave a criterion (8.33), (8.34) for how small the activity $A(X)$ must be for convergence of the Mayer expansion and exponential decay of correlations. A is built out of K_T so we need to see that K_T obeys a bound similar to (8.33), (8.34). This is where Section VIII.C comes into play. By the tree graph formula (8.51) K_T is small provided variational derivatives with respect to ϕ of the initial polymer activity $K(X, \phi)$ in the partition function (8.54) are small: we will give a partial explanation of this through the following example.

Example: suppose

$$Z(\Lambda) = e^{-V(\Lambda)}, \qquad V(\Lambda, \phi) = \lambda \int_\Lambda \phi^4 \tag{8.73}$$

Because this factors into a product over boxes in Λ, by the same argument that shows that $\mathscr{E}xp(\square) = 1$ this equals $\mathscr{E}xp(K)$ with

$$K(X, \phi) = \square(X)\, e^{-V(X, \phi)}$$

When λ is small variational derivatives of $K(X, \phi)$ are small, uniformly in ϕ, because

$$\frac{d}{d\alpha} e^{-V(\Delta, \phi + \alpha g)} = -4\lambda \int_{\Delta} \phi^3 g\, d\mathbf{r}\, e^{-\lambda \int_{\Delta} \phi^4} \sim O(\lambda^{1/4})$$

because ϕ^4 controls $\int \phi^3 g$ when ϕ is large. This is somewhat of an oversimplification because the dependence of the estimate on the test function g is not uniform. Unfortunately a gentle reference to cover these specific missing details is not available, but (Lemberger, 1995) is detailed and close in spirit to the discussion here. More general background references are (Glimm and Jaffe, 1987; Rivasseau, 1991; Brydges, 1992). The ability to work with the bounded $\exp(-\lambda \int \phi^4)$ in place of $\int \phi^4$ is half the reason why we obtain a convergent expansion when λ is small. The other half is that all formulas involve at most tree graphs whose numbers are compensated by $N!$ factors, see the discussion at the beginning of Section VIII.B.

Exponential decay of correlations for functional integrals of the form (8.54) follows as in the discussion of the polymer gas in Section VIII.B.

It is possible that polymer representations could be useful in numerical renormalization group calculations. This has been considered (Mack and Pordt, 1985; Mark and Pordt, 1989). Their program can be viewed as a natural step beyond methods that do work well for hierarchical models (Koch and Wittwer, 1991; Koch and Wittwer, 1994).

E. The Polymer Representation

In this section we indicate how exponential decay of correlations for the Coulomb system is deduced from the considerations of Section VIII.D. The missing step, outlined in this section, is to show that the Sine–Gordon representation is an integral of the form (8.54) with $Z(\Lambda, \phi) = \mathscr{E}xp(K)(\Lambda, \phi)$ for polymer activity $K(X, \phi)$ which becomes very small as the Debye–Hückel limit is approached.

As introduced in Section II.E we use units where $l_D = 1$. We also simplify the presentation by discussing a Coulomb system with two species with equal but opposite charges and equal activities z interacting by a smoothed Coulomb potential of the form $V_{\infty, L}$ with $L = l_D$. Then there is no need for the Mayer expansion of Section II.D, which complicates the original proofs.

With these simplifications the left hand side $\exp(F)$ in the "Villain" approximation (2.79) becomes the ideal gas partition function

$$\exp\left(\int_{\Lambda} d\mathscr{E}\, z^{(L)}(\mathscr{E})\, e^{-\beta^{1/2} e_{\alpha} i\phi}\right) \tag{8.74}$$

We make the dependence on Λ explicit by writing $\exp(F(\Lambda, i\phi))$. The left hand side of the Villain approximation (2.79) factors

$$e^{F(X \cup Y,\, i\phi)} = e^{F(X,\, i\phi)} e^{F(Y,\, i\phi)} \tag{8.75}$$

whenever X and Y are disjoint. The sum over h in the right hand side of the Villain approximation also factors, if X, Y are unions of cubes. From this there follows the same property

$$e^{R_3(X \cup Y,\, i\phi)} = e^{R_3(X,\, i\phi)} e^{R_3(Y,\, i\phi)} \tag{8.76}$$

for R_3.

From (2.80)

$$\Xi_{\Lambda}/(\Xi_{\text{ideal}, \Lambda} \Xi_{\text{DH}, \Lambda}) = \int d\mu_{\text{DH}}(\phi) \sum_{h} e^{-S_{\text{DH}}(-ih,\, ig)}\, e^{-S'_{\text{DH}}(-ih,\, ig;\, i\phi) + R_3(ig + i\phi)} \tag{8.77}$$

For simplicity we set the external field $\psi = 0$. In the formula (2.82) for $S_{\text{DH}}(-ih, ig)$, R_2, R_0 vanish for this simplified model. The propagator for $d\mu_{\text{DH}}(\phi)$ decays exponentially which is the property we need in order to use the expansion from Section VIII.D.

Now we write the $d\mu$ integrand in the form

$$\mathscr{E}xp(K)(\Lambda, \phi) = \sum_{N} \frac{1}{N!} \sum_{\substack{X_1, \ldots, X_N \subset \Lambda \\ \bigcup X_j = \Lambda}} \prod_{j} K(X_j, i\phi) \tag{8.78}$$

The rough idea will be that each X_j is a contour Γ_j or several conglomerated contours together with a collar of width M which is thick enough so that the effect of the contour is locked inside X_j. To take care of regions without contours there will also be the dominant possibility that X is a single cube.

The outcome of our manipulations will be a polymer activity $K(X, \phi)$ whose pth variational derivative with respect to ϕ is of size

$$\frac{p!}{a^p} \exp(\kappa \, \|\phi\|_X^2 - O(a^2) \, |X|), \qquad a = [z l_D^3]^{1/2}, \quad |X| > 1 \tag{8.79}$$

a^2 is the number of particles in a Debye sphere and is very large near the Debye–Hückel limit. The *exp*$(-O(a^2)|X|)$ is the tunneling factor promised in Section II.G. $|X|$ is the number of unit boxes in X. $\| \ \|_X$ is a norm involving $\int_X |\phi|^2$ and integrals of derivatives of ϕ. The constant κ is small enough so that $\exp(\kappa \|\phi\|_X^2)$ can be integrated with respect to $d\mu_{\mathrm{DH}}$. Since polymers never overlap this is enough for a proof that the expansion of Section VIII.D is convergent. The non-overlapping of polymers is the reason why they are useful for obtaining convergent expansions.

To understand why this crucial limitation on κ cannot be achieved unless the tunneling effects represented by contours are taken into consideration consider the one dimensional version of the Villain approximation.

$$e^{a^2 \cos(\phi/a)} = e^{R_3(\phi)} \sum_n e^{-(1/2)(\phi - 2\pi a n)^2 + a^2} \tag{8.80}$$

If we restrict $R_3(\phi)$ to the period $[-\pi a, \pi a]$ and note that it is largest at $\phi = a\pi$ we find, by throwing away all but the $n = 0$ term, an upper bound

$$e^{R_3(\phi)} \leqslant e^{(1/2) \, \kappa \phi^2}; \qquad \kappa = 1 - \frac{4}{\pi^2} < 1 \tag{8.81}$$

Since $R_3(\phi)$ is a periodic function the bound holds for all ϕ. R_3 is analytic with more or less the same Gaussian bound in the strip $\phi + iy$ with $|y|/a \ll 1$ so

$$\frac{d^p}{d\phi^p} e^{R_3(\phi)} \sim \frac{p!}{a^p} e^{(1/2) \, \kappa \phi^2} \tag{8.82}$$

$\kappa < 1$ means that $\exp(R_3)$ and all derivatives can be integrated against the one dimensional analogue of $d\mu_{\mathrm{DH}}$, namely the Gaussian $\exp(-\phi^2/2)$

$$\frac{1}{\sqrt{2\pi}} \int e^{-\phi^2/2} \frac{d^p}{d\phi^p} e^{R_3(\phi)} \, dx = \begin{cases} O(a^{-p}) & \text{if } \ p \neq 0 \\ \to 1 & \text{if } \ p = 0 \end{cases} \tag{8.83}$$

as $a \to \infty$. This fails if R_3 is instead defined as the error in the single well approximation $a^2 \cos(\phi/a) \approx 1 - \phi^2/2 + R_3$.

The tunneling phenomena contained in the Villain approximation are invisible in perturbation theory but they are the reason why perturbation theory will not converge. The appearance of $\exp(-O(a^2)\,|X|)$ in (8.79) quantifies the physical idea that the tunneling effects are very rare in the Debye–Hückel limit when a is large. This bound (8.79) together with the considerations of Section VIII.D implies the exponential decay of correlations.

The first task on the way to (8.78) is to obtain an exact version of (2.84) so that the sum over h will factor as in (2.86). Let M be a (large) integer. Given h we choose the translation g to minimize $S_{\mathrm{DH}}(-ih, ig)$ subject to the constraint that $g(\mathbf{r}) = h(\mathbf{r})$ at every point that is distant by more than $M-1$ from any contour in h. The price of imposing this constraint is that in (8.77) we no longer have $S'_{\mathrm{DH}}(-ih, ig; i\phi) = 0$ as was the case in Section II.G. Now $S'_{\mathrm{DH}}(-ih, ig; i\phi)$ is an integral of ϕ and derivatives of ϕ times derivatives of g over the surface of the region where the constraint holds. These derivatives are of order $O(\exp(-M))$ because the constraint is almost irrelevant since the minimizer without the constraint satisfies $g(\mathbf{r}) = h(\mathbf{r}) + O(\exp(-\mathrm{dist}(\mathbf{r}, \Gamma))$. We choose M large so that $S'_{\mathrm{DH}}(-ih, ig; i\phi)$ is as small as the error term $R_3(ig + i\phi)$.

With this choice of g we have an exact version of the additivity property of $S_{\mathrm{DH}}(-ih, ig)$ in (2.84): whenever $h = h_1 + h_2$,

$$S_{\mathrm{DH}}(-ih, ig) = \sum_{j=1,2} S_{\mathrm{DH}}(-ih_j, ig_j) \tag{8.84}$$

provided every contour in h_1 is separated by a distance of $2M$ or more from every contour in h_2. See the discussion below (2.85) and note that our constraint forces the cross terms to vanish. Under the same conditions we also have

$$S'_{\mathrm{DH}}(-ih, ig; i\phi) = \sum_j S'_{\mathrm{DH}}(-ih_j, ig_j; i\phi) \tag{8.85}$$

Define $K(X, \phi)$ to vanish if X is the empty set or not a connected union of cubes, otherwise

$$K(X, \phi) = e^{R_3(X,\, ig + i\phi)} \begin{cases} \displaystyle\sum_{h:\, X(h) = X} e^{-S_{\mathrm{DH}}(-ih,\, ig)}\, e^{-S'_{\mathrm{DH}}(ih,\, ig;\, i\phi)} \\ 1 \end{cases} \tag{8.86}$$

The second line applies when X is a single cube. The constraint $X(h) = X$ is defined below. The constraint[35] forces X to hold contours when it is not

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[35] If there is no h such that $X(h) = X$ then $K(X, \phi) = 0$.

a single cube and contours are responsible for the $\exp(-O(a^2)\,|X|)$ in (8.79). This definition leads to the desired representation

$$\Xi_{\Lambda}/(\Xi_{\text{ideal},\,\Lambda}\Xi_{\text{DH},\,\Lambda})=\int d\mu_{\text{DH}}(\phi)\sum_{N}\frac{1}{N!}\sum_{\substack{X_1,\dots,\,X_N\subset\Lambda\\ \bigcup X_j=\Lambda}}\prod_{j}K(X_j,\phi) \tag{8.87}$$

It is convenient to measure distance using

$$\text{dist}(\mathbf{r},\mathbf{r}')=\max_{i}\,|r_i-r_i'| \tag{8.88}$$

so that the unit cube centered on the origin is $\{\mathbf{r}\colon \text{dist}(0,\mathbf{r})<1/2\}$. $X(h)$ is defined to be the open set consisting of all points closer than M to some contour in h. To derive (8.87) note that any h occurring in the sum (8.77) determines $X(h)$ which decomposes uniquely into disjoint open connected subsets X_j. Each X_j determines a unique h_j such that

$$\begin{aligned} &X(h_j)=X_j; \qquad h_j=0 \text{ outside } \Lambda\\ &\quad h_j=h+\text{a constant when restricted to } X_j\\ &\quad h=\sum_j h_j \end{aligned} \tag{8.89}$$

The first two conditions determine h_j and the last is implied by them. Therefore the sum over h in (8.77) is equivalent to summing over N, $X_1,\dots,X_N$ followed by $h_1,\dots,h_N$. By (8.84) and the symmetry

$$e^{R_3(X_k,\,i\sum_j g_j+i\phi)}=e^{R_3(X_k,\,ig_k+i\phi)} \tag{8.90}$$

we can factor the summands. This symmetry is the one we remarked in (2.75) and it holds in this form because for $j\neq k$ $g_j=h_j$ is constant on X_k. Incidentally a fractional charge immersed in the system destroys this symmetry. See the remarks on fractional charges in Section II.G.

F. Proofs for Theorems in Section VIII

Proof of Theorems VIII.4 and VIII.5. Following (Brydges and Kennedy, 1987). Let $\chi(a\geqslant\tau)$ denote a function of τ which is 1 when $a\geqslant\tau$ and zero otherwise. Then

$$U_N\circ\boldsymbol{\sigma}(T,\mathbf{s})=\sum_{ij}\int_0^{\sigma_{ij}(T,\,\mathbf{s})}d\tau\;V_{ij}'(\tau)=\int_0^1 d\tau\sum_{ij}V_{ij}'(\tau)\,\chi(\sigma_{ij}(T,\mathbf{s})\geqslant\tau) \tag{8.91}$$

A value of τ and a tree T determine a partition of the particles = vertices of T into clusters: simply erase all bonds $ij \in T$ for which $s_{ij} < \tau$. The rest of the tree falls into connected subtrees. Each cluster consists of the vertices in each subtree. The bonds $ij \in T$ we erased are in fact eliminated by the χ in the above equation. The key point is that if lk is another bond not in T with k and l is separate clusters that used to be connected by ij then it too is eliminated by χ because $s_{ij} < \tau$ implies $\sigma_{kl}(T, \mathbf{s}) < \tau$. Therefore at each value of τ we have a τ dependent partition of the vertices into clusters C_α such that

$$\sum_{ij} V'_{ij}(\tau)\, \chi(\sigma_{ij}(T, \mathbf{s}) \geqslant \tau) = \sum_{\alpha} \sum_{ij \in C_\alpha} V'_{ij}(\tau) \tag{8.92}$$

Thus a stability estimate $\sum V'_{ij}(\tau) \geqslant -B(\tau)\, N$ is inherited by $U_N \circ \boldsymbol{\sigma}(T, \mathbf{s})$, because we can apply it to each cluster in the last equation and then integrate over τ. Theorem VIII.4 follows easily.

Theorem VIII.5. Following (Göpfert and Mack, 1981) there is a systematic way to improve stability estimates by using numerically calculated constants for small clusters. The simplest instance is to note that for clusters of single particles we have no interaction to bound so that

$$\sum_{ij} V'_{ij}(\tau)\, \chi(\sigma_{ij}(T, \mathbf{s}) \geqslant \tau) \geqslant -B(\tau)\, N_1 \tag{8.93}$$

where N_1 is the number of particles not in single clusters,

$$\begin{aligned} N_1 &= |\{i : i \in \text{some } C_j \text{ with } |C_j| > 1\}| \\ &\leqslant |\{i : s_{ij} \geqslant \tau \text{ some } ij \text{ in } T\}| \\ &\leqslant \sum_{i,\, j} \chi(s_{ij} \geqslant \tau) = 2 \sum_{ij} \chi(s_{ij} \geqslant \tau) \end{aligned} \tag{8.94}$$

Therefore

$$U_N \circ \boldsymbol{\sigma}(T, \mathbf{s}) \geqslant -\int_0^1 d\tau\, 2B(\tau) \sum_{ij} \chi(s_{ij} \geqslant \tau) \tag{8.95}$$

which is (8.18). ▮

Proof of Theorem VIII.2. We know the case $N = 2$. We assume $N > 2$ and make the inductive hypothesis that the theorem holds for all cases with less than N vertices. It is sufficient to prove that both sides have the same t derivative and agree at $t=0$. The t derivative of the right hand side is

$$\sum_{G\in\mathscr{F}}\sum_{b\in G}\int^{t} d^{G\backslash b}s\;\partial^{G}F\circ\boldsymbol{\sigma}(G,\mathbf{s})_{s_b=t} \tag{8.96}$$

We interchange the sums and obtain $\sum X_b$ where

$$X_b=\sum_{G\in\mathscr{F},\,G\ni b}\int^{t} d^{G\backslash b}s\;\partial^{G}F\circ\boldsymbol{\sigma}(G,\mathbf{s})_{s_b=t} \tag{8.97}$$

Now we fix b. To use the inductive hypothesis, we reduce N by one by rewriting X_b as a sum over all forests $\bar{G}$ on $N-1$ vertices. The $N-1$ vertices are obtained from the original vertices $\{1, 2,..., N\}$ by identifying the vertices at either end of b. The possible bonds $\bar{c}$ are viewed as sets of identified bonds on $\{1, 2,..., N\}$. For example, if $b=12$, then $1i$ and $2i$ become the same bond which we would denote by $\overline{1i}$ or $\overline{2i}$.

$\bar{\mathbf{s}}$ denotes a vector of parameters $\bar{s}_{\bar{c}}$ assigned to bonds $\bar{c}$. Given such parameters, we determine parameters $\mathbf{s}$ by assigning $\bar{s}_{\bar{c}}$ to all bonds $c\in\bar{c}$ and t to bond b. Thus define $\mathbf{s}=\mathbf{j}(\bar{\mathbf{s}})$ where the c component his given by

$$j_c(\bar{\mathbf{s}})=\begin{cases}\bar{s}_{\bar{c}} & \text{if}\quad c\neq b\\ t & \text{if}\quad c=b\end{cases} \tag{8.98}$$

To each forest $G\ni b$ on N vertices we associate a unique forest G/b on $N-1$ vertices by identifying the vertices in the pair b. Thus

$$G/b=\{\bar{c} : c\in G\} \tag{8.99}$$

For any function f of parameters $\mathbf{s}$,

$$\sum_{G\colon G/b=\bar{G}}(\partial^{G\backslash b}f)\circ\mathbf{j}(\bar{\mathbf{s}})=\partial^{\bar{G}}(f\circ\mathbf{j})(\bar{\mathbf{s}}) \tag{8.100}$$

To understand this, consider

$$\left(\frac{\partial f}{\partial u}\right)_{u=s}+\left(\frac{\partial f}{\partial v}\right)_{v=s}=\frac{\partial}{\partial s}\,(f(u,v)_{u=v=s})$$

Also, for any function f of parameters $\mathbf{s}$ and $G\ni b$,

$$\int^{t} d^{G\backslash b}s\;f\circ\boldsymbol{\sigma}(G,\mathbf{s})_{s_b=t}=\int^{t} d^{G/b}\bar{s}\;f\circ\mathbf{j}\circ\bar{\boldsymbol{\sigma}}(G/b,\bar{\mathbf{s}}) \tag{8.101}$$

The key point here is that $\sigma_c(G,\mathbf{s})_{s_b=t}$ depends only on $\bar{c}$.

We return to (8.97). By summing over G with G/b held fixed

$$X_b = \sum_{\bar{G}} \sum_{G:\, G/b = \bar{G}} \int^t d^{G \setminus b} s\, \partial^G F \circ \boldsymbol{\sigma}(G, \mathbf{s})_{s_b = t} \tag{8.102}$$

By (8.101) this equals

$$\sum_{\bar{G}} \sum_{G:\, G/b = \bar{G}} \int^t d^{\bar{G}} \bar{s}\, \partial^G F \circ \mathbf{j} \circ \bar{\boldsymbol{\sigma}}(\bar{G}, \bar{\mathbf{s}}) \tag{8.103}$$

which by (8.100), with $f = \partial_b F$ is

$$\sum_{\bar{G}} \int^t d^{\bar{G}} \bar{s} (\partial^{\bar{G}}\, \partial_b F \circ \mathbf{j}) \circ \bar{\boldsymbol{\sigma}}(\bar{G}, \bar{\mathbf{s}}) \tag{8.104}$$

which by the inductive hypothesis is

$$(\partial_b F) \circ \mathbf{j}(t \bar{\mathbb{1}}) = \partial_b F(t \mathbb{1}) \tag{8.105}$$

Therefore the t derivative of the right hand side of (8.6) is $\sum_b \partial_b F(t\mathbb{1})$ which is the t derivative of the left hand side of (8.6). ▮

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