

Quantum Mayer Graphs for Coulomb Systems and the Analog of the Debye Potential

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Within the Feynman–Kac path integral representation, the equilibrium quantities of a quantum plasma can be represented by Mayer graphs. The well known Coulomb divergencies that appear in these series are eliminated by partial resummations. In this paper, we propose a resummation scheme based on the introduction of a single effective potential ϕ that is the quantum analog of the Debye potential. A low density analysis of ϕ shows that it reduces, at short distances, to the bare Coulomb interaction between the charges (which is able to lead to bound states). At scale of the order of the Debye screening length κ_D^{-1} , ϕ approaches the classical Debye potential and, at large distances, it decays as a dipolar potential (this large distance behaviour is due to the quantum nature of the particles). The prototype graphs that result from the resummation obey the same diagrammatical rules as the classical graphs of the Abe–Meeron series. We give several applications that show the usefulness of ϕ to account for Coulombic effects at all distances in a coherent way.

KEY WORDS: Quantum plasma; Mayer graphs; Debye potential; screening.

1. INTRODUCTION

A non relativistic quantum plasma in thermal equilibrium shows a variety of phenomena, atomic and molecular recombination, ionization, collective screening, all of them originating from the basic Coulomb potential between point charges. A clear distinction and classification of these effects is only possible at low density, but even in this regime, it is a non elementary task to describe all consequences stemming from the sole Coulomb potential in a coherent way.

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The formalism of quantum Mayer graphs is particularly well suited to this program. Quantum Mayer graphs arise when the Gibbs statistical weight is expressed in terms of the Feynman–Kac path integral and is suitably reorganized to take into account the quantum statistics. According to this description, the quantum Coulomb gas is mapped into a certain classical-like gas of charged loops that carry fluctuating multipoles.⁽¹⁾ Then, the familiar Mayer expansion methods can be applied to this classical gas of loops. The resulting Mayer graphs are defined within the usual classical rules. All the quantum mechanical aspects are embodied into a generalized definition of phase space and of the corresponding Mayer bonds and weights at vertices.

This quantum Mayer diagrammatic is well suited for the low density regime since the small parameter is the activity or the density, and not the coupling constant (the electric charge). This is to be contrasted with the standard Feynman perturbation theory of the many-body problem (see, e.g., ref. 2) that has been applied to the high-temperature regime,^(3,4) and also to the high-density limit at zero temperature.⁽⁵⁾ In both cases, the Coulomb interactions can indeed be treated as small perturbations. At finite temperature, non-perturbative effects are essential. In this regime, the effective-potential method⁽⁶⁾ can be used. This first principles approach amounts to introduce an equivalent classical system of point particles with many-body potentials that incorporate all quantum effects. It has been applied to the calculation of low-density expansions up to order ρ^2 .^(7,8) However, general properties of this expansion remain quite hard to derive in this framework. Indeed, if only two-body potentials intervene at order ρ^2 , many-body potentials appear at higher orders, the effects of which cannot be accounted for within simple diagrammatical techniques. The present formalism based on loops Mayer graphs, avoids this drawback. It proves to be particularly efficient in dealing simultaneously with the collective screening effects and the quantum mechanics of small clusters of charges. Various applications have already been presented: derivation of the equation of state of a multicomponent plasma up to order $\rho^{5/2}$ in the density,^(9,10) characterization of the asymptotic behaviour of the particle and charge correlations,^(12,13) magnetized plasma.⁽¹⁴⁾

In all cases the central point is to build, by partial resummations, an integrable effective screened potential (in the same way as the classical Debye–Hückel potential arises from the chain graphs summation) that has a shorter range than the bare Coulomb potential. In quantum mechanics, there are several ways to define such an effective potential, depending on whether it includes or not multipolar interactions and quantum statistics. A proper choice of the effective potential may be dictated by the physical situation at hand and the convenience of the calculation, and several

possibilities have been considered in the above mentioned works. In this paper, we establish the properties of the most compact form of the effective potential, including multipolar interactions and quantum statistics.

In Section 2, we recall the basic rules for quantum Mayer graphs, as formulated in ref. 15. The effective potential ϕ is defined in Section 3; it is calculated with the help of a very useful lemma on Brownian bridge integrals.

Section 4 is devoted to a low density analysis of ϕ . At short distances, ϕ behaves as the bare Coulomb potential: this is the part that will control the quantum mechanical binding. At distances of the order of the classical Debye screening length, its behaviour is similar to the usual exponentially decaying Debye–Hückel potential induced by collective screening effects. At still larger distances, the effective potential displays an algebraic decay typical for unscreened multipolar interactions. These interactions are associated to the intrinsic quantum fluctuations of the charges. The dominant term in the algebraic tail of ϕ is related to a dipolar potential, and it is responsible for the non exponential decay of equilibrium particle and charge correlation functions.

In Section 5, we recall the diagrammatic rules for the so-called prototype graphs that arise when the Coulomb potential is replaced by the effective potential. The rules are simple: they involve only two bonds and are identical to those occurring in the Abe–Meeron series for the classical plasma.^(16,17) We consider resummations both in activity and density expansions and make the link between our resummed series and that introduced in earlier works. In this formalism (as well as in ref. 12 and subsequent papers) the value of a graph results of unbounded summations on particle numbers (since the number of particles in a loop is not fixed). Regarding the finiteness of a prototype graph, one can assert that spatial integrations are convergent because of the introduction of the screened potential, but convergence of infinite sums on particle numbers cannot be guaranteed in general (see discussion in Section 5.4). A prototype graph must hence be understood as a convenient compact notation for the set of all graphs with the same structure but different particle numbers in the loops (all graphs with a given number of particles are finite).

In the last section, we present several applications of the formalism that illustrate the crucial role of ϕ for a coherent description of all Coulombic phenomena. First, we revisit the derivation of various sum rules in the quantum plasma. With the prototype graphs introduced in this paper, the quantum sum rules are formally proved as the classical ones: they are direct consequences of the screening embodied in the effective potential ϕ . We also argue that the dipolar sum rule for two fixed particles of different species should not hold because of the quantum fluctuations that are properly accounted for by ϕ . Eventually, we propose a simple

approximation for the particle correlations by retaining the first graphs in the diagrammatic series. This approximate form does satisfy the charge sum rule, and it does incorporate all the physical mechanisms that control short and large distance behaviours.

2. QUANTUM MAYER GRAPHS

We consider \mathcal{S} species of point quantum charges e_α with masses m_α and spin σ_α , $\alpha = 1, \dots, \mathcal{S}$, obeying Fermi or Bose statistics (with at least one fermionic species). The charges interact by the Coulomb potential $e_\alpha e_{\alpha'} V(\mathbf{r}) = e_\alpha e_{\alpha'} / |\mathbf{r}|$. In the grand canonical ensemble, each type of charge has a chemical potential μ_α or fugacity $z_\alpha = \exp[\beta\mu_\alpha]$ with β the inverse temperature. Quantum Mayer graphs arise when the Gibbs statistical weight is expressed in terms of the Feynman–Kac path integral in which quantum fluctuations are represented by Brownian trajectories. The open trajectories associated to exchange contributions are reorganized into larger closed “loops” containing several particles. The result is that the grand partition function of the quantum gas can still be written in a classical-like form as (the so-called magic formula)

$$\Xi_A = \sum_{n=0}^{\infty} \frac{1}{n!} \int \prod_{i=1}^n d\mathcal{L}_i z(\mathcal{L}_i) \exp(-\beta U(\mathcal{L}_1, \dots, \mathcal{L}_n)) \quad (1)$$

if a suitable definition of the phase space integration and of the interaction are introduced. This formula has been derived and applied to the Coulomb system by Cornu in ref. 12. Here we follow the notations and definitions given in the review of ref. 15. An element \mathcal{L} of phase space, called a loop,

$$\mathcal{L} = (\mathbf{R}, \alpha, q, \mathbf{X}(s), 0 \leq s \leq q) = (\mathbf{R}, \chi) \quad (2)$$

is specified by its position \mathbf{R} in space, the particle species α , the number of particles q in the loop, and its shape $\mathbf{X}(s)$. The q particles that belong to the loop are located at positions

$$\mathbf{r}^{(k)} = \mathbf{R} + \lambda_\alpha \mathbf{X}(k-1), \quad k = 1, \dots, q \quad (3)$$

where

$$\lambda_\alpha = \hbar \sqrt{\frac{\beta}{m_\alpha}} \quad (4)$$

is the de Broglie thermal wavelength of the particle of type α . The path $\mathbf{R} + \lambda_\alpha \mathbf{X}(k-1+s)$, $s \in [0, 1]$, is the trajectory of the k th particle. It is

constrained to stay inside the volume Λ of the system, but we do not write this constraint explicitly since it will be trivially removed in the infinite volume limit $\Lambda \rightarrow \infty$. The collective variable

$$\chi = (\alpha, q, \mathbf{X}(\cdot)) \quad (5)$$

denotes all the internal parameters that describe the constitution of the loop. The loop can be viewed as an extended object at \mathbf{R} that has internal degree of freedom χ .

The shape of the loop $\mathbf{X}(s)$ is a Brownian bridge (a closed Brownian path), parametrized by the “time” s running in the “time interval” $[0, q]$ with $\mathbf{X}(0) = \mathbf{X}(q) = 0$. It is distributed according to the normalized Gaussian measure $D(\mathbf{X})$, with covariance

$$\int D(\mathbf{X}) X_\mu(s_1) X_\nu(s_2) = \delta_{\mu,\nu} q \left[\min\left(\frac{s_1}{q}, \frac{s_2}{q}\right) - \frac{s_1}{q} \frac{s_2}{q} \right] \quad (6)$$

The path $\mathbf{X}(s)$ is extended for convenience to a q -periodic function for all s . Integration on phase space means integration over space and summation over all internal degrees of freedom of the loop

$$\int d\mathcal{L} \cdots = \int d\mathbf{R} \sum_{\alpha=1}^{\mathcal{L}} \sum_{q=1}^{\infty} \int D(\mathbf{X}) \cdots = \int d\mathbf{R} \int d\chi \cdots \quad (7)$$

The interaction energy of n loops is the sum of two-loop potentials

$$U(\mathcal{L}_1, \dots, \mathcal{L}_n) = \sum_{1=i < j}^n e_{\alpha_i} e_{\alpha_j} V(\mathcal{L}_i, \mathcal{L}_j) \quad (8)$$

with the potential between two different loops

$$V(\mathcal{L}_i, \mathcal{L}_j) = \int_0^{q_1} ds_1 \int_0^{q_2} ds_2 \tilde{\delta}(s_1 - s_2) V(\mathbf{R}_i + \lambda_{\alpha_i} \mathbf{X}_i(s_1) - \mathbf{R}_j - \lambda_{\alpha_j} \mathbf{X}_j(s_2)) \quad (9)$$

In (9),

$$\tilde{\delta}(s) = \sum_{n=-\infty}^{\infty} e^{2i\pi ns} \quad (10)$$

is the Dirac comb ($\tilde{\delta}(s_1 - s_2)$ does not vanish only for $(s_1 - s_2)$ integer). The “equal time” condition $\tilde{\delta}(s_1 - s_2)$ naturally appears in the Feynman–Kac path integral; it can be seen as the manifestation of the quantum nature of

the particles. When it is omitted, (9) becomes identical to the pure electrostatic potential between two charged wires of shapes $\mathbf{X}_1(s)$ and $\mathbf{X}_2(s)$:

$$V_{\text{elec}}(\mathcal{L}_i, \mathcal{L}_j) = \int_0^{q_1} ds_1 \int_0^{q_2} ds_2 V(\mathbf{R}_1 + \lambda_{\alpha_1} \mathbf{X}_1(s_1) - \mathbf{R}_2 - \lambda_{\alpha_2} \mathbf{X}_2(s_2)) \quad (11)$$

To make the spatial dependence explicit, we also write

$$V(\mathcal{L}_i, \mathcal{L}_j) = V(\mathbf{R}_{ij}, \chi_i, \chi_j), \quad \mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j \quad (12)$$

In (1), the activity $z(\mathcal{L}) = z(\chi)$ of a loop

$$z(\mathcal{L}) = (2\sigma_\alpha + 1) \frac{(\eta_\alpha)^{q-1}}{q} \frac{z_\alpha^q}{(2\pi q \lambda_\alpha^2)^{3/2}} \exp(-\beta U(\mathcal{L})), \quad z_\alpha = e^{\beta \mu_\alpha} \quad (13)$$

incorporates the effects of quantum statistics ($\eta_\alpha = 1$ for bosons and $\eta_\alpha = -1$ for fermions), the spin degeneracy as well as the internal interaction $U(\mathcal{L}) = U(\chi)$ of the particles in the same loop with

$$U(\mathcal{L}) = \frac{e_\alpha^2}{2} \int_0^q ds_1 \int_0^q ds_2 (1 - \delta_{[s_1], [s_2]}) \tilde{\delta}(s_1 - s_2) V(\lambda_\alpha (\mathbf{X}(s_1) - \mathbf{X}(s_2))) \quad (14)$$

Here $[s] =$ integer part of s and the term with the Kronecker symbol $\delta_{[s_1], [s_2]}$ subtracts out the self-energies of the particles. Notice that $z(\chi)$ may take negative values for fermions, but since all the interactions between the particles that belong to the same loop are repulsive, one has the bound

$$|z(\chi)| \leq \frac{(2\sigma_\alpha + 1)}{q} \frac{z_\alpha^q}{(2\pi q \lambda_\alpha^2)^{3/2}} \quad (15)$$

The above rules define the statistical mechanics of the system of charged loops. Notice that loops with arbitrary shapes carry multipoles of all orders, and all possible shapes are randomly distributed. Because of the structure of the partition function (1) and of the interaction energy (8), the classical technique of Mayer expansions clearly applies to this system. The bonds are

$$f(\mathcal{L}_i, \mathcal{L}_j) = \exp(-\beta e_{\alpha_i} e_{\alpha_j} V(\mathcal{L}_i, \mathcal{L}_j)) - 1 \quad (16)$$

the weights at vertices are $z(\mathcal{L}_i)$, and the integration upon the vertices variables \mathcal{L}_i have to be performed according to (7). For instance, the loop

density $\rho(\mathcal{L})$ is represented by the activity expansion (see for example ref. 18)

$$\rho(\mathcal{L}) = \sum_{\mathbf{G}} \frac{1}{S_{\mathbf{G}}} \int \prod_{n=1}^N d\mathcal{L}_n z(\mathcal{L}_n) \left[\prod f \right]_{\mathbf{G}} \quad (17)$$

where the sum runs over all unlabeled topologically different connected diagrams \mathbf{G} with one root point \mathcal{L} and $N=0, 1, \dots$ internal points (by convention, the term $N=0$ is $z(\mathcal{L})$). The symmetry factor $S_{\mathbf{G}}$ is the number of permutations of the internal points \mathcal{L}_n that leave the integrand invariant.

At large distance (namely $|\mathbf{R}_1 - \mathbf{R}_2| \gg \lambda_{\alpha_1}$ and λ_{α_2}), the interaction (9) behaves as the Coulomb potential between two point charges $q_1 e_{\alpha_1}$ and $q_2 e_{\alpha_2}$

$$e_{\alpha_1} e_{\alpha_2} V(\mathcal{L}_1, \mathcal{L}_2) \sim \frac{q_1 e_{\alpha_1} q_2 e_{\alpha_2}}{|\mathbf{R}_1 - \mathbf{R}_2|} \quad (18)$$

so that the bonds $f(\mathcal{L}_i, \mathcal{L}_j)$ are not integrable and resummations are needed.

3. THE EFFECTIVE POTENTIAL ϕ

3.1. Definition and Formal Calculation of ϕ

We consider the linear part

$$f_{\mathbf{C}}(\mathcal{L}_i, \mathcal{L}_j) = -\beta_{ij} V(\mathcal{L}_i, \mathcal{L}_j) \equiv \bigcirc \text{---} \bigcirc \quad (19)$$

of the bond (16) with the abbreviation $\beta_{ij} = \beta e_{\alpha_i} e_{\alpha_j}$. Similarly to what Abe and Meeron did for classical particles, we define the effective potential $\phi(\mathcal{L}_a, \mathcal{L}_b)$ between two loops \mathcal{L}_a and \mathcal{L}_b as the sum of all the chain graphs with the linearized bond (19):

$$-\beta_{ab} \phi(\mathcal{L}_a, \mathcal{L}_b) \equiv \bigcirc \text{---} \bigcirc + \bigcirc \text{---} \bullet \text{---} \bigcirc + \bigcirc \text{---} \bullet \text{---} \bullet \text{---} \bigcirc + \dots \quad (20)$$

This definition of $\phi(\mathcal{L}_a, \mathcal{L}_b)$ differs from the one used in previous works by the fact that it includes both quantum statistics and multipolar interactions. In ref. 19, $\phi(\mathcal{L}_a, \mathcal{L}_b)$ is calculated in the Maxwell–Boltzmann approximation, retaining only loops with $q=1$. In ref. 12 (and subsequent works), a multipolar decomposition of the loop interaction is performed, and only chains of monopolar interactions are summed. In spite of its complexity,

the summation on chain graphs (20) can be performed in a translation invariant system.

We decompose $\phi(\mathcal{L}_a, \mathcal{L}_b)$ into

$$\phi(\mathcal{L}_a, \mathcal{L}_b) = V(\mathcal{L}_a, \mathcal{L}_b) + \phi_{\text{ch}}(\mathcal{L}_a, \mathcal{L}_b) \quad (21)$$

with $-\beta_{ab}\phi_{\text{ch}}(\mathcal{L}_a, \mathcal{L}_b)$ the sum of all chains having at least an intermediate black point. According to the rules of Section 2, the N th order term of $\phi_{\text{ch}}(\mathcal{L}_a, \mathcal{L}_b)$ (with N black points and $N+1$ bonds) is

$$\begin{aligned} & \phi_{\text{ch}}^{(N)}(\mathbf{R}_{ab}, \chi_a, \chi_b) \\ &= (-\beta)^N \int d\mathcal{L}_1 \cdots d\mathcal{L}_N z(\mathcal{L}_1) \cdots z(\mathcal{L}_N) \\ & \quad \times e_{\alpha_1} V(\mathbf{R}_{a1}, \chi_a, \chi_1) e_{\alpha_1} e_{\alpha_2} V(\mathbf{R}_{12}, \chi_1, \chi_2) e_{\alpha_2} \cdots e_{\alpha_N} V(\mathbf{R}_{Nb}, \chi_N, \chi_b) \end{aligned} \quad (22)$$

We introduce the Fourier transform of the loop potential

$$\tilde{V}(\mathbf{k}, \chi_1, \chi_2) = \int d\mathbf{R} e^{-i\mathbf{k} \cdot \mathbf{R}} V(\mathbf{R}, \chi_1, \chi_2) \quad (23)$$

$$= \tilde{V}(\mathbf{k}) \int_0^{q_1} ds_1 \int_0^{q_2} ds_2 \tilde{\delta}(s_1 - s_2) e^{i\mathbf{k} \cdot [\lambda_{\alpha_1} \mathbf{X}_1(s_1) - \lambda_{\alpha_2} \mathbf{X}_2(s_2)]} \quad (24)$$

and this is further decomposed with the help of (10) into

$$\tilde{V}(\mathbf{k}, \chi_1, \chi_2) = \tilde{V}(\mathbf{k}) \sum_{n=-\infty}^{\infty} c_n(\mathbf{k}, \chi_1) c_n^*(\mathbf{k}, \chi_2) \quad (25)$$

where $\tilde{V}(\mathbf{k}) = 4\pi/|\mathbf{k}|^2$ and

$$c_n(\mathbf{k}, \chi) \equiv \int_0^q ds e^{2i\pi ns} e^{i\mathbf{k} \cdot \lambda_{\alpha} \mathbf{X}(s)} \quad (26)$$

Hence, using the invariance of $z(\mathcal{L}) = z(\chi)$ under translations, the convolution theorem gives for the N th order term, in the Fourier representation,

$$\begin{aligned} & \tilde{\phi}_{\text{ch}}^{(N)}(\mathbf{k}, \chi_a, \chi_b) = -(-\tilde{V}(\mathbf{k}))^{N+1} \\ & \quad \times \sum_{n_1, \dots, n_{N+1}} g_{n_1 n_2}(k) g_{n_2 n_3}(k) \cdots g_{n_N n_{N+1}}(k) c_{n_1}(\mathbf{k}, \chi_a) c_{n_{N+1}}^*(\mathbf{k}, \chi_b) \end{aligned} \quad (27)$$

where

$$g_{n_1, n_2}(k) \equiv \beta \int d\chi e^{\alpha z(\chi)} c_{n_1}^*(\mathbf{k}, \chi) c_{n_2}(\mathbf{k}, \chi) \quad (28)$$

includes the integration on the internal variables of the loop at a black point. The integral (28) is simplified by the application of the following lemma on a change of variable in a Brownian integral.

Lemma 1. For any $u \in \mathbb{R}$, the Gaussian measure $D(\mathbf{X})$ is invariant under

$$\mathbf{X}(s) \rightarrow \mathbf{X}(s+u) - \mathbf{X}(u) \quad (29)$$

Hence for any functional $G(\mathbf{X}(\cdot))$, one has

$$\int D(\mathbf{X}) G(\mathbf{X}(\cdot)) = \int D(\mathbf{X}) G(\mathbf{X}(\cdot + u) - \mathbf{X}(u)) \quad (30)$$

The proof proceeds by an explicit verification that the covariance (6) is left invariant under (29) (see ref. 20, Lemma 2).

We recall that the path $\mathbf{X}(s)$ is extended to a q -periodic function for all $s \in \mathbb{R}$. If we replace the factor $(1 - \delta_{[s_1], [s_2]})$ in (14) by the periodic expression $(1 - \delta_{[s_1 \bmod q], [s_2 \bmod q]})$, the invariance of $U(\chi)$ and $z(\chi)$ under the transformation (29) is obvious, since the integrand in (14) is q -periodic in both s_1 and s_2 . The part of (28) that involves the Brownian integral reduces therefore to, according to (26),

$$\begin{aligned} & \int_0^q ds_1 \int_0^q ds_2 \int D(\mathbf{X}) z(\chi) e^{-ik \cdot \lambda_\alpha [\mathbf{X}(s_1) - \mathbf{X}(s_2)]} e^{-2i\pi n_1 s_1} e^{2i\pi n_2 s_2} \\ &= \int_0^q ds_1 \int_0^q ds_2 \int D(\mathbf{X}) z(\chi) e^{ik \cdot \lambda_\alpha \mathbf{X}(s_2 - s_1)} e^{-2i\pi n_1 s_1} e^{2i\pi n_2 s_2} \\ &= q \delta_{n_1, n_2} \int_0^q ds \int D(\mathbf{X}) z(\chi) e^{ik \cdot \lambda_\alpha \mathbf{X}(s)} e^{2i\pi n_2 s} \end{aligned} \quad (31)$$

The second line results of the application of (30) with $u = -s_1$. Hence $g_{n_1, n_2}(k)$ is diagonal in the frequency indices, and we can write

$$g_{n_1, n_2}(k) = \frac{1}{4\pi} \delta_{n_1, n_2} \kappa^2(k, n_1) \quad (32)$$

with

$$\kappa^2(k, n) \equiv 4\pi\beta \sum_{\alpha} e_{\alpha}^2 \sum_q q \int_0^q ds \int D(\mathbf{X}) z(\chi) e^{ik \cdot \lambda_{\alpha} \mathbf{X}(s)} e^{2i\pi ns} \quad (33)$$

Thus N frequency summations in (27) are readily performed

$$\begin{aligned} \phi_{\text{ch}}^{(N)}(\mathbf{k}, \chi_a, \chi_b) &= \int_0^{q_a} ds_a \int_0^{q_b} ds_b e^{ik \cdot [\lambda_a \mathbf{X}_a(s_a) - \lambda_b \mathbf{X}_b(s_b)]} \\ &\times \sum_{n=-\infty}^{\infty} \frac{4\pi}{k^2} \left(-\frac{\kappa^2(k, n)}{k^2} \right)^N e^{2i\pi n(s_a - s_b)} \end{aligned} \quad (34)$$

Summing (34) on $N \geq 1$ leads eventually to the expression of the chain potential:

$$\begin{aligned} \tilde{\phi}_{\text{ch}}(\mathbf{k}, \chi_a, \chi_b) &= \int_0^{q_a} ds_a \int_0^{q_b} ds_b e^{ik \cdot [\lambda_a \mathbf{X}_a(s_a) - \lambda_b \mathbf{X}_b(s_b)]} \\ &\times \sum_{n=-\infty}^{\infty} \frac{-4\pi\kappa^2(k, n)}{k^2[k^2 + \kappa^2(k, n)]} e^{2i\pi n(s_a - s_b)} \end{aligned} \quad (35)$$

The effective potential is obtained by adding $\tilde{V}(\mathbf{k}, \chi_a, \chi_b)$ to (35). Thus, according to (24),

$$\begin{aligned} \tilde{\phi}(\mathbf{k}, \chi_a, \chi_b) &= \int_0^{q_a} ds_a \int_0^{q_b} ds_b e^{ik \cdot [\lambda_a \mathbf{X}_a(s_a) - \lambda_b \mathbf{X}_b(s_b)]} \\ &\times \sum_{n=-\infty}^{\infty} \frac{4\pi}{k^2 + \kappa^2(k, n)} e^{2i\pi n(s_a - s_b)} \end{aligned} \quad (36)$$

The expression (36) is our main formula and generalizes the effective potential of ref. 19 to any quantum statistics. We establish in the next section the convergence of the sum over n and show that ϕ is a smooth function of its arguments.

We note that, if the sum of chains (20) is calculated with the classical electrostatic interaction (11) instead of the loop interaction (9), the result for the effective potential is just the term $n = 0$ of (36). This part $\phi^{n=0}$ decays faster than any inverse power of \mathbf{r} (see Section 3.2), as it is expected for a classical Coulomb gas. The part $\phi^{n \neq 0}$ associated to the non-zero frequency terms in (36) embody purely quantum effects that arise from the difference between the loop interaction (9) and the electrostatic interaction (11).

3.2. Finiteness and Regularity of ϕ

In order to show that $\tilde{\phi}(\mathbf{k}, \chi_a, \chi_b)$ is a well defined continuous function at low density (for $\mathbf{k} \neq \mathbf{0}$), we start by studying the “screening coefficients” $\kappa^2(k, n)$. Using (31), they are given by

$$\kappa^2(k, n) = 4\pi\beta \sum_{\alpha} e_{\alpha}^2 \sum_q \int \mathbf{D}(\mathbf{X}) z(\chi) \left| \int_0^q ds e^{i\mathbf{k} \cdot \lambda_{\alpha} \mathbf{X}(s)} e^{2i\pi n s} \right|^2 \quad (37)$$

When z_{α} is less than one, the series is convergent. Indeed, using the bound (15) and $|\int_0^q ds \exp[i\mathbf{k} \cdot \lambda_{\alpha} \mathbf{X}(s)] \exp[2i\pi n s]| \leq q$,

$$|\kappa^2(k, n)| \leq 4\pi\beta \sum_{\alpha} e_{\alpha}^2 \frac{(2\sigma_{\alpha} + 1)}{(2\pi\lambda_{\alpha}^2)^{3/2}} \sum_{q=1}^{\infty} \frac{z_{\alpha}^q}{\sqrt{q}} < \infty, \quad z_{\alpha} < 1 \quad (38)$$

for all k and n . The term $q = 1$ in the above sum is nothing but the inverse of the square of the classical screening length λ_{D} :

$$\kappa_{\text{D}}^2 = 4\pi\beta \sum_{\alpha} e_{\alpha}^2 \frac{(2\sigma_{\alpha} + 1) z_{\alpha}}{(2\pi\lambda_{\alpha}^2)^{3/2}} = \lambda_{\text{D}}^{-2} \quad (39)$$

We deduce hence from (38) the uniform estimate

$$|\kappa^2(k, n)| \leq \kappa_{\text{D}}^2 [1 + \mathcal{O}(z)] \quad (40)$$

where $z = \sup_{\alpha} z_{\alpha}$. In the special case $k = 0$ and $n = 0$, we have moreover the equality

$$\kappa^2(0, 0) = \kappa_{\text{D}}^2 [1 + \mathcal{O}(z)] \quad (41)$$

The notation $\kappa^2(k, n)$ as squares is justified by the properties

$$\kappa^2(k, 0) > 0, \quad k \geq 0 \quad (42)$$

and

$$\kappa^2(k, n) > 0, \quad k > 0, \quad n \neq 0 \quad (43)$$

if z is sufficiently small (notice that $\kappa^2(0, n) = 0$, $n \neq 0$). This positivity property is not trivial since for fermions $z(\chi)$ may be negative if q is greater than one (in the Maxwell–Boltzmann approximation, only loops with $q = 1$ are retained and $\kappa_{\text{MB}}^2(k, n)$ is manifestly positive). For a bosonic species, the terms in (37) are clearly positive, so it is sufficient to consider a fermionic species α . The idea is to single out the term $q = 1$ in (37) and show

that it dominates all the others at low density. For a one particle loop, $z(\chi)$ reduces to $(2\sigma_\alpha + 1) z_\alpha (2\pi\lambda_\alpha^2)^{-3/2}$; for a q -particle loop, $q \geq 2$, $z(\chi) \geq -(2\sigma_\alpha + 1) q^{-1} z_\alpha^q (2\pi q \lambda_\alpha^2)^{-3/2}$ by (15). Hence the q -sum in (37) for a fermionic species α is minorized by

$$\frac{(2\sigma_\alpha + 1)}{(2\pi\lambda_\alpha^2)^{3/2}} \left[z_\alpha u_1(k, n) - \sum_{q=2}^{\infty} \frac{z_\alpha^q}{\sqrt{q}} u_q(k, n) \right] \quad (44)$$

with

$$u_q(k, n) = \int_0^1 ds e^{2i\pi nqs} e^{-\frac{1}{2}k^2\lambda_\alpha^2qs(1-s)} \geq 0 \quad (45)$$

The quantity (45) results of the calculation of the functional integral

$$\begin{aligned} \int \mathbf{D}(\mathbf{X}) \left| \int_0^q ds e^{i\mathbf{k} \cdot \lambda_\alpha \mathbf{X}(s)} e^{2i\pi ns} \right|^2 &= q \int_0^q ds e^{2i\pi ns} \int \mathbf{D}(\mathbf{X}) e^{i\mathbf{k} \cdot \lambda_\alpha \mathbf{X}(s)} \\ &= q^2 u_q(k, n) \end{aligned} \quad (46)$$

where we have used that $\mathbf{D}(\mathbf{X})$ is a Gaussian measure with the covariance (6), and changed s into qs in the time integral. One has clearly $u_q(k, 0) \leq u_1(k, 0)$, so that (44) is positive if $n = 0$ for z_α sufficiently small. This proves (42). For $n \neq 0$, we show in appendix A that there exists a positive constant C such that for all $q = 1, 2, \dots$,

$$u_q(k, n) \leq C q^{3/2} u_1(k, n), \quad n \neq 0 \quad (47)$$

For z_α sufficiently small, (44) is therefore also positive for $n \neq 0$ (if $k > 0$) and (43) is proved.

In the chain potential (35), the sum over n is absolutely convergent. Indeed, using the positivity of $\kappa^2(k, n)$ at low density and (10), it is sufficient to find an upper bound for

$$\sum_n \kappa^2(k, n) = 4\pi\beta \int d\chi e_\alpha^2 z(\chi) q \int_0^q ds e^{i\mathbf{k} \cdot \lambda_\alpha \mathbf{X}(s)} \tilde{\delta}(s) \quad (48)$$

Using (15) and $|\sum_{m=1}^q \exp[i\mathbf{k} \cdot \lambda_\alpha \mathbf{X}(m-1)]| \leq q$, we recover the convergent series (38), from which we deduce the upper bound

$$\sum_n \kappa^2(k, n) \leq \kappa_D^2 [1 + \mathcal{O}(z)] \quad (49)$$

The sum over n therefore converges and the effective potential $\phi = V + \phi_{\text{ch}}$ is hence a well defined continuous function of \mathbf{k} for $\mathbf{k} \neq \mathbf{0}$ at low density.

We mention another proof of the convergence of $\sum_n \kappa^2(k, n)$, which is based on a bound for the decay of $\kappa^2(k, n)$ for large n . From (37), (15) and (46), we have

$$\kappa^2(k, n) \leq 4\pi\beta \sum_{\alpha} e_{\alpha}^2 \frac{(2\sigma_{\alpha} + 1) z_{\alpha}}{(2\pi\lambda_{\alpha}^2)^{3/2}} \sum_{q=1}^{\infty} \frac{z_{\alpha}^{q-1}}{\sqrt{q}} u_q(k, n) \quad (50)$$

Two integrations by parts of the factor $\exp[i2\pi nqs]$ in (45) show that

$$u_q(k, n) \leq \frac{1}{n^2} k^2 \lambda^2 (1 + k^2 \lambda^2), \quad n \neq 0 \quad (51)$$

with $\lambda = \sup_{\alpha} \lambda_{\alpha}$. Inserting this bound in (50) gives

$$\kappa^2(k, n) \leq \frac{\kappa_D^2}{n^2} C(z) k^2 \lambda^2 (1 + k^2 \lambda^2), \quad n \neq 0 \quad (52)$$

where $C(z)$ is a finite function of z if $z < 1$. The decay of $\kappa^2(k, n)$ for large n is therefore fast enough to ensure the convergence of $\sum_n \kappa^2(k, n)$.

3.3. Large Distance Decay of ϕ

The asymptotic behaviour of $\phi(\mathbf{r}, \chi_a, \chi_b)$ as $|\mathbf{r}| \rightarrow \infty$ is very similar to that of ϕ^{MB} (the Maxwell–Boltzmann approximation of ϕ) obtained in ref. 19. It is determined by the possible non analytic part of $\tilde{\phi}(\mathbf{k}, \chi_a, \chi_b)$ as $\mathbf{k} \rightarrow \mathbf{0}$.

We determine first the small k behaviour of the ‘‘screening coefficients’’ $\kappa^2(k, n)$. By expanding in a Taylor series $\exp[i\mathbf{k} \cdot \lambda_{\alpha} \mathbf{X}(s)]$ in (37), we find

$$\kappa^2(k, n) = \kappa^2 \delta_{n,0} + \gamma_n k^2 + \mathcal{O}(\kappa_D^2 \lambda^4 k^4) \quad (53)$$

with

$$\kappa^2 \equiv 4\pi\beta \int d\chi e_{\alpha}^2 q^2 z(\chi) \quad (54)$$

and

$$\gamma_n \equiv \frac{4\pi\beta}{3} \int d\chi e_{\alpha}^2 \lambda_{\alpha}^2 z(\chi) \left| \int_0^q ds \mathbf{X}^2(s) e^{i2\pi ns} \right|^2 = \mathcal{O}\left(\frac{\kappa_D^2 \lambda^2}{n^2}\right) \quad (55)$$

In writing (55), we have taken into account that the measure $D(\mathbf{X})$ and $z(\chi)$ are invariant under space inversion and rotations. The estimate $1/n^2$ follows from (15) and direct evaluation of the functional integral (and the time integration over s) with the covariance (6). The estimate for the remainder in (53) is obtained by writing the latter, using (33), as

$$\begin{aligned} \kappa^2(k, n) - \kappa^2 \delta_{n,0} - \gamma_n k^2 &= 4\pi\beta \int d\chi e_{\alpha}^2 q \int_0^q ds z(\chi) \\ &\times \left(e^{i\mathbf{k} \cdot \lambda_{\alpha} \mathbf{X}(s)} - \sum_{m=0}^3 \frac{1}{m!} (i\mathbf{k} \cdot \lambda_{\alpha} \mathbf{X}(s))^m \right) e^{i2\pi ns} \end{aligned} \quad (56)$$

where odd terms in $\mathbf{X}(s)$ have been freely subtracted, and by using the bounds $|\exp[ix] - \sum_{m=0}^3 (ix)^m/m!| \leq C|x|^4$ and (15).

The zero frequency coefficient $\kappa^2(k, 0)$ does not vanish at $k=0$, contrary to the non-zero frequency terms. We split therefore the effective potential into

$$\tilde{\phi}(\mathbf{k}, \chi_a, \chi_b) = \tilde{\phi}^{n=0}(\mathbf{k}, \chi_a, \chi_b) + \tilde{\phi}^{n \neq 0}(\mathbf{k}, \chi_a, \chi_b) \quad (57)$$

where

$$\tilde{\phi}^{n=0}(\mathbf{k}, \chi_a, \chi_b) = \int_0^{q_a} d\tau_a \int_0^{q_b} d\tau_b e^{i\mathbf{k}[\lambda_a \mathbf{X}_a(\tau_a) - \lambda_b \mathbf{X}_b(\tau_b)]} \frac{4\pi}{k^2 + \kappa^2(k, 0)} \quad (58)$$

$$\tilde{\phi}^{n \neq 0}(\mathbf{k}, \chi_a, \chi_b) = \int_0^{q_a} d\tau_a \int_0^{q_b} d\tau_b e^{i\mathbf{k}[\lambda_a \mathbf{X}_a(\tau_a) - \lambda_b \mathbf{X}_b(\tau_b)]} \sum_{n \neq 0} \frac{4\pi}{k^2 + \kappa^2(k, n)} e^{2i\pi n(\tau_a - \tau_b)} \quad (59)$$

Since all moments of the Gaussian measure $D(\mathbf{X})$ are finite, $\kappa^2(k, n)$ has a Taylor expansion in \mathbf{k} at arbitrary order and is hence an infinitely differentiable function of \mathbf{k} . Using (53) and (42), $\tilde{\phi}^{n=0}(\mathbf{k}, \chi_a, \chi_b)$ is also an infinitely differentiable function of \mathbf{k} implying that its Fourier transform decays faster than any inverse power of \mathbf{r} . Recalling (41), the zero frequency part $\phi^{n=0}$ describes collective screening effects with an inverse length κ^{-1} that is asymptotic to the classical Debye screening length κ_D^{-1} as $z \rightarrow 0$.

The part $\phi^{n \neq 0}$ is not exponentially screened because of the different small k behaviour $\kappa^2(k, n) \sim \gamma_n k^2$ for $n \neq 0$. Taking into account $\int_0^q d\tau \exp[2i\pi n\tau] = 0$ and (53), the leading term of (59) as $k \rightarrow 0$ is

$$\phi^{n \neq 0}(\mathbf{k}, \chi_a, \chi_b) \underset{k \rightarrow 0}{\sim} \int_0^{q_a} d\tau_a \int_0^{q_b} d\tau_b h(\tau_a - \tau_b) \frac{(\mathbf{k} \cdot \lambda_a \mathbf{X}_a(\tau_a))(\mathbf{k} \cdot \lambda_b \mathbf{X}_b(\tau_b))}{k^2} \quad (60)$$

where $h(\tau) = \sum_{n \neq 0} \frac{e^{2in\tau}}{1+\gamma_n}$. Hence $\phi(\mathbf{r}, \chi_a, \chi_b)$ decays as a dipolar potential

$$\phi(\mathbf{r}, \chi_a, \chi_b) \underset{r \rightarrow \infty}{\sim} - \int_0^{q_a} d\tau_a \int_0^{q_b} d\tau_b h(\tau_a - \tau_b) (\lambda_a \mathbf{X}_a(\tau_a) \cdot \nabla) (\lambda_b \mathbf{X}_b(\tau_b) \cdot \nabla) \frac{1}{r} \quad (61)$$

This unscreened dipolar tail is responsible for the algebraic decay of particles and charge correlations in the quantum Coulomb gas. ^(21, 12)

4. LOW DENSITY BEHAVIOUR OF ϕ

We consider in this section a low density limit that corresponds to a regime of low degeneracy ($\lambda_a \ll a$, a : mean interparticle distance) and low coupling ($\Gamma \equiv \beta e^2/a \ll 1$). In this regime,

$$z \ll 1 \quad \text{and} \quad \kappa_D \lambda \ll 1 \quad (62)$$

The first low density deviations of $\phi(\mathcal{L}_a, \mathcal{L}_b)$ from the Coulomb potential $V(\mathcal{L}_a, \mathcal{L}_b)$ are of order κ_D , and can conveniently be obtained from the formula (36). All contributions to ϕ that are $\kappa_D \mathcal{O}(z)$ or $\kappa_D \mathcal{O}(\kappa_D \lambda)$ will be neglected (see the end result (71)).

We decompose again ϕ according to (57) and consider first the inverse Fourier transform of the zero frequency part $\phi^{n=0}$:

$$\begin{aligned} \phi^{n=0}(\mathbf{r}, \chi_a, \chi_b) &= \frac{1}{(2\pi)^3} \int d\mathbf{k} \int_0^{q_a} d\tau_a \int_0^{q_b} d\tau_b e^{ik[\mathbf{r} + \lambda_a \mathbf{X}_a(\tau_a) - \lambda_b \mathbf{X}_b(\tau_b)]} \\ &\quad \times \frac{4\pi}{k^2 + \kappa^2(k, 0)} \end{aligned} \quad (63)$$

We rewrite the fraction $4\pi/[k^2 + \kappa^2(k, 0)]$ as

$$\frac{4\pi}{k^2 + \kappa_D^2} + \frac{4\pi}{k^2 + \kappa_D^2} \frac{\kappa_D^2 - \kappa^2(k, 0)}{k^2 + \kappa^2(k, 0)} \quad (64)$$

The first term, once inverse Fourier transformed in (63), gives the classical screened Debye potential between loops:

$$\phi_D(\mathbf{r}, \chi_a, \chi_b) = \int_0^{q_a} d\tau_a \int_0^{q_b} d\tau_b \frac{e^{-\kappa_D |\mathbf{r} + \lambda_a \mathbf{X}_a(\tau_a) - \lambda_b \mathbf{X}_b(\tau_b)|}}{|\mathbf{r} + \lambda_a \mathbf{X}_a(\tau_a) - \lambda_b \mathbf{X}_b(\tau_b)|} \quad (65)$$

The contribution of the second term of (64) is $\kappa_D[\mathcal{O}(z) + \mathcal{O}(\kappa_D\lambda)]$. Indeed, inserting absolute values in (63) and using the positivity (42), we can majorize this contribution by

$$\frac{4\pi q_a q_b}{(2\pi)^3} \int d\mathbf{k} \frac{1}{k^2 + \kappa_D^2} \frac{|\kappa_D^2 - \kappa^2(k, 0)|}{k^2} \quad (66)$$

We split the integral over \mathbf{k} into the regions: $|\mathbf{k}| < \lambda^{-1}$ and $|\mathbf{k}| > \lambda^{-1}$. From the bound (40), the integral over the region $|\mathbf{k}| > \lambda^{-1}$ is $\kappa_D \mathcal{O}(\kappa_D\lambda)$. To control the small k behaviour of the integrand, we write

$$|\kappa_D^2 - \kappa^2(k, 0)| \leq |\kappa_D^2 - \kappa^2| + |\kappa^2 - \kappa^2(k, 0)| \quad (67)$$

From (41), the contribution of the first term of (67) to $\phi^{n=0}$ is $\kappa_D \mathcal{O}(z)$, as seen after introducing the change of variables $\mathbf{k} = \kappa_D \mathbf{q}$. The estimate

$$\frac{\kappa^2(k, 0) - \kappa^2}{k^2} = 4\pi\beta \int d\chi q \int_0^q ds e_\alpha^2 z(\chi) \frac{e^{ik \cdot \lambda_\alpha X(s)} - 1}{k^2} = \mathcal{O}(\kappa_D^2 \lambda^2) \quad (68)$$

that follows from the invariance of $\mathbf{D}(\mathbf{X})$ and $z(\chi)$ under space inversion together with the majorations (15) and $|\exp[ix] - 1 - ix| \leq Cx^2$, shows that the second term of (67) gives a contribution $\kappa_D \mathcal{O}(\kappa_D\lambda)$ to ϕ .

We consider now the non-zero frequency part $\phi^{n \neq 0}$. The fraction $4\pi/[k^2 + \kappa^2(k, n)]$ in (59) is rewritten as

$$\frac{4\pi}{k^2} - \frac{4\pi}{k^2} \frac{\kappa^2(k, n)}{k^2 + \kappa^2(k, n)} \quad (69)$$

When inserted in (59) and inverse Fourier transformed, the first term of (69) gives $V - V_{\text{elec}}$, where V_{elec} is the electrostatic potential between loops (11). To estimate the contribution to ϕ of the second term of (69), we split as before the \mathbf{k} integral into the regions $|\mathbf{k}| > \lambda^{-1}$ and $|\mathbf{k}| < \lambda^{-1}$ and introduce the majoration (using the positivity (43))

$$\sum_{n \neq 0} \frac{\kappa^2(k, n)}{k^2 + \kappa^2(k, n)} \leq \frac{1}{k^2} \sum_{n \neq 0} \kappa^2(k, n) \quad (70)$$

The bound (49) shows that the integral over the region $|\mathbf{k}| > \lambda^{-1}$ is $\kappa_D \mathcal{O}(\kappa_D\lambda)$. Using (52), the integral over the complementary region is also $\kappa_D \mathcal{O}(\kappa_D\lambda)$.

Collecting the above results, we obtain the low density asymptotic behaviour of the effective potential

$$\begin{aligned} \phi(\mathbf{r}, \chi_a, \chi_b) = & V(\mathbf{r}, \chi_a, \chi_b) + \phi_D(\mathbf{r}, \chi_a, \chi_b) \\ & - V_{\text{elec}}(\mathbf{r}, \chi_a, \chi_b) + \kappa_D [\mathcal{O}(z) + \mathcal{O}(\kappa_D \lambda)] \end{aligned} \quad (71)$$

where the estimate for the remainder is uniform with respect to \mathbf{r} . This expression allows to derive the following various behaviours of ϕ that depend on the scale of $|\mathbf{r}|$.

(a) Short Distance Behaviour

If $r \ll \kappa_D^{-1}$, the exponential in ϕ_D can be linearized and (71) becomes

$$\phi(\mathbf{r}, \chi_a, \chi_b) = V(\mathbf{r}, \chi_a, \chi_b) - q_a q_b \kappa_D + \kappa_D [\mathcal{O}(z) + \mathcal{O}(\kappa_D \lambda)], \quad r, \lambda_\alpha \ll \kappa_D^{-1} \quad (72)$$

The effective potential differs at short distance from the bare Coulomb potential only by a constant shift at lowest order. The next corrections will depend on the positions and shapes of the loops.

(b) Classical Screening at Scale $r \sim \kappa_D^{-1}$

On the scale $r \sim \kappa_D^{-1}$, the term $V - V_{\text{elec}}$ in (71) behaves as λ^2/r^3 , as can be seen by introducing the multipolar expansion

$$\begin{aligned} \frac{1}{|\mathbf{r} + \lambda_a \mathbf{X}_a(\tau_a) - \lambda_b \mathbf{X}_b(\tau_b)|} = & \frac{1}{|\mathbf{r}|} + [\lambda_a \mathbf{X}_a(\tau_a) - \lambda_b \mathbf{X}_b(\tau_b)] \cdot \nabla \frac{1}{|\mathbf{r}|} \\ & + \frac{1}{2} ([\lambda_a \mathbf{X}_a(\tau_a) - \lambda_b \mathbf{X}_b(\tau_b)] \cdot \nabla)^2 \frac{1}{|\mathbf{r}|} + \mathcal{O}\left(\frac{1}{|\mathbf{r}|^4}\right) \end{aligned} \quad (73)$$

The term ϕ_D behaves on the other hand as $\exp[-\kappa_D r]/r$. At distances $r \sim \kappa_D^{-1}$, $V - V_{\text{elec}}$ is hence smaller than ϕ_D by a factor $\kappa_D^2 \lambda^2$, so that

$$\phi(\mathbf{r}, \chi_a, \chi_b) = q_a q_b \frac{e^{-\kappa_D r}}{r} + \kappa_D [\mathcal{O}(z) + \mathcal{O}(\kappa_D \lambda)], \quad r \sim \kappa_D^{-1} \quad (74)$$

On this scale, the effective potential reduces to the standard Debye potential that describes the classical collective screening effects.

(c) Large Distance Behaviour

The large distance behaviour of ϕ has already been obtained non perturbatively in Section 3.3. It is given by the dipolar tail (61) that involves

the function $h(\tau_a - \tau_b)$. Notice that this function reduces at low density to $\tilde{\delta}(\tau_a - \tau_b) - 1$ since $\gamma_n = \mathcal{O}(\kappa_D^2 \lambda^2)$. In the zero density limit, this tail corresponds to the asymptotic behaviour $r \rightarrow \infty$ of $V - V_{\text{elec}}$.

The previous results are interpreted as follows. Since $\kappa_D^{-1} \gg \lambda_\alpha$, the particles can be treated classically at relative distances $r \sim \kappa_D^{-1}$. Therefore, the screened potential is expected to behave as its classical counterpart for such distances. In other words, in the chain summation (20), the leading contributions arise from configurations such that all loop potentials can be replaced by the Coulomb potential (18). Only loops with $q = 1$ are retained since $z_\alpha \ll 1$. Then, ϕ does reduce to its Debye classical expression (74) where the classical screening length κ_D^{-1} appears because the system is weakly degenerate.

The result (72) can be recovered with similar arguments. By definition, the effective potential satisfies

$$\phi(\mathcal{L}_a, \mathcal{L}_b) = V(\mathcal{L}_a, \mathcal{L}_b) - \beta \int d\mathcal{L}_1 z(\mathcal{L}_1) e_{\alpha_1}^2 V(\mathcal{L}_a, \mathcal{L}_1) \phi(\mathcal{L}_1, \mathcal{L}_b) \quad (75)$$

If $|\mathbf{r}_a - \mathbf{r}_b|$ and λ_α are much smaller than κ_D^{-1} , the leading contribution to the convolution $V \star \phi$ arises, at low density, from the regions where the loop \mathcal{L}_1 is far enough from the loops \mathcal{L}_a and \mathcal{L}_b so that $V(\mathcal{L}_a, \mathcal{L}_1) \simeq q_a q_1 / |\mathbf{r}_a - \mathbf{r}_1|$ and $\phi(\mathcal{L}_1, \mathcal{L}_b) \simeq q_1 q_b \exp[-\kappa_D |\mathbf{r}_1 - \mathbf{r}_b|] / |\mathbf{r}_1 - \mathbf{r}_b|$. The contribution of these regions to the convolution is

$$\int d\mathbf{r}_1 \frac{1}{|\mathbf{r}_a - \mathbf{r}_1|} \frac{e^{-\kappa_D |\mathbf{r}_1 - \mathbf{r}_b|}}{|\mathbf{r}_1 - \mathbf{r}_b|} \simeq \frac{4\pi}{\kappa_D}, \quad |\mathbf{r}_a - \mathbf{r}_b| \ll \kappa_D^{-1} \quad (76)$$

The expression (76) is indeed the leading contribution, since it grows like κ_D^{-1} while the contribution from the region close to the loops \mathcal{L}_a and \mathcal{L}_b remains finite in the zero density limit. Inserting (76) into (75) and retaining only the term $q_1 = 1$, we recover the low density result (72) at short distances.

The effective potential defined in (20) incorporates into a single function all the basic collective phenomena that screen the interactions of quantum charges (loops) at short, intermediate and long distance. It will serve in Section 5 as the basic object in the resummed Mayer diagrammatics, which involves graphs with bonds defined in terms of ϕ rather than V .

We mention that the above low density analysis of ϕ allows to derive useful upper bounds on $\phi_{\text{ch}} = \phi - V$ that are uniform in the loop variables. The contribution $\phi_D - V_{\text{elec}}$ in (71) can indeed be majorized uniformly in \mathbf{r} , χ_a, χ_b by

$$\frac{4\pi q_a q_b}{(2\pi)^3} \int d\mathbf{k} \frac{\kappa_D^2}{k^2(k^2 + \kappa_D^2)} = q_a q_b \mathcal{O}(\kappa_D) \quad (77)$$

The estimate $\mathcal{O}(\kappa_D)$ follows from the change of variables $\mathbf{k} = \kappa_D \mathbf{q}$. At low density, there exists therefore a constant C independent of the loop variables such that

$$|\phi_{\text{ch}}(\mathbf{r}, \chi_a, \chi_b)| \leq C q_a q_b \kappa_D \quad (78)$$

The bound (78) does not capture the decay of ϕ_{ch} with distance. Since $\phi \sim 1/r^3$, $\phi_{\text{ch}}(\mathbf{r}, \chi_a, \chi_b) = \phi(\mathbf{r}, \chi_a, \chi_b) - V(\mathbf{r}, \chi_a, \chi_b)$ decreases as (minus) the Coulomb potential itself. In fact, one can show that ϕ_{ch} is majorized at low density by the electrostatic potential (11):

$$|\phi_{\text{ch}}(\mathbf{r}, \chi_a, \chi_b)| \leq C V_{\text{elec}}(\mathbf{r}, \chi_a, \chi_b) \quad (79)$$

where the constant C is independent of the distance \mathbf{r} and the loop arguments χ_a, χ_b . The proof of this statement can be found in appendix B.

5. RESUMMED DIAGRAMMATICS

5.1. Prototype Graphs in Activity

As pointed out after (17), every Mayer graph diverges because of the long range of the bond f . Just as in the classical Coulomb gas, systematic resummations can be performed to obtain so-called prototype graphs where the Coulomb potential is replaced by an integrable effective potential. The precise form of the effective potential depends on the chosen decomposition of the bond f into a long range and a short range part. Several decompositions have already been considered in the literature and the resulting diagrammatic rules were studied in details.^(10, 12) The starting point of the resummation leading to the effective potential ϕ studied in the previous section is the decomposition

$$f(\mathcal{L}_i, \mathcal{L}_j) = -\beta_{ij} V(\mathcal{L}_i, \mathcal{L}_j) + \frac{1}{2} \beta_{ij}^2 V^2(\mathcal{L}_i, \mathcal{L}_j) + f_{\text{T}}(\mathcal{L}_i, \mathcal{L}_j) \quad (80)$$

which defines the truncated bond $f_{\text{T}}(\mathcal{L}_i, \mathcal{L}_j)$. We mention only the main steps of the resummation procedure, skipping all the technical details, since they are almost identical to those occurring in the above mentioned works. The replacement of each Mayer bond by its decomposition (80) provides new graphs built with three kinds of bonds: $-\beta V$, $\frac{1}{2} \beta^2 V^2$ and f_{T} . Points in these diagrams that are either intermediate points in a convolution of two bonds $-\beta V$, or connected only by the single bond $\frac{1}{2} \beta^2 V^2$, are called

Coulomb points. The prototype graphs are then obtained by integrating over all Coulomb points. By a combinatoric formula,⁽¹⁰⁾ the set of Mayer graphs is transformed into a new set of prototype graphs, obeying the following rules. The bonds can be either

$$F_C(\mathcal{L}_a, \mathcal{L}_b) = -\beta_{ab}\phi(\mathcal{L}_a, \mathcal{L}_b) \quad (81)$$

where $\phi(\mathcal{L}_a, \mathcal{L}_b)$ is the effective potential (36), or

$$F_R(\mathcal{L}_a, \mathcal{L}_b) = e^{F_C(\mathcal{L}_a, \mathcal{L}_b)} - 1 - F_C(\mathcal{L}_a, \mathcal{L}_b) \quad (82)$$

The points in the prototype graphs have two kinds of weight $\omega(\mathcal{L})$:

$$\omega(\mathcal{L}) = \begin{cases} z(\mathcal{L}) & \text{(bare loop)} \\ z(\mathcal{L})(e^{I(\mathcal{L})} - 1) & \text{(dressed loop)} \end{cases} \quad (83)$$

In (83), $I(\mathcal{L})$ is the sum of all rings and reduces to

$$I(\mathcal{L}) = -\frac{1}{2} \beta e_\alpha^2 \phi_{\text{ch}}(\mathbf{0}, \chi, \chi) \quad (84)$$

The bound (78) shows that this quantity is finite. The prototype graphs obey the usual topological rules of Mayer graphs, with two additional rules to prevent double counting:

- The convolution of two bonds F_C with an intermediate bare loop is forbidden.

- A bond F_R that would be the only link between a bare loop and the rest of the diagram is forbidden and must be replaced by the bond $F_R^* = F_R - \frac{1}{2} F_C^2$.

The symmetry factor S_G attached to a prototype graph G is defined as usual: it is the number of permutations of the loops that leave the integrand (the product of the bonds and the weights) invariant. The resummed series representing the loop density $\rho(\mathcal{L})$ is eventually written as (compare with (17))

$$\rho(\mathcal{L}) = \sum_G \frac{1}{S_G} \int \prod_{n=1}^N d\mathcal{L}_n \omega(\mathcal{L}_n) \left[\prod_{F_C, F_R, F_R^*} F \right]_G \quad (85)$$

where the sum runs over all unlabelled topologically different prototype graphs G with one root point \mathcal{L} , and ω and F denote the various kinds of weights and bonds. The loop correlations $\rho(\mathcal{L}_1, \dots, \mathcal{L}_n)$ admit Mayer

diagrammatic representations similar to (17), but where the graphs have n root points $\mathcal{L}_1, \dots, \mathcal{L}_n$.

5.2. Prototype Graphs in Density

The principle of topological reduction allows to write the Mayer expansions of the loop correlations $\rho(\mathcal{L}_1, \dots, \mathcal{L}_n)$ in terms of graphs with points carrying the weight $\rho(\mathcal{L})$ rather than $z(\mathcal{L})$. Topologically, the graphs in density differ from the graphs in activity only by the absence of articulation points³ (and the different weight attached to the points). The Coulomb divergencies in the density Mayer graphs can be removed by a slightly modified version of the resummation procedure described above.

We calculate first the effective potential ϕ_ρ resummed in density. As before, ϕ_ρ is defined as the sum of the chain graphs (20), but where the intermediate loops carry the weight $\rho(\mathcal{L})$. Let us denote by $\mathcal{L}^{[u]} = (\alpha, q, \mathbf{R} + \lambda_\alpha \mathbf{X}(u), \mathbf{X}(\cdot + u) - \mathbf{X}(u))$, $u \in \mathbb{R}$, the loop \mathcal{L} with the origin set at $\mathbf{R} + \lambda_\alpha \mathbf{X}(u)$ instead of \mathbf{R} ($\mathcal{L}^{[u]}$ describes indeed the same path $\mathbf{R} + \lambda_\alpha \mathbf{X}(\cdot)$ as \mathcal{L} but with the time parameter shifted by u). The loop density $\rho(\mathcal{L})$ satisfies then

$$\rho(\mathcal{L}^{[u]}) = \rho(\mathcal{L}), \quad \forall u \in \mathbb{R} \quad (86)$$

To prove (86), recall that, by definition,

$$\begin{aligned} \rho(\mathcal{L}_1^{[u]}) &= \frac{1}{\Xi_A} \sum_{n=1}^{\infty} \frac{1}{(n-1)!} \int d\mathcal{L}_2 \cdots d\mathcal{L}_n z(\mathcal{L}_1^{[u]}) z(\mathcal{L}_2) \cdots z(\mathcal{L}_n) \\ &\quad \times \exp[-\beta U(\mathcal{L}_1^{[u]}, \mathcal{L}_2, \dots, \mathcal{L}_n)] \end{aligned} \quad (87)$$

Introducing the change of variables $\mathbf{R}_i \rightarrow \mathbf{R}_i + \lambda_\alpha \mathbf{X}_i(u)$, $i = 2, \dots, N$ and using the invariance (30) on the measures $D(\mathbf{X}_2), \dots, D(\mathbf{X}_n)$, we find

$$\begin{aligned} \rho(\mathcal{L}_1^{[u]}) &= \frac{1}{\Xi_A} \sum_{n=1}^{\infty} \frac{1}{(n-1)!} \int d\mathcal{L}_2 \cdots d\mathcal{L}_n z(\mathcal{L}_1^{[u]}) \cdots z(\mathcal{L}_n^{[u]}) \\ &\quad \times \exp[-\beta U(\mathcal{L}_1^{[u]}, \dots, \mathcal{L}_n^{[u]})] \end{aligned} \quad (88)$$

We obtain (86) by noting that $U(\mathcal{L}_1^{[u]}, \dots, \mathcal{L}_n^{[u]}) = U(\mathcal{L}_1, \dots, \mathcal{L}_n)$ from (8) and (9) and that $z(\mathcal{L}^{[u]}) = z(\mathcal{L})$ from (13) and (14).

³ An articulation point is a point such that when it is suppressed, the graph breaks into two (or more) parts, at least one of them containing no root point.

Using (86), the loop density $\rho(\chi)$ of a homogeneous system is thus invariant under (29), just as $z(\chi)$. This allows one to calculate ϕ_ρ exactly in the same way as the potential ϕ resummed in activity. We find therefore

$$\tilde{\phi}_\rho(\mathbf{k}, \chi_a, \chi_b) = \int_0^{q_a} ds_a \int_0^{q_b} ds_b e^{i\mathbf{k} \cdot [\lambda_a \mathbf{X}_a(s_a) - \lambda_b \mathbf{X}_b(s_b)]} \sum_{n=-\infty}^{\infty} \frac{4\pi}{k^2 + \kappa_\rho^2(k, n)} e^{2i\pi n(s_a - s_b)} \quad (89)$$

with the screening coefficients

$$\kappa_\rho^2(k, n) \equiv 4\pi\beta \sum_\alpha e_\alpha^2 \sum_q q \int_0^q ds \int D(\mathbf{X}) \rho(\chi) e^{i\mathbf{k} \cdot \lambda_\alpha \mathbf{X}(s)} e^{2i\pi ns} \quad (90)$$

Here, we must be aware that $\rho(\mathcal{L})$ is only known through its low-fugacity expansion (85). However, at sufficiently low fugacities, it is expected that $\rho(\mathcal{L})$ is close to $z(\mathcal{L})$, and consequently the properties of $\kappa_\rho^2(k, n)$ should be analogous to that of $\kappa^2(k, n)$. In particular, the positivity property $\kappa_\rho^2(0, 0) > 0$ must hold because the polarization cloud around a specified charge e_α of the system must have the sign opposite to e_α (see ref. 12 or the review of ref. 15).

In the resummation scheme in density, it is not necessary anymore (because of the absence of articulation points) to add and subtract the term $\frac{1}{2}\beta^2 V^2$ in the decomposition (80) and there is only one type of weight, namely $\rho(\mathcal{L})$. As in the activity expansion, the resummation generates two kinds of bonds: the bond issued from the chain summation $-\beta\phi_\rho$, and the bond $\exp[-\beta\phi_\rho] - 1 + \beta\phi_\rho$. The prototype graphs in density obey topological rules identical to those of the Mayer graphs, with a single exception that prevents doublecounting: the convolution of two bonds $-\beta\phi_\rho$ is forbidden.

5.3. Link with the ‘‘Multipole’’ Prototype Graphs

The prototype graphs (in activity or density) obtained by the above resummation schemes are particularly convenient, because they obey diagrammatic rules that are the same as the classical rules first derived by Meeron. In particular, only two resummed bonds are present, as compared to the four bonds (F_{cc} , F_{cm} , F_{mc} and F_R) of the ‘‘multipole’’ diagrammatics.⁽¹²⁾ The link between these two resummations can be made explicit by introducing in every bond of (20) the multipole decomposition of the loop potential:

$$V(\mathcal{L}_1, \mathcal{L}_2) = V_{cc}(\mathcal{L}_1, \mathcal{L}_2) + V_{cm}(\mathcal{L}_1, \mathcal{L}_2) + V_{mc}(\mathcal{L}_1, \mathcal{L}_2) + V_{mm}(\mathcal{L}_1, \mathcal{L}_2) \quad (91)$$

where

$$V_{cc} = q_1 q_2 V(\mathbf{R}_1 - \mathbf{R}_2) \quad (92)$$

$$V_{cm} = q_1 \int_0^{q_2} ds_2 (V(\mathbf{R}_1 - \mathbf{R}_2 - \lambda_{\alpha_2} \mathbf{X}_2(s_2)) - V(\mathbf{R}_1 - \mathbf{R}_2)) \quad (93)$$

$$V_{mc} = q_2 \int_0^{q_1} ds_1 (V(\mathbf{R}_1 + \lambda_{\alpha_1} \mathbf{X}_1(s_1) - \mathbf{R}_2) - V(\mathbf{R}_1 - \mathbf{R}_2)) \quad (94)$$

$$\begin{aligned} V_{mm} = & \int_0^{q_1} ds_1 \int_0^{q_2} ds_2 \tilde{\delta}(s_1 - s_2) V(\mathbf{R}_1 + \lambda_{\alpha_1} \mathbf{X}_1(s_1) - \mathbf{R}_2 - \lambda_{\alpha_2} \mathbf{X}_2(s_2)) \\ & - V_{cc} - V_{cm} - V_{mc} \end{aligned} \quad (95)$$

In the prototype graphs defined in ref. 12, the bond F_{cc} is the sum of the chains of monopole-monopole interactions V_{cc} . The bond $F_{cm}(\mathcal{L}_1, \mathcal{L}_2)$ corresponds to the sum of all chains made of monopole interactions for the intermediate loops and a monopole-multipole interaction $V_{cm}(\bullet, \mathcal{L}_2)$ for the end loop \mathcal{L}_2 . F_{mc} is the same as F_{cm} with the arguments interchanged and the bond F_{mm} results from the sum of the chains of monopole interactions with monopole-multipole interactions at both end points. From these definitions, we see that the bond F_C in our prototype graphs corresponds to an infinite sum of chain graphs of ref. 12 of arbitrary length, made with bonds⁴ F_{cc} , F_{cm} , F_{mc} and F_{mm} .

5.4. On the Integrability of the Prototype Graphs

There are some important comments to be made about the finiteness of the prototype graphs. First of all, we recall that the divergence of the Coulomb potential $V(\mathbf{r})$ at the origin does not lead to singularities in the quantum Mayer graphs. Indeed, point charges with opposite sign do not collapse in quantum mechanics, and no ad-hoc short-ranged regularization is needed. Mathematically, these Coulomb divergencies are smoothed out by the functional integrations over the shapes of the loops. For example, the expression

$$\int D(\mathbf{X}) \exp \left[\beta e^2 \int_0^q ds \frac{1}{|\mathbf{r} + \lambda \mathbf{X}(s)|} \right] < C \quad (96)$$

⁴In ref. 12, the bond F_{mm} does not appear in fact by itself, but is part of the bond $F_R = (F_R - F_{mm}) + F_{mm}$.

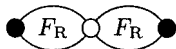
is bounded uniformly in \mathbf{r} . This follows directly from the finiteness of the matrix element $\langle \mathbf{r} | \exp[-\beta q \mathbf{H}] | \mathbf{r} \rangle$ for the hydrogen Hamiltonian $\mathbf{H} = \mathbf{p}^2/2m - e^2/|\mathbf{r}|$. As a corollary, for all \mathbf{r} ,

$$\int \mathbf{D}(\mathbf{X}) \left(\int_0^q ds \frac{1}{|\mathbf{r} + \lambda \mathbf{X}(s)|} \right)^m < C, \quad m = 1, 2, \dots \quad (97)$$

thus any power of the Coulomb potential is integrable (at short distances) in the Mayer graphs. In the prototype graphs, we are lead to calculate functional integrals over powers of V and ϕ_{ch} . The local integrability of ϕ_{ch} will follow from that of V_{elec} by the bound (79). Notice that the functional integrals over V_{elec} do not have simple quantum mechanical matrix elements equivalents. However, they are finite as proved in appendix C.

In the thermodynamic limit, for the infinitely extended system, there are two potentially dangerous unbounded parameters in the loop variables (2), namely the \mathbf{R} -integration extends over the whole space and the q -summation extends over loops with unlimited numbers of particles.⁵ Both can lead to divergences.

The present formalism of prototype graphs is devised to cure the divergences arising from the long range of the Coulomb potential in such a way that prototype graphs are now finite as far as spatial integrations are concerned. In view of (61), $F_C(a, b)$ is at the border of integrability, like in a dipole gas, and $F_R(a, b) \sim |\mathbf{r}_a - \mathbf{r}_b|^{-6}$ is integrable at large distances. Integrations on the variables of a loop connected by a single bond F_C are finite if integration on the shape of the loop is performed first. This is argued in more details in ref. 12. However the convergence of q -summations is not guaranteed in this formalism. Indeed, the charges in a given graph are distributed into loops and interact according to the bonds (product of F_C and F_R) and to the self energy factors $\exp[-\beta U(\mathcal{L})]$. This set of interactions does not contain in general all the necessary mutual interactions between the charges to ensure stability of the system when the number of particles in the loops becomes very large. For example, the graph



presents an excess of Coulomb binding energy when the black and white loops carry charges of opposite sign because of the absence of repulsive interaction between the two black loops. The point is that individual

⁵ The integration on the shape of the loop is not dangerous because the measure $\mathbf{D}(\mathbf{X})$ has a Gaussian small weight for large loops.

prototype graphs, which are made of interacting loops, are not in one to one correspondence with physical processes that involve clusters of charges with all mutual interactions included. A prototype graph must hence be understood as a convenient compact notation for the set of all graphs having the same structure as the prototype graph but in which the points are loops with specified particle species α and number of particles q .

The “compact” notation for prototype graphs is especially useful if one wishes to derive exact relations between physical quantities (such as in the applications presented in Section 6). Obtaining such relations requires dealing with *all* graphs together in a compact way, including the effects of quantum statistics: the present formalism is particularly efficient in this respect. If wished, infinite particle summations occurring in intermediate steps can be made finite by introducing a cut-off $q \leq Q < \infty$ which can be removed when the initial and end points of the calculation represent well defined quantities.

If the formalism is used to derive explicit forms of low density expansions, such as a virial expansion for ionized or recombined phases, the resummed diagrammatic series must be understood to consist of prototype graphs with loops having a fixed number of particles. Then, at a given order in density, only a finite number of such graphs need to be retained. This is the point of view adopted in refs. 12 and 14 to establish the low density equation of state. To go beyond the plasma phase and to derive equation of states for atomic and molecular gases, it will be convenient to introduce another resummation scheme (the screened virial expansion) where charges are not basically reorganized into loops but into clusters of finitely many nuclei and electrons that have the full set of pair interactions between them. This is the subject of a companion paper in preparation.⁽²²⁾

6. APPLICATIONS

6.1. Sum Rules in Quantum Plasmas

The equilibrium correlations of a plasma obey sum rules that express the screening of the system’s internal charges, as well as that of any external classical charge distribution.⁽²³⁾ In this last section, we retrieve such sum rules for the quantum multicomponent plasma using the prototype graphs defined in Section 5. The resummation in terms of a single effective potential proves to be particularly efficient for this purpose. It allows us to prove the quantum sum rules via a simple extension of the method used in the classical case. This diagrammatical method was apparently first devised

by F. Cornu.^(12,14) In order to connect the screening properties of loops to those of particles, it is necessary to establish the relations between the *particle* correlations $\rho(\alpha_1, \mathbf{r}_1, \dots, \alpha_n, \mathbf{r}_n)$ and the *loop* correlations $\rho(\mathcal{L}_1, \dots, \mathcal{L}_n)$. The relations for the one and the two-point functions are found in ref. 12. In Appendix D, we introduce an efficient way to derive the connexion between loop and particle correlations of higher order that is based on the invariance (30) of the measure $D(\mathbf{X})$.

The simplest sum rule is the local neutrality equation

$$\sum_{\alpha} e_{\alpha} \rho_{\alpha}(\mathbf{r}) = 0 \quad (99)$$

We will also derive the charge sum rules

$$\int d\mathbf{r} \sum_{\alpha} e_{\alpha} \rho_{T, \text{c.p.}}(\alpha, \mathbf{r} | \alpha_1, \mathbf{r}_1, \dots, \alpha_n, \mathbf{r}_n) = 0 \quad (100)$$

for $n = 1$ and 2 . The notation $\rho_{T, \text{c.p.}}$ means that the correlation function is truncated with respect to the n particles located at $\mathbf{r}_1, \dots, \mathbf{r}_n$, and that the contribution of coincident particles is included, namely

$$\begin{aligned} \rho_{T, \text{c.p.}}(\alpha, \mathbf{r} | \alpha_1, \mathbf{r}_1, \dots, \alpha_n, \mathbf{r}_n) &= \rho(\alpha, \mathbf{r}, \alpha_1, \mathbf{r}_1, \dots, \alpha_n, \mathbf{r}_n) \\ &\quad - \rho(\alpha, \mathbf{r}) \rho(\alpha_1, \mathbf{r}_1, \dots, \alpha_n, \mathbf{r}_n) \\ &\quad + \sum_{j=1}^n \delta_{\alpha, \alpha_j} \delta(\mathbf{r} - \mathbf{r}_j) \rho(\alpha_1, \mathbf{r}_1, \dots, \alpha_n, \mathbf{r}_n) \end{aligned} \quad (101)$$

The function $\rho_{T, \text{c.p.}}$ is, after division by $\rho(\alpha_1, \mathbf{r}_1, \dots, \alpha_n, \mathbf{r}_n)$, the excess particle density of species α at \mathbf{r} when there are particles of species $\alpha_1, \dots, \alpha_n$ located at $\mathbf{r}_1 \neq \dots \neq \mathbf{r}_n$. The full set of charge sum rules (100) for arbitrary n is expected to hold in the one and multi-component quantum plasmas: they directly follow from the structure of the equation of motion for imaginary time Green's functions (Section III and V of ref. 21). Another derivation has been proposed in ref. 24 based on the Bogoliubov hierarchy equations for reduced density matrices. The latter derivation is based on a priori assumptions on the clustering rate of these reduced density matrices that also involve their off-diagonal parts. We will see that the charge sum rules (100) are direct consequences of sum rules obeyed by the *loop* correlations that can easily be derived (at least formally) from their diagrammatic series.

At low densities, the classical plasma obeys multipolar sum rules stating that the multipoles generated by any configuration of internal charges

are exactly compensated on average by those of the corresponding screening cloud. The simplest relation is the classical dipolar sum rule

$$\int d\mathbf{r} \sum_{\alpha} e_{\alpha} \mathbf{r} \rho_{T, \text{c.p.}}^{\text{classical}}(\alpha, \mathbf{r} | \alpha_1, \mathbf{r}_1, \alpha_2, \mathbf{r}_2) = \mathbf{0} \quad (102)$$

If the charges are quantum mechanical, this relation still holds for the homogeneous one component plasma, a consequence of the special fact that in this system the total current operator is proportional to the total momentum operator, which is a constant of the motion (Section III of ref. 21). For a multicomponent quantum plasma, we will argue, on the basis of the resummed diagrammatic series, that the dipolar sum rule (102) for different species cannot hold because of the quantum fluctuations of individual charges. The fate of higher order multipolar sum rules is similar for both the one and multi-component quantum plasmas: they are no longer valid as it can be seen from the Wigner–Kirkwood semi-classical expansion.⁽²¹⁾

6.1.1. Local Neutrality

It is shown in Appendix D that $\rho(\alpha, \mathbf{r})$ is given by (D.4). The average charge density hence becomes

$$\sum_{\alpha} e_{\alpha} \rho(\alpha, \mathbf{r}) = \int d\chi e_{\alpha} q \rho(\mathcal{L}) \quad (103)$$

We derive the neutrality relation (99) by using the resummed diagrammatic series in activity of $\rho(\mathcal{L})$. Let us call \mathcal{L} a Coulomb root point in a prototype graph of this series if \mathcal{L} is a bare loop (see (83)) and is linked to the rest of the diagram by exactly one bond F_C , and split the density of loops accordingly:

$$\rho(\mathcal{L}) = \rho^{\text{c}}(\mathcal{L}) + \rho^{\text{nc}}(\mathcal{L}) \quad (104)$$

where $\rho^{\text{c}}(\mathcal{L})$ ($\rho^{\text{nc}}(\mathcal{L})$) is the sum of the \mathbb{G} -diagrams where \mathcal{L} is (is not) a Coulomb point. Because convolutions of Coulomb points are forbidden in prototype graphs, this definition implies immediately the integral equation

$$\rho^{\text{c}}(\mathcal{L}) = \int d\mathcal{L}_1 z(\mathcal{L}) F_C(\mathcal{L}, \mathcal{L}_1) \rho^{\text{nc}}(\mathcal{L}_1) \quad (105)$$

and thus

$$\rho(\mathcal{L}) = \int d\mathcal{L}_1 H(\mathcal{L} | \mathcal{L}_1) \rho^{\text{nc}}(\mathcal{L}_1) \quad (106)$$

with

$$H(\mathcal{L} | \mathcal{L}_1) \equiv \delta(\mathcal{L}, \mathcal{L}_1) + z(\mathcal{L}) F_C(\mathcal{L}, \mathcal{L}_1) \quad (107)$$

The formula (106) can be represented graphically by

$$\rho(\mathcal{L}) = \bigcirc \leftarrow \text{wavy bond} \bullet^{\rho^{\text{nc}}(\mathcal{L}_1)} \quad (108)$$

where the bond represents the function $H(\mathcal{L} | \mathcal{L}_1)$. The proofs of the sum rules will all rely on such “dressing” of the root points with the bond H .

For a homogeneous system, $H(\mathcal{L} | \mathcal{L}_1) = H(\mathbf{R} - \mathbf{R}_1; \chi | \chi_1)$ and $\rho^{\text{nc}}(\mathcal{L}_1) = \rho^{\text{nc}}(\chi_1)$. The average charge density therefore reads, from (103) and (106),

$$\sum_{\alpha} e_{\alpha} \rho_{\alpha} = \lim_{k \rightarrow 0} \int d\chi \int d\chi_1 e_{\alpha} q H(\mathbf{k}; \chi | \chi_1) \rho^{\text{nc}}(\chi_1) \quad (109)$$

The Fourier transform of the bond H , and its small k behaviour, can be evaluated from the analysis of ϕ of Section 3. We find that it satisfies

$$\int d\chi e_{\alpha} q H(\mathbf{k}; \chi | \chi') = e_{\alpha'} \left[\sum_n \frac{k^2}{k^2 + \kappa^2(k, n)} \int_0^{q'} ds' e^{-i\mathbf{k} \cdot \lambda_{\alpha'} \mathbf{X}'(s')} e^{i2\pi ns'} - \sum_{k=2}^{q'} (e^{-i\mathbf{k} \cdot \lambda_{\alpha'} \mathbf{X}'(k-1)} - 1) \right] = \mathcal{O}(k) \quad (110)$$

The integral in (109) therefore vanishes in the limit $k \rightarrow 0$ and the local neutrality is proved.

To obtain (110), we write the Fourier transform of the bond H using the explicit form (36) of $\tilde{\phi}(\mathbf{k}, \chi, \chi')$:

$$\begin{aligned} \tilde{H}(\mathbf{k}; \chi | \chi') &= \delta(\chi, \chi') + z(\chi)(-\beta) e_{\alpha} e_{\alpha'} \int_0^q ds \int_0^{q'} ds' e^{i\mathbf{k} \cdot [\lambda_{\alpha} \mathbf{X}(s) - \lambda_{\alpha'} \mathbf{X}'(s')]} \\ &\times \sum_n \frac{4\pi}{k^2 + \kappa^2(k, n)} e^{i2\pi n(s-s')} \end{aligned} \quad (111)$$

From the definition (33) of $\kappa^2(k, n)$, one has

$$\int d\chi e_{\alpha} q \tilde{H}(\mathbf{k}; \chi | \chi') = e_{\alpha'} \left\{ q' - \sum_n \left(\frac{\kappa^2(k, n)}{k^2 + \kappa^2(k, n)} \right) \int_0^{q'} ds' e^{-i\mathbf{k} \cdot \lambda_{\alpha'} \mathbf{X}'(s')} e^{-i2\pi ns'} \right\} \quad (112)$$

Adding and subtracting 1 in the parenthesis, the rhs of (112) becomes

$$e_{\alpha'} \left\{ q' + \sum_n \frac{k^2}{k^2 + \kappa^2(k, n)} \int_0^{q'} ds' e^{-ik \cdot \lambda_{\alpha'} X'(s')} e^{i2\pi ns'} - \sum_{k=1}^{q'} e^{-ik \cdot \lambda_{\alpha'} X'(k-1)} \right\} \quad (113)$$

which is equivalent to (110). The small k behaviour $\mathcal{O}(k)$ follows from (53).

6.1.2. Charge Sum Rule

We prove in this section the charge sum rules (100) for $n = 1$ and 2. (The case $n = 1$ has already been derived in the ‘‘multipole’’ resummation scheme by F. Cornu⁽¹²⁾).

The relations between the particle correlations and the loop correlations are given in Appendix D. From (D.10), the charge sum rule (100) for $n = 1$ becomes

$$\int d\mathcal{L} e_{\alpha} q \sum_{q_1} q_1 \int D(\mathbf{X}_1) \rho_{T, c.p.}(\mathcal{L} | \mathcal{L}_1) = 0 \quad (114)$$

and for $n = 2$, from (D.11) and (30),

$$\int d\mathcal{L} e_{\alpha} q \left[\sum_{q_1, q_2} q_1 q_2 \int D(\mathbf{X}_1) \int D(\mathbf{X}_2) \rho_{T, c.p.}(\mathcal{L} | \mathcal{L}_1, \mathcal{L}_2) + \delta_{\alpha_1, \alpha_2} \sum_{q_1} \int D(\mathbf{X}_1) \sum_{k=2}^{q_1} \delta(\mathbf{r}_1^{(k)} - \mathbf{r}_2) \rho_{T, c.p.}(\mathcal{L} | \mathcal{L}_1) \right] = 0 \quad (115)$$

In these formulae, the excess loop densities $\rho_{T, c.p.}(\mathcal{L} | \mathcal{L}_1, \dots, \mathcal{L}_n)$ are defined in the same way as (101).

For convenience, we use from now on the prototype graphs in density rather than in activity. We omit however to write the index ρ in the effective potential (89) for the sake of notational simplicity. Thus $F_C(\mathcal{L}_a, \mathcal{L}_b) = -\beta_{ab} \phi(\mathcal{L}_a, \mathcal{L}_b)$ involves the effective potential (89) and the definition of the bond H is modified according to

$$H(\mathcal{L} | \mathcal{L}') \equiv \delta(\mathcal{L}, \mathcal{L}') + \rho(\mathcal{L}) F_C(\mathcal{L}, \mathcal{L}') \quad (116)$$

With these new definitions, it is remarkable that the property (110) still holds without any change. This is due to the similarity between the formulae (89) and (36) for the effective potentials, and the formulae (90) and (33) for the screening coefficients. Since the truncation in the loop correlations $\rho_{T, c.p.}(\mathcal{L} | \mathcal{L}_1, \dots, \mathcal{L}_n)$ is made only with respect to the group of loops

$\mathcal{L}_1, \dots, \mathcal{L}_n$, the diagrammatic expansions of these functions involve graphs in which the root loop \mathcal{L} is connected to at least one of the loops $\mathcal{L}_1, \dots, \mathcal{L}_n$ (apart from this, these n loops may be disconnected). Just as the local neutrality, the charge sum rules can be proved by “dressing” with the bond H the root point \mathcal{L} . We define therefore the function $\rho^\circ(\mathcal{L} | \mathcal{L}_1, \dots, \mathcal{L}_n)$ ($\rho^{\text{nc}}(\mathcal{L} | \mathcal{L}_1, \dots, \mathcal{L}_n)$) as the sum of the graphs where \mathcal{L} is (is not) coulombic. As before, \mathcal{L} is a Coulomb root point if it is linked by exactly one bond F_C to the rest of the diagram. The proof of the sum rules proceeds now by following the derivation of the equivalent classical sum rules.

Case $n=1$. Using the above definitions, we split $\rho_{\text{T, c.p.}}(\mathcal{L} | \mathcal{L}_1)$ according to

$$\rho_{\text{T, c.p.}}(\mathcal{L} | \mathcal{L}_1) = \rho_{\text{T}}^\circ(\mathcal{L} | \mathcal{L}_1) + \rho_{\text{T}}^{\text{nc}}(\mathcal{L} | \mathcal{L}_1) + \delta(\mathcal{L}, \mathcal{L}_1) \rho(\mathcal{L}_1) \quad (117)$$

Since $\rho_{\text{T}}^\circ(\mathcal{L} | \mathcal{L}_1)$ satisfies the integral equation

$$\rho_{\text{T}}^\circ(\mathcal{L} | \mathcal{L}_1) = \rho(\mathcal{L}) F_C(\mathcal{L}, \mathcal{L}_1) \rho(\mathcal{L}_1) + \rho(\mathcal{L}) \int d\mathcal{L}' F_C(\mathcal{L}, \mathcal{L}') \rho_{\text{T}}^{\text{nc}}(\mathcal{L}' | \mathcal{L}_1) \quad (118)$$

we have the dressing relation

$$\rho_{\text{T, c.p.}}(\mathcal{L} | \mathcal{L}_1) = \rho(\mathcal{L}_1) H(\mathcal{L} | \mathcal{L}_1) + \int d\mathcal{L}' H(\mathcal{L} | \mathcal{L}') \rho_{\text{T}}^{\text{nc}}(\mathcal{L}' | \mathcal{L}_1) \quad (119)$$

Graphically, (119) can be represented by

$$\rho_{\text{T, c.p.}}(\mathcal{L} | \mathcal{L}_1) = \begin{array}{c} \mathcal{L} \\ \circ \leftarrow \text{wavy} \circ \end{array} \rho(\mathcal{L}_1) + \begin{array}{c} \mathcal{L} \\ \circ \leftarrow \text{wavy} \bullet \end{array} \begin{array}{c} \mathcal{L}' \\ \circ \end{array} \begin{array}{c} \mathcal{L}_1 \\ \circ \end{array} \rho_{\text{T}}^{\text{nc}} \quad (120)$$

In the above diagram, all points have weight unity, unless stated otherwise (like $\rho(\mathcal{L}_1)$). The “narrow part” of the asymmetric bond $\rho_{\text{T}}^{\text{nc}}$ is associated to the non coulombic loop. In Fourier representation, the convolution on the intermediate loop \mathcal{L}' in (119) becomes a product:

$$\tilde{\rho}_{\text{T, c.p.}}(\mathbf{k}; \chi | \chi_1) = \rho(\chi_1) \tilde{H}(\mathbf{k}; \chi | \chi_1) + \int d\chi' \tilde{H}(\mathbf{k}; \chi | \chi') \tilde{\rho}_{\text{T}}^{\text{nc}}(\mathbf{k}, \chi' | \chi_1) \quad (121)$$

To obtain the sum rule (114), we perform the integral $\int d\chi e_{\alpha q} \sum_{q_1} q_1 \int D(\mathbf{X}_1)$ over this expression and take the limit $k \rightarrow 0$. This limit is zero by the property (110) and hence the sum rule is proved.

Notice that we can infer from (121) a relation stronger than (114), namely that

$$\lim_{k \rightarrow 0} \int d\chi e_{\alpha} q \tilde{\rho}_{T, \text{c.p.}}(\mathbf{k}, \chi | \chi_1) = 0 \tag{122}$$

or, singling out the contribution of coincident points,

$$\int d\mathbf{r} \int d\chi \frac{\rho_T(\mathbf{r}, \chi | \chi_1)}{\rho(\chi_1)} = -e_{\alpha} q_1, \quad \forall \chi_1 \tag{123}$$

This is a charge sum rule for the system of loops. It states that *the cloud of loops induced around a fixed loop \mathcal{L}_1 of the system carries a total charge exactly opposite to that of the loop \mathcal{L}_1* . The quantum charge sum rule (100) for $n = 1$ is hence a direct consequence of the sum rule (123) obeyed by the system of loops.

Case $n=2$. The second term of (115) is zero by the sum rule (123), so we only have to consider

$$\int d\mathcal{L} e_{\alpha} q \sum_{q_1, q_2} q_1 q_2 \int D(\mathbf{X}_1) \int D(\mathbf{X}_2) \rho_{T, \text{c.p.}}(\mathcal{L} | \mathcal{L}_1, \mathcal{L}_2) \tag{124}$$

The truncated correlation $\rho_{T, \text{c.p.}}(\mathcal{L} | \mathcal{L}_1, \mathcal{L}_2)$ satisfies the integral equation

$$\begin{aligned} \rho_{T, \text{c.p.}}(\mathcal{L} | \mathcal{L}_1, \mathcal{L}_2) = & \int d\mathcal{L}' H(\mathcal{L} | \mathcal{L}') \rho_T^{\text{nc}}(\mathcal{L}' | \mathcal{L}_1, \mathcal{L}_2) \\ & + H(\mathcal{L} | \mathcal{L}_1) \rho(\mathcal{L}_1, \mathcal{L}_2) + H(\mathcal{L} | \mathcal{L}_2) \rho(\mathcal{L}_1, \mathcal{L}_2) \end{aligned} \tag{125}$$

where the last two terms take into account the contribution of the coincident points and the situations where \mathcal{L} is connected with a single bond F_C directly to the loops \mathcal{L}_1 and \mathcal{L}_2 . Graphically, this dressing relation is

$$\rho_{T, \text{c.p.}}(\mathcal{L} | \mathcal{L}_1, \mathcal{L}_2) = \text{Diagram 1} + \text{Diagram 2} + \text{Diagram 3} \tag{126}$$

Taking the Fourier transform of $\rho_{T, \text{c.p.}}(\mathbf{r}, \chi | \mathcal{L}_1, \mathcal{L}_2)$ with respect to \mathbf{r} , we find

$$\begin{aligned} \tilde{\rho}_{T, \text{c.p.}}(\mathbf{k}, \chi | \mathcal{L}_1, \mathcal{L}_2) &= \int d\chi' \tilde{H}(\mathbf{k}; \chi | \chi') \tilde{\rho}_T^{\text{nc}}(\mathbf{k}, \chi' | \mathcal{L}_1, \mathcal{L}_2) \\ &\quad + e^{-i\mathbf{k} \cdot \mathbf{r}_1} \tilde{H}(\mathbf{k}; \chi | \chi_1) \rho(\mathcal{L}_1, \mathcal{L}_2) \\ &\quad + e^{-i\mathbf{k} \cdot \mathbf{r}_2} \tilde{H}(\mathbf{k}; \chi | \chi_2) \rho(\mathcal{L}_1, \mathcal{L}_2) \end{aligned} \quad (127)$$

Performing $\int d\chi e_\alpha q$ over this expression, we see from (110) that this integral vanishes in the limit $k \rightarrow 0$, so that the sum rule (100) for $n = 2$ is established. The charge sum rules for $n \geq 3$ can in principle be proved by the same method, but the formulae become rapidly very lengthy.

6.1.3. Dipolar Sum Rule

In this section, we argue that the dipolar sum rule does not hold in general in quantum plasmas, because of the quantum fluctuations of the charges. The breakdown of this sum rule can already be suspected from the screening formula (110). The expression (110) has indeed a non vanishing term of order \mathbf{k} and this term is related to the dipole moment of the screening cloud induced around a fixed loop χ .

We consider a weakly degenerate multicomponent plasma and work in the Maxwell–Boltzmann approximation. All exchange contributions are neglected, and hence only loops with $q = 1$ remain (all q -sums are restricted from now on to the terms $q = 1$). Using the formula (D11) for $\rho_{T, \text{c.p.}}(\alpha_1, \mathbf{r}_1 | \alpha_2, \mathbf{r}_2, \alpha_3, \mathbf{r}_3)$, the total dipole moment reads

$$\int d\mathcal{L}_1 e_{\alpha_1} \mathbf{r}_1 \int D(\mathbf{X}_2) \int D(\mathbf{X}_3) \rho_{T, \text{c.p.}}(\mathbf{r}_1, \chi_1 | \mathcal{L}_2, \mathcal{L}_3) \quad (128)$$

This dipole moment is most easily calculated from the term linear in \mathbf{k} in the Fourier transform

$$\int d\chi_1 e_{\alpha_1} \int D(\mathbf{X}_2) \int D(\mathbf{X}_3) \tilde{\rho}_{T, \text{c.p.}}(\mathbf{k}, \chi_1 | \mathcal{L}_2, \mathcal{L}_3) \quad (129)$$

and we recall that the truncated loop correlation obey the dressing relation (127). At low density ($\Gamma = \beta e^2 / a \ll 1$, a : mean interparticle distance), the first term of (127) can be neglected because it is smaller than the others by a factor $\Gamma^{3/2}$. After calculating $\int d\chi_1 \tilde{H}(\mathbf{k}, \chi_1 | \chi_i)$, $i = 2, 3$ with the help of (110), (129) becomes

$$\int \mathbf{D}(\mathbf{X}_2) \int \mathbf{D}(\mathbf{X}_3) \sum_n \frac{k^2}{k^2 + \kappa^2(k, n)} \times \int_0^1 ds [e_{\alpha_2} e^{-ik \cdot \lambda_2 \mathbf{X}_2(s)} + e_{\alpha_3} e^{-ik \cdot \lambda_3 \mathbf{X}_3(s)}] e^{i2\pi ns} \rho(\mathcal{L}_2, \mathcal{L}_3) \quad (130)$$

In the limit $k \rightarrow 0$, this expression vanishes and we recover the charge sum rule (100) for two fixed particles. Extracting the terms linear in \mathbf{k} , the dipole moment is found to be, at low density,

$$\int \mathbf{D}(\mathbf{X}_2) \int \mathbf{D}(\mathbf{X}_3) \int_0^1 ds h(s) [\lambda_{\alpha_2} e_{\alpha_2} \mathbf{X}_2(s) + \lambda_{\alpha_3} e_{\alpha_3} \mathbf{X}_3(s)] \rho(\mathcal{L}_2, \mathcal{L}_3) \quad (131)$$

where $h(s) \simeq \delta(s) - 1$ was defined in (61). Using $\rho(\mathcal{L}_2, \mathcal{L}_3) = \rho(\mathcal{L}_3, \mathcal{L}_2)$, the invariance of this correlation function under space inversion [$\rho(\mathbf{r}; \alpha_2, \mathbf{X}_2; \alpha_3, \mathbf{X}_3) = \rho(-\mathbf{r}; \alpha_2, -\mathbf{X}_2; \alpha_3, -\mathbf{X}_3)$] and the rotational invariance of the measure $\mathbf{D}(\mathbf{X})$, (131) can be rewritten as

$$\int \mathbf{D}(\mathbf{X}_2) \int \mathbf{D}(\mathbf{X}_3) \int_0^1 ds h(s) \mathbf{X}_2(s) \times [e_{\alpha_2} \lambda_{\alpha_2} \rho(\mathbf{r}_2 - \mathbf{r}_3; \alpha_2, \mathbf{X}_2; \alpha_3, \mathbf{X}_3) + e_{\alpha_3} \lambda_{\alpha_3} \rho(\mathbf{r}_2 - \mathbf{r}_3; \alpha_3, -\mathbf{X}_2; \alpha_2, \mathbf{X}_3)] \quad (132)$$

If $\alpha_2 = \alpha_3$, the expression in brackets is even in \mathbf{X}_2 and thus $\int \mathbf{D}(\mathbf{X}_2)$ vanishes by parity. In the general case $\alpha_2 \neq \alpha_3$, this symmetry no longer holds and the dipolar sum rule is expected to break down.

6.2. A Simple Approximation for the Particle Correlations

At low densities, the diagrammatic series provide simple approximations for the particle correlations by retaining only the first graphs. A possible one, that preserves the charge sum rules, is, for the loop correlations,

$$\rho_T(\mathcal{L}_1 | \mathcal{L}_2) = \text{Diagram 1} + \text{Diagram 2} \quad (133)$$

From (D.8), the corresponding particle correlations $\rho_T(\alpha_1, \mathbf{r}_1 | \alpha_2, \mathbf{r}_2)$ are obtained by inserting (133) into

$$\rho_T(\alpha_1, \mathbf{r}_1 | \alpha_2, \mathbf{r}_2) = \sum_{q_1, q_2} q_1 q_2 \int \mathbf{D}(\mathbf{X}_1) \int \mathbf{D}(\mathbf{X}_2) \rho_T(\mathcal{L}_1 | \mathcal{L}_2) + \delta_{\alpha_1, \alpha_2} \sum_{q_2} q_2 \sum_{k=2}^{q_2} \int \mathbf{D}(\mathbf{X}_2) \delta(\mathbf{r}_2^{(k)} - \mathbf{r}_1) \rho(\mathcal{L}_2) \quad (134)$$

In (133), we notice that the first term is nothing but the loop correlations in the mean-field (Debye-like) approximation. By virtue of (110), we see that the charge sum rule is already satisfied within this approximation. The next term in (133) also obeys to this sum rule because the bond F_R is dressed with H : the charge sum rule is there enforced as a consequence of (110) that accounts for the basic screening mechanisms in the system of loops.

The degeneracy effects are expected to be weak at low densities. Thus, it is legitimate to keep only the contributions of loops with $q=1$ in the above approximation. It is clear that the second term of (134), which is due to exchange effects, no longer contributes to $\rho_T^{\text{MB}}(\alpha_1, \mathbf{r}_1 | \alpha_2, \mathbf{r}_2)$. Inserting the decomposition (116) into (133), we find

$$\rho_T^{\text{MB}}(\alpha_1, \mathbf{r}_1 | \alpha_2, \mathbf{r}_2) = \int D(\mathbf{X}_1) \int D(\mathbf{X}_2) \left\{ \begin{array}{l} \text{(a)} \\ \text{(b)} \\ \text{(c)} \\ \text{(d)} \end{array} \right\} \quad (135)$$

In (135), all densities $\rho(\mathcal{L}_i)$ have been replaced by $z(\mathcal{L}_i) = (2\sigma_\alpha + 1) z_\alpha / (2\pi\lambda_\alpha^2)^{3/2}$. The bond in the graph (a) is the Mayer bond $\exp(-\beta\phi^{\text{MB}}) - 1$, where the Maxwell-Boltzmann version ϕ^{MB} of ϕ is given by (89) with $\kappa_\rho^2(k, n)$ taking the value

$$4\pi\beta \sum_\alpha e_\alpha^2 \frac{(2\sigma_\alpha + 1) z_\alpha}{(2\pi\lambda_\alpha^2)^{3/2}} \int_0^1 ds e^{-\frac{1}{2}k^2\lambda_\alpha^2 s(1-s)} e^{i2\pi ns} \quad (136)$$

The bonds F_C and F_R in the graphs (b), (c) and (d) are of course also evaluated with the effective potential ϕ^{MB} . We stress that (135) still satisfies the charge sum rule, since both the dressed structure of (133) and the property (110) are conserved within the Maxwell-Boltzmann description.

The properties of ϕ^{MB} , identical to those of ϕ , enforce the approximation (135) to reproduce the exact behaviours at short and large distances. When $|\mathbf{r}_1 - \mathbf{r}_2| \rightarrow 0$, ϕ^{MB} behaves as V , and the first term in (135) is, at lowest order,

$$\frac{(2\sigma_{\alpha_1} + 1) z_{\alpha_1}}{(2\pi\lambda_{\alpha_1}^2)^{3/2}} \frac{(2\sigma_{\alpha_2} + 1) z_{\alpha_2}}{(2\pi\lambda_{\alpha_2}^2)^{3/2}} \langle \mathbf{r}_1, \mathbf{r}_2 | e^{-\beta H_{\alpha_1, \alpha_2}} - e^{-\beta H_{\alpha_1}} e^{-\beta H_{\alpha_2}} | \mathbf{r}_1, \mathbf{r}_2 \rangle \quad (137)$$

where $H_\alpha = \mathbf{p}^2/2m_\alpha$ is the Hamiltonian of a free particle and H_{α_1, α_2} is the Hamiltonian of two quantum particles interacting via the Coulomb potential. The next terms in (135) provide small contributions compared to (137), which is indeed the expected form of the pair correlations at low densities. It is obvious that (137) incorporates non-perturbative effects with respect to interactions and quantum mechanics. In particular, if $\alpha_1 = e$ and $\alpha_2 = p$, (137) involves contributions of the hydrogen atom that results from the quantum mechanical binding of one electron and one proton.

At intermediate distances $r \sim \kappa_D^{-1}$, $\phi^{\text{MB}}(\mathbf{r}, \chi_1, \chi_2) \sim \exp[-\kappa_D r]/r$, and (135) becomes

$$\rho_T(\alpha_1, \mathbf{r}_1 | \alpha_2, \mathbf{r}_2) \simeq -\beta e_{\alpha_1} e_{\alpha_2} \frac{e^{-\beta|\mathbf{r}_1 - \mathbf{r}_2|}}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad |\mathbf{r}_1 - \mathbf{r}_2| \sim \kappa_D^{-1} \quad (138)$$

that entirely arises from the graph (a) of (135) with linearized bond $-\beta_{12}\phi^{\text{MB}}(\mathcal{L}_1, \mathcal{L}_2)$. We recover the familiar classical Debye–Hückel formula which is indeed valid for distances $r \sim \kappa_D^{-1}$ since the size λ_α of quantum fluctuations of the particles is much smaller than κ_D^{-1} .

At very large distances, $|\mathbf{r}_1 - \mathbf{r}_2| \rightarrow \infty$, ϕ^{MB} behaves as a dipolar potential

$$-\int_0^1 d\tau_a \int_0^1 d\tau_b (\delta(\tau_a - \tau_b) - 1) (\lambda_a \mathbf{X}_a(\tau_a) \cdot \nabla) (\lambda_b \mathbf{X}_b(\tau_b) \cdot \nabla) \frac{1}{|\mathbf{r}|} \quad (139)$$

The linear contribution of ϕ^{MB} to (135) vanishes after the functional integrations for parity reasons. The square of (139) provides in all the terms (a)–(d) of (135) $1/r^6$ contributions, the sum of which does coincide with the low-density algebraic $1/r^6$ -tail of the correlations.⁽¹²⁾

Notice that the simplest mean-field approximation, described by the first term in (133), neither captures the local structure nor the large-distance behaviour. Indeed, non perturbative effects (such as binding) are crucial at short-distances. Moreover, because of rotational symmetry, the contributions of this first term, linear in ϕ , are short-ranged while the $1/r^6$ -tails arise from the fluctuations of ϕ , that is ϕ^2 . According to the above considerations, (135) should be a quite accurate approximation at low densities. Numerical calculations, and comparisons to quantum Monte Carlo results, are postponed to a next paper.

APPENDIX A. PROOF OF THE INEQUALITY (47)

The function $u_q(k, n)$ defined in (45) can be expressed as $(\lambda_\alpha^2/2\pi)^{3/2}$ times the integral

$$v_q(k, n) = q^{3/2} \int d\mathbf{p} e^{-\beta q E_p} \int_0^1 dS e^{-\beta q S (E_{\mathbf{p}+\mathbf{k}} - E_p)} e^{i2\pi n q S} \quad (A.1)$$

where $E_p = \hbar^2 \mathbf{p}^2 / 2m_\alpha$. The “time” integration over s can be carried out explicitly. The result is, using the fact that q and $n \neq 0$ are integers and keeping only the real value since $u_q(k, n) \geq 0$ (see (45)),

$$v_q(k, n) = q^{3/2} \int d\mathbf{p} (e^{-\beta q E_p} - e^{-\beta q E_{p+k}}) \frac{\beta q (E_{p+k} - E_p)}{(2\pi n q)^2 + \beta^2 q^2 (E_{p+k} - E_p)^2} \quad (\text{A.2})$$

Introducing the change of variable $\mathbf{p} \rightarrow \mathbf{p} - \mathbf{k}/2$, the integrand becomes

$$v_q(k, n) = 4 \sqrt{q} \int d\mathbf{p} \frac{e^{-\beta q (E_p + E_{k/2})} \sinh(q \frac{\beta \hbar^2}{2m_\alpha} |\mathbf{p} \cdot \mathbf{k}|)}{(2\pi n)^2 + \beta^2 (E_{p+\frac{k}{2}} - E_{p-\frac{k}{2}})^2} \frac{\beta \hbar^2}{2m_\alpha} |\mathbf{p} \cdot \mathbf{k}| \quad (\text{A.3})$$

where the absolute values were freely introduced since $x \sinh(x)$ is an even function of x . Notice that the integrand in (A3) is non-negative function. To compare $v_q(k, n)$ with $v_1(k, n)$, we rewrite (A3) as

$$v_q(k, n) = 4 \sqrt{q} \int d\mathbf{p} \frac{e^{-\beta (E_p + E_{k/2})} \sinh(\frac{\beta \hbar^2}{2m_\alpha} |\mathbf{p} \cdot \mathbf{k}|)}{(2\pi n)^2 + \beta^2 (E_{p+\frac{k}{2}} - E_{p-\frac{k}{2}})^2} \frac{\beta \hbar^2}{2m_\alpha} |\mathbf{p} \cdot \mathbf{k}| \\ \times \left[e^{-(q-1) \frac{\beta \hbar^2}{2m_\alpha} (p^2 + \frac{k^2}{4})} \frac{\sinh(q \frac{\beta \hbar^2}{2m_\alpha} |\mathbf{p} \cdot \mathbf{k}|)}{\sinh(\frac{\beta \hbar^2}{2m_\alpha} |\mathbf{p} \cdot \mathbf{k}|)} \right] \quad (\text{A.4})$$

Using $\mathbf{p}^2 + \mathbf{k}^2/4 \geq |\mathbf{p} \cdot \mathbf{k}|$, the expression in brackets is majorized by

$$r_q(x) \equiv e^{-(q-1)x} \frac{\sinh(qx)}{\sinh(x)}, \quad x = \frac{\beta \hbar^2}{2m_\alpha} |\mathbf{p} \cdot \mathbf{k}| \geq 0 \quad (\text{A.5})$$

An analysis of the function $r_q(x)$ shows that there exists a constant $C > 0$ such that $r_q(x) \leq Cq$ uniformly in $x \geq 0$ and $q \geq 1$. Inserting this majoration in (A.4) gives

$$v_q(k, n) \leq Cq^{3/2} v_q(k, n) \quad (\text{A.6})$$

which is equivalent to the assertion (47).

APPENDIX B. PROOF OF THE BOUND (79)

The inverse Fourier transform of (35) is

$$\tilde{\phi}_{\text{ch}}(\mathbf{r}, \chi_a, \chi_b) = \int_0^{q_a} ds_a \int_0^{q_b} ds_b G(\mathbf{r} + \lambda_a \mathbf{X}_a(s_a) - \lambda_b \mathbf{X}_b(s_b), s_a - s_b) \quad (\text{B.1})$$

where

$$G(\mathbf{r}, s) = \frac{1}{(2\pi)^3} \int d\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}} \sum_n \frac{-4\pi\kappa^2(k, n)}{k^2[k^2 + \kappa^2(k, n)]} e^{2i\pi ns} \quad (\text{B.2})$$

$$= \frac{1}{r} \left(-\frac{2}{\pi} \int_0^\infty dk \frac{\sin(kr)}{k} \sum_n \frac{\kappa^2(k, n)}{k^2 + \kappa^2(k, n)} e^{2i\pi ns} \right) \quad (\text{B.3})$$

Proving (79) amounts to show that the expression in braces is bounded uniformly in $|\mathbf{r}|$ and s at low density. We split the k integral according to $G(\mathbf{r}, s) = -2/(\pi r)[G_{\text{SR}}(r, s) + G_{\text{LR}}(r, s)]$ where

$$G_{\text{SR}}(r, s) = \int_0^{\kappa_{\text{D}}} dk \frac{\sin(kr)}{k} H(k, s), \quad G_{\text{LR}}(r, s) = \int_{\kappa_{\text{D}}}^\infty dk \frac{\sin(kr)}{k} H(k, s) \quad (\text{B.4})$$

and

$$H(k, s) = \sum_n \frac{\kappa^2(k, n)}{k^2 + \kappa^2(k, n)} e^{2i\pi ns} \quad (\text{B.5})$$

From (49) and the positivity $\kappa^2(k, n) \geq 0$, $|H(k, s)|$ is bounded at low density by $\kappa_{\text{D}}^2[1 + \mathcal{O}(z)]/k^2$. Hence, using $|\sin(kr)| \leq 1$, we obtain the uniform bound $|G_{\text{LR}}(r, s)| \leq [1 + \mathcal{O}(z)]/2$. Regarding $G_{\text{SR}}(r, s)$, more care has to be exercised because we have to take profit of the oscillations of the function $\sin(kr)$. Notice that, from (43) and (52),

$$|H(k, s)| \leq 1 + \sum_{n \neq 0} \frac{\kappa^2(k, n)}{k^2 + \kappa^2(k, n)} = 1 + \mathcal{O}(\kappa_{\text{D}}^2 \lambda^2), \quad k < \lambda^{-1} \quad (\text{B.6})$$

The function $H(k, s)$ is therefore bounded uniformly in s and k in the short range region $k \leq \kappa_{\text{D}} \ll \lambda^{-1}$. Introducing $H_{\text{T}}(k, s) = H(k, s) - H(0, s)$, the short range part $G_{\text{SR}}(r, s)$ is given by

$$G_{\text{SR}}(r, s) = H(0, s) \int_0^{\kappa_{\text{D}}} dk \frac{\sin(kr)}{k} + \int_0^{\kappa_{\text{D}}} dk \frac{\sin(kr)}{k} H_{\text{T}}(k, s) \quad (\text{B.7})$$

Since $H(0, s)$ is bounded uniformly in s and the integral $\int_0^{\kappa_{\text{D}}} dk \sin(kr)/k = \text{Si}(\kappa_{\text{D}} r)$ is bounded uniformly in r , it remains only to consider the

second term of (B.7). Using $|\sin(kr)| \leq 1$, the latter term is smaller or equal to

$$\int_0^1 dp \frac{|H_T(\kappa_D p, s)|}{p} \quad (\text{B.8})$$

An analysis of the function

$$H_T(k, s) = \frac{k^2}{k^2 + \kappa^2(k, 0)} + \sum_{n \neq 0} \left(\frac{\kappa^2(k, n)}{k^2 + \kappa^2(k, n)} - \frac{\gamma_n}{1 + \gamma_n} \right) e^{i2\pi ns} \quad (\text{B.9})$$

where we used (53), shows that the integral (B.8) is finite. Indeed, using the positivity $\gamma_n > 0$, which follows from (43), $|H_T(k, s)|$ can be bounded by

$$|H_T(k, s)| \leq \frac{k^2}{\kappa^2(k, 0)} + \frac{1}{k^2} \sum_{n \neq 0} |\kappa^2(k, n) - \gamma_n k^2| \quad (\text{B.10})$$

The term $k^2/\kappa^2(k, 0)$ gives a finite contribution to the integral (B.8). According to (52) and (55), we have

$$|\kappa^2(k, n) - \gamma_n k^2| = \mathcal{O} \left(\frac{k^2}{n^2} \right) \quad (\text{B.11})$$

This bound can be combined with the estimate of the remainder in (53) to yield

$$|\kappa^2(k, n) - \gamma_n k^2| = \mathcal{O} \left(\left(\frac{k^2}{n^2} \right)^{\alpha_1} (k^4 \lambda^2)^{\alpha_2} \right), \quad n \neq 0 \quad (\text{B.12})$$

where $\alpha_1 + \alpha_2 = 1$. Choosing $\alpha_1 = 3/4$, we see that the contribution of the second term in (B.10) to (B.8) is finite, since both the summation over n and the p integral converge. The proof of (79) is hence completed.

APPENDIX C. LOCAL INTEGRABILITY OF V_{elec}^n

In this appendix, we prove that any power of the electrostatic potential (11) is locally integrable:

$$\int D(\mathbf{X}_a) \int D(\mathbf{X}_b) \left(\int_0^{q_a} d\tau_a \int_0^{q_b} d\tau_b \frac{1}{|\mathbf{r} + \lambda_a \mathbf{X}_a(\tau_a) - \lambda_b \mathbf{X}_b(\tau_b)|} \right)^n < C \quad (\text{C.1})$$

uniformly in \mathbf{r} and $n = 1, 2, \dots$.

The integral (C.1) can be evaluated using the covariance (6). We find

$$\begin{aligned} & \int \mathbf{D}(\mathbf{X}_a) \int \mathbf{D}(\mathbf{X}_b) \left(\frac{1}{(2\pi)^3} \int_0^{q_a} d\tau_a \int_0^{q_b} d\tau_b \int d\mathbf{k} e^{-i\mathbf{k} \cdot [\mathbf{r} + \lambda_a \mathbf{X}_a(\tau_a) - \lambda_b \mathbf{X}_b(\tau_b)]} \frac{4\pi}{k^2} \right)^n \\ &= \int \left(\prod_{i=1}^n d\mathbf{k}_i \frac{4\pi}{|\mathbf{k}_i|^2} \frac{e^{-i\mathbf{k}_i \cdot \mathbf{r}}}{(2\pi)^3} \right) \int_0^{q_a} d\tau_1 \cdots d\tau_n \int \mathbf{D}(\mathbf{X}_a) e^{-i\lambda_a \sum_m \mathbf{k}_m \cdot \mathbf{X}_a(\tau_m)} \\ & \quad \times \int_0^{q_b} d\tau'_1 \cdots d\tau'_n \int \mathbf{D}(\mathbf{X}_b) e^{i\lambda_b \sum_m \mathbf{k}_m \cdot \mathbf{X}_b(\tau'_m)} \end{aligned} \quad (\text{C.2})$$

$$\begin{aligned} &= \int \left(\prod_{i=1}^n d\mathbf{k}_i \frac{4\pi}{|\mathbf{k}_i|^2} \frac{e^{-i\mathbf{k}_i \cdot \mathbf{r}}}{(2\pi)^3} \right) \left(\int_0^{q_a} d\tau_1 \cdots d\tau_n e^{-\frac{1}{2} \lambda_a^2 \sum_{i,j=1}^n \mathbf{k}_i \cdot \mathbf{k}_j \text{cov}(\tau_i, \tau_j)} \right) \\ & \quad \times \left(\int_0^{q_b} d\tau'_1 \cdots d\tau'_n e^{-\frac{1}{2} \lambda_b^2 \sum_{i,j=1}^n \mathbf{k}_i \cdot \mathbf{k}_j \text{cov}(\tau'_i, \tau'_j)} \right) \end{aligned} \quad (\text{C.3})$$

Using $\exp[-\frac{1}{2} \lambda_b^2 \sum_{i,j=1}^n \mathbf{k}_i \cdot \mathbf{k}_j \text{cov}(\tau'_i, \tau'_j)] \leq 1$, we obtain the upper bound

$$\begin{aligned} (\text{C.1}) &\leq q_b^n \int \left(\prod_{i=1}^n d\mathbf{k}_i \frac{4\pi}{|\mathbf{k}_i|^2} \frac{1}{(2\pi)^3} \right) \int_0^{q_a} d\tau_1 \cdots d\tau_n e^{-\frac{1}{2} \lambda_a^2 \sum_{i,j=1}^n \mathbf{k}_i \cdot \mathbf{k}_j \text{cov}(\tau_i, \tau_j)} \\ &\leq q_b^n \int \mathbf{D}(\mathbf{X}_a) \left(\int_0^{q_a} ds \frac{1}{|\lambda_a \mathbf{X}_a(s)|} \right)^n \end{aligned} \quad (\text{C.4})$$

The finiteness of (C.1) follows hence from that of (97).

APPENDIX D. PARTICLE AND LOOP CORRELATIONS

In this appendix, we establish the relations between the loop correlations $\rho(\mathcal{L}_1, \dots, \mathcal{L}_n)$ and the particle correlations $\rho(\alpha_1, \mathbf{r}_1, \dots, \alpha_n, \mathbf{r}_n)$ using a systematic procedure based on the invariance (30) of the measure $\mathbf{D}(\mathbf{X})$. Since loops themselves involve several particles, we have to distinguish between particles belonging to the same loop and to different loops. We illustrate the method in the simple cases of the particle density $\rho(\alpha, \mathbf{r})$ and of the two-particle correlations $\rho(\alpha_1, \mathbf{r}_1, \alpha_2, \mathbf{r}_2)$, and state the result for the three-point function.

For a configuration of particles distributed in a set of loops $\{\mathcal{L}_i\}$, we can write the particle density observable $\hat{\rho}(\alpha, \mathbf{r})$ as a summation on the loop index i

$$\hat{\rho}(\alpha, \mathbf{r}) = \sum_i \delta_{\alpha_i, \alpha} \sum_{k=1}^{q_i} \delta(\mathbf{r}_i^{(k)} - \mathbf{r}) \quad (\text{D.1})$$

where, according to (3), $\mathbf{r}_i^{(k)} = \mathbf{R}_i + \lambda_{\alpha_i} \mathbf{X}_i(k-1)$, $k = 1, \dots, q_i$, are the positions of the particles belonging to the loop i . Taking the average of $\hat{\rho}(\alpha, \mathbf{r})$ on the ensemble of loops gives the particle density at \mathbf{r} :

$$\rho(\alpha, \mathbf{r}) = \sum_q \int \mathbf{D}(\mathbf{X}) \sum_{k=1}^q \rho(\alpha, q, \mathbf{r} - \lambda_{\alpha} \mathbf{X}(k-1), \mathbf{X}) \quad (\text{D.2})$$

The main point relies in the simplification of formulae like (D.2). In the present case, we need only to recall the invariance property (86) of $\rho(\mathcal{L})$. For the integer value $u = k-1$, (86) state that the loop density is invariant under a reassignment of the origin of the loop \mathcal{L} on its k th particle:

$$\rho(\mathcal{L}) = \rho(\mathcal{L}^{[k-1]}) = \rho(\alpha, q, \mathbf{r}^{(k)}, \mathbf{X}(\cdot + k-1) - \mathbf{X}(k-1)), \quad k = 1, \dots, q \quad (\text{D.3})$$

Inserting (D.3) in (D.2) and using (30), we recover the result

$$\rho(\alpha, \mathbf{r}) = \sum_q q \int \mathbf{D}(\mathbf{X}) \rho(\alpha, q, \mathbf{r}, \mathbf{X}) \quad (\text{D.4})$$

The two-point function $\rho(\alpha_1, \mathbf{r}_1, \alpha_2, \mathbf{r}_2)$ is given in the ensemble of loops by the average

$$\begin{aligned} \rho(\alpha_1, \mathbf{r}_1, \alpha_2, \mathbf{r}_2) = & \left\langle \sum_{i \neq j} \delta_{\alpha_i, \alpha_1} \delta_{\alpha_j, \alpha_2} \sum_{k=1}^{q_i} \sum_{k'=1}^{q_j} \delta(\mathbf{r}_i^{(k)} - \mathbf{r}_1) \delta(\mathbf{r}_j^{(k')} - \mathbf{r}_2) \right. \\ & \left. + \delta_{\alpha_1, \alpha_2} \sum_i \delta_{\alpha_i, \alpha_1} \sum_{\substack{k, k'=1 \\ k \neq k'}}^{q_i} \delta(\mathbf{r}_i^{(k)} - \mathbf{r}_1) \delta(\mathbf{r}_i^{(k')} - \mathbf{r}_2) \right\rangle_{\text{loops}} \quad (\text{D.5}) \end{aligned}$$

The first contribution in (D.5) refers to particles in different loops and the second contribution to particles within the same loop. In terms of the loop correlations, (D.5) becomes,

$$\begin{aligned} & \rho(\alpha_1, \mathbf{r}_1, \alpha_2, \mathbf{r}_2) \\ & = \sum_{q_1, q_2} \int \mathbf{D}(\mathbf{X}_1) \mathbf{D}(\mathbf{X}_2) \sum_{k=1}^{q_1} \sum_{k'=1}^{q_2} \\ & \quad \times \rho(\alpha_1, q_1, \mathbf{r}_1 - \lambda_1 \mathbf{X}_1(k-1), \mathbf{X}_1; \alpha_2, q_2, \mathbf{r}_2 - \lambda_2 \mathbf{X}_2(k'-1), \mathbf{X}_2) \\ & \quad + \delta_{\alpha_1, \alpha_2} \sum_{q_2} \int \mathbf{D}(\mathbf{X}_2) \sum_{\substack{k, k'=1 \\ k \neq k'}}^{q_2} \delta(\mathbf{r}_1 - \lambda_2 \mathbf{X}_2(k-1) - \mathbf{r}_2 + \lambda_2 \mathbf{X}_2(k'-1)) \\ & \quad \times \rho(\alpha_2, q_2, \mathbf{r}_2 - \lambda_2 \mathbf{X}_2(k-1), \mathbf{X}_2) \quad (\text{D.6}) \end{aligned}$$

To simplify this formula, one uses the fact that the n -point correlations $\rho(\mathcal{L}_1, \dots, \mathcal{L}_n)$ are invariant under changing the origin of any loop \mathcal{L}_i on another particle within the same loop:

$$\rho(\mathcal{L}_1, \dots, \mathcal{L}_i, \dots, \mathcal{L}_n) = \rho(\mathcal{L}_1, \dots, \mathcal{L}_i^{[k-1]}, \dots, \mathcal{L}_n), \quad k = 1, \dots, q_i \quad (\text{D.7})$$

This invariance follows from the special forms of (13), (14) and (9) which are insensitive to the choice of the origin. Inserting (D.7) in (D.6) and using the invariance (30) of the measure $D(\mathbf{X})$, we find

$$\begin{aligned} \rho(\alpha_1, \mathbf{r}_1, \alpha_2, \mathbf{r}_2) &= \sum_{q_1, q_2} q_1 q_2 \int D(\mathbf{X}_1) D(\mathbf{X}_2) \rho(\mathcal{L}_1, \mathcal{L}_2) \\ &\quad + \delta_{\alpha_1, \alpha_2} \sum_{q_2} q_2 \sum_{k=2}^{q_2} \int D(\mathbf{X}_2) \delta(\mathbf{r}_2^{(k)} - \mathbf{r}_1) \rho(\mathcal{L}_2) \end{aligned} \quad (\text{D.8})$$

where the loops \mathcal{L}_1 and \mathcal{L}_2 are located at \mathbf{r}_1 and \mathbf{r}_2 . For the three-particle correlations, we find similarly

$$\begin{aligned} &\rho(\alpha_1, \mathbf{r}_1, \alpha_2, \mathbf{r}_2, \alpha_3, \mathbf{r}_3) \\ &= \sum_{q_1, q_2, q_3} q_1 q_2 q_3 \int D(\mathbf{X}_1) D(\mathbf{X}_2) D(\mathbf{X}_3) \rho(\mathcal{L}_1, \mathcal{L}_2, \mathcal{L}_3) \\ &\quad + \delta_{\alpha_1, \alpha_3} \sum_{q_2} q_2 \sum_{q_3} q_3 \sum_{k=2}^{q_3} \int D(\mathbf{X}_2) D(\mathbf{X}_3) \delta(\mathbf{r}_3^{(k)} - \mathbf{r}_1) \rho(\mathcal{L}_2, \mathcal{L}_3) \\ &\quad + \delta_{\alpha_1, \alpha_2} \sum_{q_3} q_3 \sum_{q_2} q_2 \sum_{k=2}^{q_2} \int D(\mathbf{X}_2) D(\mathbf{X}_3) \delta(\mathbf{r}_2^{(k)} - \mathbf{r}_1) \rho(\mathcal{L}_2, \mathcal{L}_3) \\ &\quad + \delta_{\alpha_2, \alpha_3} \sum_{q_1} q_1 \sum_{q_2} q_2 \sum_{k=2}^{q_2} \int D(\mathbf{X}_1) D(\mathbf{X}_2) \delta(\mathbf{r}_2^{(k)} - \mathbf{r}_3) \rho(\mathcal{L}_1, \mathcal{L}_2) \\ &\quad + \delta_{\alpha_1, \alpha_2} \delta_{\alpha_2, \alpha_3} \sum_{q_1} q_1 \sum_{\substack{k, k' \geq 2 \\ k \neq k'}}^{q_1} \int D(\mathbf{X}_1) \delta(\mathbf{r}_1^{(k)} - \mathbf{r}_2) \delta(\mathbf{r}_1^{(k')} - \mathbf{r}_3) \rho(\mathcal{L}_1) \end{aligned} \quad (\text{D.9})$$

All terms except the first one come from exchange: the last term corresponds to all particles in the same loop whereas in the three others only two particles are in the same loop. The above formulae are also valid in an inhomogeneous system.

The charge sum rules (100) involve the excess particle densities (101) that include coincident points. These densities are easily obtained from the above results. For $n = 1$, the excess particle density reads

$$\begin{aligned} \rho_{T, \text{c.p.}}(\alpha_1, \mathbf{r}_1 | \alpha_2, \mathbf{r}_2) &= \sum_{q_1, q_2} q_1 q_2 \int \mathbf{D}(\mathbf{X}_1) \mathbf{D}(\mathbf{X}_2) \rho_T(\mathcal{L}_1 | \mathcal{L}_2) \\ &+ \delta_{\alpha_1, \alpha_2} \sum_{q_2} q_2 \sum_{k=1}^{q_2} \int \mathbf{D}(\mathbf{X}_2) \delta(\mathbf{r}_2^{(k)} - \mathbf{r}_1) \rho(\mathcal{L}_2) \quad (\text{D.10}) \end{aligned}$$

Notice that the truncation in $\rho_T(\mathcal{L}_1 | \mathcal{L}_2) = \rho(\mathcal{L}_1, \mathcal{L}_2) - \rho(\mathcal{L}_1) \rho(\mathcal{L}_2)$ originates from the second term in the rhs of (101) when (D.4) is used, and that the contribution of coincident points gives the term $k = 1$ of the sum in (D.10). For $n = 2$, we find similarly

$$\begin{aligned} \rho_{T, \text{c.p.}}(\alpha_1, \mathbf{r}_1 | \alpha_2, \mathbf{r}_2, \alpha_3, \mathbf{r}_3) &= \sum_{q_1, q_2, q_3} q_1 q_2 q_3 \int \mathbf{D}(\mathbf{X}_1) \mathbf{D}(\mathbf{X}_2) \mathbf{D}(\mathbf{X}_3) \rho_T(\mathcal{L}_1 | \mathcal{L}_2, \mathcal{L}_3) \\ &+ \delta_{\alpha_1, \alpha_3} \sum_{q_2, q_3} q_2 q_3 \sum_{k=1}^{q_3} \int \mathbf{D}(\mathbf{X}_2) \mathbf{D}(\mathbf{X}_3) \delta(\mathbf{r}_3^{(k)} - \mathbf{r}_1) \rho(\mathcal{L}_2, \mathcal{L}_3) \\ &+ \delta_{\alpha_1, \alpha_2} \sum_{q_2, q_3} q_2 q_3 \sum_{k=1}^{q_2} \int \mathbf{D}(\mathbf{X}_2) \mathbf{D}(\mathbf{X}_3) \delta(\mathbf{r}_2^{(k)} - \mathbf{r}_1) \rho(\mathcal{L}_2, \mathcal{L}_3) \\ &+ \delta_{\alpha_2, \alpha_3} \sum_{q_1, q_2} q_1 q_2 \sum_{k=2}^{q_2} \int \mathbf{D}(\mathbf{X}_1) \mathbf{D}(\mathbf{X}_2) \delta(\mathbf{r}_2^{(k)} - \mathbf{r}_3) \rho_T(\mathcal{L}_1 | \mathcal{L}_2) \\ &+ \delta_{\alpha_1, \alpha_2} \delta_{\alpha_2, \alpha_3} \sum_{q_1} q_1 \sum_{\substack{k, k'=1 \\ k \neq k'}}^{q_1} \int \mathbf{D}(\mathbf{X}_1) \delta(\mathbf{r}_1^{(k)} - \mathbf{r}_2) \delta(\mathbf{r}_1^{(k')} - \mathbf{r}_3) \rho(\mathcal{L}_1) \quad (\text{D.11}) \end{aligned}$$

The truncations in $\rho_T(\mathcal{L}_1 | \mathcal{L}_2, \mathcal{L}_3) = \rho(\mathcal{L}_1, \mathcal{L}_2, \mathcal{L}_3) - \rho(\mathcal{L}_1) \rho(\mathcal{L}_2, \mathcal{L}_3)$ and in $\rho_T(\mathcal{L}_1 | \mathcal{L}_2)$ come, as before, from the second term of (101) after substitution of (D.8). The contribution of coincident points gives the terms $k = 1$ in the second and third line of (D.11) and, after a minor rewriting of the exchange contribution in (D.8), the terms $k = 1, k' \geq 2$ and $k' = 1, k \geq 2$ in the last line of (D.11).

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