Virial expansions for quantum plasmas: Fermi-Bose statistics

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This paper is devoted to the calculation of the density expansions (at fixed non-zero temperature) of the thermodynamic functions for quantum plasmas. The Maxwell-Boltzmann forms of these expansions have been studied in two previous papers. Here we include the exchange contributions due to Fermi or Bose statistics, via a perturbative scheme where the reference ingredients are computed in the framework of Maxwell-Boltzmann statistics. The whole scheme is based on the Feynman-Kac path integral representation which amounts to introducing classical auxiliary systems made of extended objects, the filaments. The quantities of interest are then evaluated by applying familiar diagrammatical methods of classical statistical mechanics. The exact density expansions of the free energy and of the pressure are explicitly calculated up to order $\rho^{5/2}$ in the density ρ. The corresponding expressions include, in a systematic and coherent way, the contributions of various physical effects such as screening, diffraction, recombination, scattering, and exchange. At order ρ^2, we recover the expansions obtained via the effective-potential method. Our terms of order $\rho^{5/2}$ correctly reproduce results which are known in some particular limits. Moreover, the high-temperature expansions which can be easily inferred from our virial expansions do coincide with those obtained from the Feynman graphs in the usual many-body theory. [S1063-651X(96)04205-5]

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I. INTRODUCTION

This paper is the third of a series devoted to the study of the density expansions of the thermodynamic quantities for quantum plasmas. We consider a multicomponent system $\mathscr{S}$ made of electrons and nuclei which are assumed to be point particles. Each particle has a mass m_α and carries a charge e_α and a spin σ_α, where α is a species index which specifies the nature of the particle. The Hamiltonian of $\mathscr{S}$ is nonrelativistic and only involves two-body Coulomb interactions of the form $e_\alpha e_\beta / r$ for two charges separated by a distance r. It does not depend on the spins of the particles. Such a purely Coulombic description of matter is well suited for a very large variety of physical situations. Besides their own conceptual interest, the virial expansions are useful in practice for studying regimes where the density is not too high and the temperature is not too low (for instance, these conditions are met in the core of the sun).

In a first paper [1], we derived a diagrammatic representation for the particle correlations of $\mathscr{S}$ in the framework of Maxwell-Boltzmann statistics. As in the work by Ginibre [2], the application of the Feynman-Kac formula [3] to the density matrix leads to the introduction of an auxiliary classical system $\mathscr{S}^*$ made of closed filaments. Since the filaments interact via two-body forces, all the familiar diagrammatical methods [4] can be applied to $\mathscr{S}^*$. However, the corresponding Mayer-like graphs diverge because of the long-range Coulombic nature of the interaction potential between two filaments. These long-range divergencies are removed via the chain resummations introduced by Mayer [5] and Salpeter [6] for classical point charges. In fact, inspired by the works of Meeron [7] and Abe [8] for classical Coulomb systems, we have shown that the whole set of Mayer graphs defining the correlations of $\mathscr{S}^*$ can be transformed exactly into a new set of prototype graphs Π built with resummed bonds. This provides a well-behaved diagrammatic representation for the particle correlations of $\mathscr{S}$, where the integrability of each graph is guaranteed by a sufficiently fast decay of the resummed bonds. We stress that some resummed bonds decay only algebraically, in agreement with the absence of exponential screening in the quantum case [9–12].

In a second paper [13], the above diagrammatical representation was used for studying the density expansions of the Maxwell-Boltzmann (MB) thermodynamic functions (at fixed inverse temperature β) in a systematic way. On the basis of simple scaling arguments, we have shown that the virial expansions involve half-integer powers of the densities and integer powers of the logarithm of the densities (the presence of logarithmic terms was conjectured by Friedman [14]). We also gave detailed prescriptions for selecting the graphs (in finite number) which contribute to a given order in ρ^{MB}, where ρ^{MB} is a generic notation for the MB particle densities. This allows us to recover the known results up to order $(\rho^{\mathrm{MB}})^2$, and to calculate exactly the next term of order $(\rho^{\mathrm{MB}})^{5/2}$.

As announced previously [1], the above expansions are term to term well defined despite the macroscopic collapse of the Maxwell-Boltzmann system [15]. In the present paper, the exchange contributions due to Fermi or Bose statistics are now evaluated via a perturbative scheme, in which the MB quantities are the reference ingredients. A brief description of this scheme has already been given in a Letter [16], as well as the complete form of the virial expansion up to order $\rho^{5/2}$.

The present paper is organized as follows. In Sec. II we define the model and recall the theorems which guarantee the existence of the thermodynamic limit. In Sec. III we write the Slater expansion of the grand-partition function Ξ in configuration and spin spaces. Such an expansion is organized

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with respect to the number n of exchanged particles. The term $n=0$ corresponds to Maxwell-Boltzmann statistics, while the terms $n \geqslant 2$ describe exchange effects due to Fermi or Bose statistics.

As shown in Sec. IV, the application of the Feynman-Kac formula to the spatial matrix elements of the quantum Gibbs factor allows expression of each exchange contribution to Ξ in terms of quantities relative to n opened filaments $\mathscr{F}$ immersed in a large system $\mathscr{S}^*$ made of closed filaments $\mathscr{E}$. This inhomogeneous situation can be dealt with via a perturbative scheme, where the equilibrium correlations of the homogeneous system $\mathscr{S}^*$ (without any opened filament) are the key ingredients. As described in Sec. V, the density expressions of the thermodynamic functions of $\mathscr{S}$ are then derived by taking advantage of our knowledge of $\mathscr{S}^*$ [1,13]. In particular, once the MB densities have been eliminated in favor of the real densities ρ, these expansions reduce to double integer series in $\rho^{1/2}$ and $\ln\rho$. Such a nonanalytical structure reflects the collective screening of the bare Coulomb potential.

In Sec. VI the density expansion of the pressure is calculated explicitly up to order $\rho^{5/2}$. For this, in the above Slater expansion with respect to the number n of exchanged particles, it is sufficient to keep only the MB ($n=0$) and the two-body exchange ($n=2$) contributions. The density expansions of the other thermodynamic functions are then readily obtained through thermodynamic identities.

The physical nature of the various contributions to the density expansions is discussed in Sec. VII. There are purely classical terms which arise from Debye screening at large distances. The short-range quantum effects associated with bound and scattering states enter in suitably truncated traces of the quantum Gibbs factors for a finite number of charges. There are diffraction terms which appear as quantum corrections to a classical treatment of the long-range part of the interactions. Eventually, the exchange contributions are expressed in terms of off-diagonal matrix elements of the n-body density matrix. All these physical effects should be coupled together at higher orders in the density.

Also in Sec. VII, comparisons to previous results and checkings are also decribed. Of course, the virial expansions can be studied by using other first-principles formalisms. First, the effective-potential method formulated by Morita [17] for quantum systems with two-body interactions has been applied to the present Coulomb case by Ebeling [18]. This method consists in introducing classical equivalent systems made of point objects with second-, third-, and higher-order many-body effective interactions. In practice, only two-body effective potentials have been retained [18–20]. This amounts to considering well-behaved classical systems with two-body Coulomb interactions that are regularized at short distances (quantum effects smooth out the singularity of $1/r$ at the origin). The corresponding calculations [19,20] provide the exact form of the virial expansions up to order ρ^2, which is indeed recovered by our formalism [16]. However, the expressions proposed for the $\rho^{5/2}$ term [20] are not complete because the three-body effective potentials do contribute at this order [21]. Our formalism allows a precise evaluation of this missing contribution which is of the diffraction type. We stress that the presence of this additional diffraction term is crucial for recovering the Wigner-Kirkwood $\hbar^2$ corrections [22] to the classical quantities for the one-component plasma. By the way, we also do recover the virial expansion for the classical one-component plasma calculated by Cohen and Murphy [23].

Another possible approach is based on the standard many-body perturbative expansions with respect to the Coulomb interaction potential $v_c(r)=1/r$ in the framework of the grand-canonical ensemble. These expansions can be written in terms of graphs similar to those which appear in field theory, where fermionic or bosonic loops associated to imaginary-time free propagators are connected at different times by an arbitrary number of interaction lines v_c [24]. The long-range Coulomb divergencies are eliminated via the well-known ring resummations [25,26]. To our knowledge, analytic evaluations of the corresponding Feynman graphs have been restricted to the high-density regime at zero temperature [25], and to the high-temperature limit [27–29]. Explicit calculations of the virial coefficients at finite nonzero temperature should also be possible by following Rogers's idea [30]. This author proposed a classical treatment of the ring resummations combined with a proper account of the ladder graphs that describe quantum effects at short distances. In this procedure, some terms are left over since they are expected to be quantitatively small in the physical regimes considered by the author [31] (i.e., at moderately high densities where complex entities made of several charges may be formed). A detailed control of these terms should allow recovery of the virial expansions calculated by the above formalisms. At the moment, we have checked that the high-temperature expansions of our virial coefficients do coincide with the terms found by DeWitt [28] and more recently by DeWitt *et al.* [29].

II. THE MODEL

We consider a multicomponent system $\mathscr{S}$, with an arbitrary number of species made of point particles. Each particle of species α (an electron or a nuclei in practical applications) has a mass m_α and carries a charge e_α and a spin σ_α. Two charges e_α and e_β separated by a distance r interact instantaneously via the usual two-body Coulomb potential $e_\alpha e_\beta v_c(r)$ with $v_c(r)=1/r$. The corresponding Hamiltonian for N particles enclosed in a box with volume Λ is

$$H_N=-\sum_i \frac{\hbar^2}{2m_i}\Delta_i+\frac{1}{2}\sum_{i\neq j}\frac{e_i e_j}{|\vec{r}_i-\vec{r}_j|}, \tag{2.1}$$

where $i=[{}^{\kappa}_{\alpha}]$ is a double index, while k runs from 1 to the number N_α of charges of species α, and α runs from 1 to the number n_s of species ($N=\Sigma_\alpha N_\alpha$). The boundary conditions which define H_N are of the Dirichlet type, i.e., the eigenwave-functions of H_N vanish at the surface of the box. This nonrelativistic Coulomb Hamiltonian is well suited for practical applications where the mean velocity of the particles is small compared to the speed of light.

Let the system be in thermal equilibrium at temperature $T(\beta=1/k_BT)$. The grand-partition function of the finite system reads

$$\Xi_\Lambda = \mathrm{Tr}_\Lambda \exp\left[-\beta \left(H_N - \sum_\alpha \mu_\alpha N_\alpha \right) \right], \tag{2.2}$$

where μ_α is the chemical potential of species α. In the definition (2.2), the trace Tr_Λ is taken over all the states satisfying the above boundary conditions and symmetrized according to the statistics of each species. Note that the total charge $\Sigma_\alpha e_\alpha N_\alpha$ carried by each of these states may be different from zero.

Lieb and Lebowitz [15] have shown that the thermodynamic limit (TL) of the present system exists if and only if at least one species obeys Fermi statistics (see also Lieb [32], Dyson and Lenard [33]). The TL is defined as the infinite volume limit ($\Lambda \to \infty$), while the chemical potential μ_α and the temperature T are kept fixed. The existence of the TL means that the thermodynamic quantities relative to the infinite system have the right extensive properties. In particular, the bulk pressure P given through

$$\beta P = \lim_{\mathrm{TL}} \frac{1}{\Lambda} \ln \Xi_\Lambda \tag{2.3}$$

is a well-behaved function of the intensive parameters μ_α and β which does not depend on the shapes of the finite boxes considered in the TL. If the fugacities $z_\alpha = \exp(\beta \mu_\alpha)$ are small enough (at given temperature), the system surely is in a fluid phase. The local density of any species α then becomes uniform in the TL and reduces to

$$\rho_\alpha = z_\alpha \frac{\partial}{\partial z_\alpha} \left[\lim_{\mathrm{TL}} \frac{1}{\Lambda} \ln \Xi_\Lambda \right] \Bigg|_\beta . \tag{2.4}$$

Furthermore, the infinite system is locally neutral, i.e.,

$$\sum_\alpha e_\alpha \rho_\alpha = 0 \tag{2.5}$$

for any set of fugacities.

III. SLATER EXPANSION OF THE GRAND-PARTITION FUNCTION

The trace (2.2) defining the grand-partition function can be taken over the symmetrized Slater sums built with one-body states $|\vec{r} \sigma^z\rangle$ which describe a particle localized at $\vec{r}$ with the projection of its spin along a given z axis equal to σ^z [1]. This gives

$$\Xi_\Lambda = \sum_{N_\alpha = 0}^{\infty} \frac{\Pi_\alpha z_\alpha^{N_\alpha}}{\Pi_\alpha N_\alpha !} \sum_{\mathscr{P}_\alpha} \prod_\alpha \epsilon_\alpha(\mathscr{P}_\alpha) \sum_{\{\sigma_i^z\}} \prod_i \langle \sigma^z_{\mathscr{P}_\alpha(i)} | \sigma_i^z \rangle \times \int_{\Lambda^N} \prod_i d\vec{r}_i \langle \vec{r}_{\mathscr{P}_\alpha(i)} | \otimes_i | \exp(-\beta H_N) | \otimes_i | \vec{r}_i \rangle . \tag{3.1}$$

In (3.1), $\mathscr{P}_\alpha$ is a permutation of $(1, \ldots, N_\alpha)$, $\mathscr{P}_\alpha(i) = (\mathscr{P}_\alpha(k), \alpha)$, and $\epsilon_\alpha(\mathscr{P}_\alpha)$ is either 1 if the particles of species α are bosons (σ_α integer) or the signature (± 1) of $\mathscr{P}_\alpha$ in the fermionic case (σ_α half integer). Notice that the spin part of the matrix elements contributes the degeneracy factor $\Sigma_{\{\sigma_i^z\}} \Pi_i \langle \sigma^z_{\mathscr{P}_\alpha(i)} | \sigma_i^z \rangle$ which only depends on the permutations $\mathscr{P}_\alpha$.

The Slater-sum representation (3.1) of Ξ_Λ provides a natural perturbative scheme for treating the exchange contributions. The term where $\mathscr{P}_\alpha$ reduces to the identity for any α obviously corresponds to Maxwell-Boltzmann statistics [1]. All the other terms describe exchange effects associated with Fermi or Bose statistics. They can be reorganized with respect to the number n of exchanged particles, i.e., the number n of indexes i such that $\mathscr{P}_\alpha(i) \neq i$. This allows us to rewrite (3.1) as

$$\Xi_\Lambda = \Xi_\Lambda^{\mathrm{MB}} + \sum_{n=2}^{\infty} \Xi_\Lambda^{(n)} , \tag{3.2}$$

where each $\Xi_\Lambda^{(n)}$ denotes the whole contribution of all the terms in (3.1) with n exchanged particles.

The first term ($n=0$) in (3.2) which corresponds to MB statistics reads [1]

$$\Xi_\Lambda^{\mathrm{MB}} = \sum_{N_\alpha = 0}^{\infty} \prod_\alpha \frac{z_\alpha^{N_\alpha}}{N_\alpha !} (2\sigma_\alpha + 1)^{N_\alpha} \times \int_{\Lambda^N} \prod_i d\vec{r}_i \langle \vec{R}_N | \exp(-\beta H_N) | \vec{R}_N \rangle , \tag{3.3}$$

with $|\vec{R}_N\rangle = \otimes_i |\vec{r}_i\rangle$. Each spin degeneracy factor relative to species α reduces to $(2\sigma_\alpha + 1)^{N_\alpha}$ and the matrix element

$$\langle \vec{R}_N | \exp(-\beta H_{N,\Lambda}) | \vec{R}_N \rangle \tag{3.4}$$

is diagonal with respect to all the positions $\vec{r}_i$.

The second term ($n=2$) in (3.2) is obtained by collecting the contributions to (3.1) of all the sets of permutations which exchange two given indexes associated to the given species α and leave unchanged the remaining ones. For each species α, there are $N_\alpha(N_\alpha - 1)/(2!)$ such sets of permutations which give identical contributions. The corresponding spin degeneracy factor now reduces to $(2\sigma_\alpha + 1)^{N_\alpha - 1}$ because the product of $\langle \sigma^z_{\mathscr{P}_\alpha(i)} | \sigma_i^z \rangle$ is different from zero only when the two exchanged particles are in the same spin state; the other degeneracy factors for $\gamma \neq \alpha$ are obviously equal to $(2\sigma_\alpha + 1)^{N_\gamma}$ as in the MB case. We then obtain

$$\Xi_\Lambda^{(2)} = \sum_\alpha (-1)^{2\sigma_\alpha} (2\sigma_\alpha + 1) \frac{z_\alpha^2}{2!} \times \sum_{N_\alpha = 2}^{\infty} \frac{z_\alpha^{N_\alpha - 2}}{(N_\alpha - 2)!} (2\sigma_\alpha + 1)^{N_\alpha - 2} \times \sum_{N_\gamma = 0}^{\infty} \frac{\Pi_{\gamma \neq \alpha} z_\gamma^{N_\gamma}}{\Pi_{\gamma \neq \alpha} (N_\gamma !)} (2\sigma_\gamma + 1)^{N_\gamma} \times \int d\vec{r}_1 d\vec{r}_2 d\vec{R}_{N-2} \langle \vec{r}_2 \vec{r}_1 \vec{R}_{N-2} | e^{-\beta H_N} | \vec{r}_1 \vec{r}_2 \vec{R}_{N-2} \rangle , \tag{3.5}$$

where $\vec{r}_1$ and $\vec{r}_2$ are the positions of the two particles of species α which are exchanged and $\vec{R}_{N-2}$ is a collective notation for the $(N-2)$ positions of the other particles. The matrix element

$$\langle \vec{r}_2 \vec{r}_1 \vec{R}_{N-2} | e^{-\beta H_N} | \vec{r}_1 \vec{r}_2 \vec{R}_{N-2} \rangle \tag{3.6}$$

is off diagonal with respect to the positions of the two exchanged particles and diagonal with respect to the positions of the $(N-2)$ other particles.

Expressions similar to (3.5) can be easily found for the other Ξ_Λ^n's ($n \geqslant 3$). In particular, the spin degeneracy factors are readily evaluated by identifying the spins of the exchanged particles which are involved in a given cyclic permutation (any permutation of n objects is a product of p cycles). Moreover, like (3.6), the matrix elements of $\exp(-\beta H_N)$ are off diagonal with respect to the positions of the n exchanged particles and diagonal with respect to the positions of the $(N-n)$ other particles.

The perturbative representation (3.2) is particularly well suited for calculating the first terms in the density expansions of the thermodynamic quantities. Indeed, since the off-diagonal matrix elements of $\exp(-\beta H_N)$ are short ranged, the contributions to intensive quantities (like the pressure) of each $\Xi_\Lambda^{(n)}$ are at least of order ρ^n, roughly speaking [34]. Therefore, at a given order in ρ, only a finite number of terms in (3.2) must be retained.

IV. FEYNMAN-KAC REPRESENTATION

A. The Feynman-Kac formula for the density matrix

According to the original path integral formulation introduced by Feynman and Hibbs [35], the matrix elements of $\exp(-\beta H_N)$ in configuration space read

$$\langle \vec{R}'_N | \exp[-\beta H_N] | \vec{R}_N \rangle = \sum_{\text{all paths}} \exp\left(\frac{-S\{\vec{r}_i(t)\}}{\hbar} \right), \tag{4.1}$$

where $S\{\vec{r}_i(t)\}$ is the classical action

$$S\{\vec{r}_i(t)\} = \int_0^{\beta\hbar} dt \left\{ \sum_i \frac{m_i}{2} \left[\frac{d\vec{r}_i(t)}{dt} \right]^2 + \frac{1}{2} \sum_{i \neq j} e_i e_j v_c[|\vec{r}_i(t) - \vec{r}_j(t)|] \right\} \tag{4.2}$$

for paths $\vec{r}_i(t)$ going from $\vec{r}_i$ to $\vec{r}'_i$ in a ''time'' $\beta\hbar$. The summation in (4.1) is taken over all such paths. The variable changes $t = s\beta\hbar$ and $\vec{r}_i(t) = (1-s)\vec{r}_i + s\vec{r}'_i + \lambda_i \vec{\xi}_i(s)$ with $\vec{\xi}_i(0) = \vec{\xi}_i(1) = \vec{0}$ in (4.1) and (4.2) lead to the so-called Feynman-Kac (FK) formula [3]

$$\langle \vec{R}'_N | \exp[-\beta H_N] | \vec{R}_N \rangle = \prod_i \frac{\exp[-(\vec{r}_i - \vec{r}'_i)^2/(2\lambda_i^2)]}{(2\pi\lambda_i^2)^{3/2}} \times \int \prod_i \mathscr{D}(\vec{\xi}_i) \exp\left[-\frac{\beta}{2} \sum_{i \neq j} e_i e_j \times \int_0^1 ds\, v_c[|(1-s)(\vec{r}_i - \vec{r}_j) + s(\vec{r}'_i - \vec{r}'_j) + \lambda_i \vec{\xi}_i(s) - \lambda_j \vec{\xi}_j(s)|] \right]. \tag{4.3}$$

In (4.3), the Gaussian prefactors arise from the kinetic contribution to the action S of the free motion part $[(1-s)\vec{r}_i + s\vec{r}'_i]$ of $\vec{r}_i(t)$. The corresponding kinetic factor $\exp[-\frac{1}{2}\int_0^1 ds\, \dot{\vec{\xi}}^2(s)]$ associated with each $\vec{\xi}$ is absorbed in a normalized Gaussian measure $\mathscr{D}(\vec{\xi})$ which defines the functional integration over all the Brownian bridges $\vec{\xi}(s)$ subjected to the constraint $\vec{\xi}(0) = \vec{\xi}(1) = \vec{0}$. This measure is intrinsic, i.e., independent of all the physical parameters, and its covariance is given by

$$\int \mathscr{D}(\vec{\xi}) \xi_\mu(s) \xi_\nu(t) = \delta_{\mu\nu} \times \begin{cases} s(1-t), & s \leqslant t \\ t(1-s), & t \leqslant s. \end{cases} \tag{4.4}$$

Eventually, the Boltzmann-like factors obviously arise from the potential part of the action S.

B. The Maxwell-Boltzmann term

As shown in Ref. [1], use of the FK formula (4.3) for the diagonal matrix element (3.4) leads to the introduction of an auxiliary classical system $\mathscr{S}^*$ made of closed filaments interacting via two-body forces. Each filament is characterized by its spatial position $\vec{r}$ and two internal degrees of freedom, the dimensionless path $\vec{\xi}(s)$ associated with its shape, and the species index α which specifies its spatial extension λ_α, and the strength e_α of its coupling with the other filaments. We denote by $\mathscr{E} = (\alpha, \vec{r}, \vec{\xi})$ the state of such a filament. Two filaments in states $\mathscr{E}$ and $\mathscr{E}'$ interact via the two-body potential $e_\alpha e_{\alpha'} v(\mathscr{E}, \mathscr{E}')$ with

$$v(\mathscr{E}, \mathscr{E}') = \int_0^1 ds\, v_c[|\vec{r} + \lambda_\alpha \vec{\xi}(s) - \vec{r}' - \lambda_{\alpha'} \vec{\xi}'(s)|]. \tag{4.5}$$

Defining the phase-space measure $d\mathscr{E}$ for a filament such that $d\mathscr{E} = d\alpha d\vec{r} \mathscr{D}(\vec{\xi})$ ($d\alpha$ means a discrete summation) and setting $z(\mathscr{E}) = (2\sigma_\alpha + 1) z_\alpha / (2\pi\lambda_\alpha^2)^{3/2}$ for its fugacity, we find that the MB grand-partition function given by (3.3) is identical to the grand-partition function of $\mathscr{S}^*$ [1],

$$\Xi_\Lambda^{\mathrm{MB}} = \Xi_\Lambda(\mathscr{S}^*) = \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{k=1}^{N} d\mathscr{E}_k z(\mathscr{E}_k) \times \left[-\frac{\beta}{2} \sum_{k \neq l} e_{\alpha_k} e_{\alpha_l} v(\mathscr{E}_k, \mathscr{E}_l) \right]. \tag{4.6}$$

C. Exchange terms

First, we consider the two-body exchange term (3.5). It is quite natural to interpret the FK representation (4.3) of the off-diagonal matrix element (3.6) in terms of two opened filaments $\mathscr{F}_{12}^{\alpha}$ and $\mathscr{F}_{21}^{\alpha}$ immersed in a bath of closed filaments. Each opened filament $\mathscr{F}_{kl}^{\alpha}$ describes the exchange of a particle α from the position $\vec{r}_k$ to the position $\vec{r}_l$ and its shape is parametrized by

$$\vec{\omega}_{kl}^{\alpha}(s)=(1-s)\vec{r}_k+s\vec{r}_l+\lambda_{\alpha}\vec{\xi}_k(s). \tag{4.7}$$

The closed filaments $\mathscr{C}$ are associated with the $(N-2)$ unexchanged particles (see Fig. 1). All the opened and closed filaments interact via the two-body potentials of the type (4.5). Inserting the FK representation of the matrix element (3.6) into the expression (3.5), we then obtain

$$\Xi_{\Lambda}^{(2)}=\frac{1}{2!}\sum_{\alpha}(-1)^{2\sigma_{\alpha}}(2\sigma_{\alpha}+1)\frac{z_{\alpha}^2}{(2\pi\lambda_{\alpha}^2)^3}\int_{\Lambda^2}d\vec{r}_1 d\vec{r}_2\int\mathscr{D}(\vec{\xi}_1)\mathscr{D}(\vec{\xi}_2)\exp\left[\frac{-(\vec{r}_2-\vec{r}_1)^2}{\lambda_{\alpha}^2}-\beta e_{\alpha}^2 v(\mathscr{F}_{12}^{\alpha},\mathscr{F}_{21}^{\alpha})\right]$$
$$\times\left\{\sum_{N=0}^{\infty}\frac{1}{N!}\int\prod_{k=1}^{N}d\mathscr{C}_k z(\mathscr{C}_k)\exp[-\beta e_{\alpha}e_{\alpha_k}v(\mathscr{F}_{12}^{\alpha},\mathscr{C}_k)-\beta e_{\alpha}e_{\alpha_k}v(\mathscr{F}_{21}^{\alpha},\mathscr{C}_k)]\exp\left[-\frac{\beta}{2}\sum_{k\neq l}e_{\alpha_k}e_{\alpha_l}v(\mathscr{C}_k,\mathscr{C}_l)\right]\right\}, \tag{4.8}$$

where the phase-space measure $d\mathscr{C}$ and the fugacity $z(\mathscr{C})$ for the closed filaments are defined as above. The sum $\Sigma_{N=0}^{\infty}\ldots$ in the right-hand side of (4.8) is nothing but the grand-partition function $\Xi_{\Lambda}(\mathscr{S}^{\star}|\mathscr{F}_{12}^{\alpha},\mathscr{F}_{21}^{\alpha})$ of the system $\mathscr{S}^{\star}$ in the presence of the external one-body potential $e_{\alpha}e_{\alpha'}[v(\mathscr{F}_{12}^{\alpha},\mathscr{C}')+v(\mathscr{F}_{21}^{\alpha},\mathscr{C}')]$ created by the two opened filaments.

It is convenient to rewrite $\Xi_{\Lambda}(\mathscr{S}^{\star}|\mathscr{F}_{12}^{\alpha},\mathscr{F}_{21}^{\alpha})$ as

$$\Xi_{\Lambda}(\mathscr{S}^{\star}|\mathscr{F}_{12}^{\alpha},\mathscr{F}_{21}^{\alpha})=\Xi_{\Lambda}(\mathscr{S}^{\star})\exp\left\{-\beta\int_0^1 dg\int d\mathscr{C}'\rho_g(\mathscr{C}'|\mathscr{F}_{12}^{\alpha},\mathscr{F}_{21}^{\alpha})e_{\alpha}e_{\alpha'}[v(\mathscr{F}_{12}^{\alpha},\mathscr{C}')+v(\mathscr{F}_{21}^{\alpha},\mathscr{C}')]\right\}, \tag{4.9}$$

which follows from a standard coupling-parameter integration technique. In (4.9), $\rho_g(\mathscr{C}'|\mathscr{F}_{12}^{\alpha},\mathscr{F}_{21}^{\alpha})$ is the one-body density of the inhomogeneous system $\mathscr{S}^{\star}$ when the external potential due to the opened filaments is multiplied by the dimensionless coupling constant g [the fugacity $z(\mathscr{C})$ and the temperature being kept fixed]. Moreover, $\Xi_{\Lambda}(\mathscr{S}^{\star})$, which corresponds to the cage $g=0$, reduces to the grand-partition function of the homogeneous system introduced in Sec. IV B. The replacement of $\Xi_{\Lambda}(\mathscr{S}^{\star}|\mathscr{F}_{12}^{\alpha},\mathscr{F}_{21}^{\alpha})$ by (4.9) in (4.8) then gives

$$\Xi_{\Lambda}^{(2)}=\Xi_{\Lambda}(\mathscr{S}^{\star})E_{\Lambda}^{(2)}, \tag{4.10}$$

where the two-body exchange factor $E_{\Lambda}^{(2)}$ reads

$$E_{\Lambda}^{(2)}=\frac{1}{2!}\sum_{\alpha}(-1)^{2\sigma_{\alpha}}(2\sigma_{\alpha}+1)\frac{z_{\alpha}^2}{(2\pi\lambda_{\alpha}^2)^3}\int_{\Lambda^2}d\vec{r}_1 d\vec{r}_2\int\mathscr{D}(\vec{\xi}_1)\mathscr{D}(\vec{\xi}_2)\exp\left[\frac{-(\vec{r}_2-\vec{r}_1)^2}{\lambda_{\alpha}^2}-\beta e_{\alpha}^2 v(\mathscr{F}_{12}^{\alpha},\mathscr{F}_{21}^{\alpha})\right]$$
$$\times\exp\left\{-\beta\int_0^1 dg\int d\mathscr{C}'\rho_g(\mathscr{C}'|\mathscr{F}_{12}^{\alpha},\mathscr{F}_{21}^{\alpha})e_{\alpha}e_{\alpha'}[v(\mathscr{F}_{12}^{\alpha},\mathscr{C}')+v(\mathscr{F}_{21}^{\alpha},\mathscr{C}')]\right\}. \tag{4.11}$$

Starting from the FK formula (4.3) for the off-diagonal matrix elements of $\exp(-\beta H_N)$ and following the same methods as above, we readily find for any $n\geq 3$

$$\Xi_{\Lambda}^{(n)}=\Xi_{\Lambda}(\mathscr{S}^{\star})E_{\Lambda}^{(n)}, \tag{4.12}$$

where the exchange factor $E_{\Lambda}^{(n)}$ can be expressed in terms of n opened filaments $\mathscr{F}_{kl}^{\alpha}$ similarly to (4.11). Apart from simple permutation, spin, and z^n factors, $E_{\Lambda}^{(n)}$ reduces to integrals over the opened-filament extremities and shapes of the product of the two exponentials

$$\exp\left[-\sum_{\mathscr{F}}r_{kl}^2/2\lambda_{\alpha}^2-\frac{\beta}{2}\sum_{\mathscr{F}\neq\mathscr{F}'}e_{\alpha}e_{\alpha'}v(\mathscr{F},\mathscr{F}')\right] \tag{4.13a}$$

and

$$\exp\left[-\beta\int_0^1 dg\int d\mathscr{C}'\rho_g(\mathscr{C}'|\{\mathscr{F}\})\sum_{\mathscr{F}}e_{\alpha}e_{\alpha'}v(\mathscr{F},\mathscr{C}')\right]. \tag{4.13b}$$

The first one, (4.13a), corresponds to the exchange of n particles in the vacuum. The second one, (4.13b), takes into account the presence of the surrounding particles which are described by MB statistics. This many-body effect on the exchange is entirely determined by the one-body density $\rho_g(\mathscr{C}'|\{\mathscr{F}\})$ of the inhomogeneous system $\mathscr{S}^{\star}$ submitted to the external potential $g\Sigma_{\mathscr{F}}e_{\alpha}e_{\alpha'}v(\mathscr{F},\mathscr{C}')$.

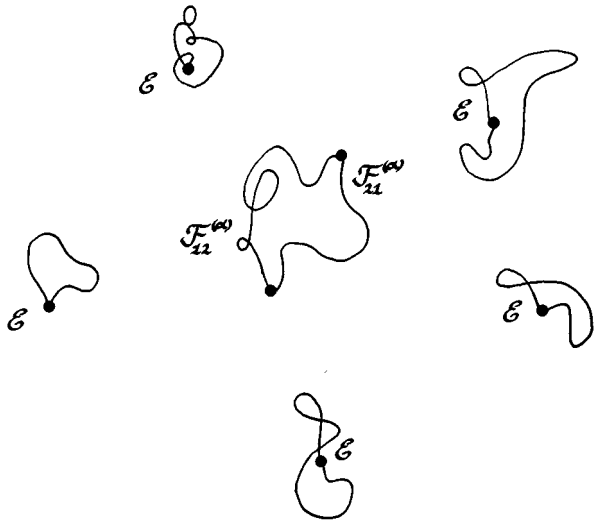

FIG. 1. The two opened filaments $\mathscr{F}_{12}^{\alpha}$ and $\mathscr{F}_{21}^{\alpha}$ immersed in a bath of closed filaments $\mathscr{E}$. The black circles denote either the extremities of the opened filaments or the positions of the closed ones. The curves represent the shapes of the filaments.

D. The grand-partition function

Inserting the FK expressions (4.6) and (4.12) of $\Xi_{\Lambda}^{\mathrm{MB}}$ and $\Xi_{\Lambda}^{(n)}$, respectively, into the series (3.2), we find

$$\Xi_{\Lambda}=\Xi_{\Lambda}(\mathscr{S}^{\star})\left\{1+\sum_{n=2}^{\infty}E_{\Lambda}^{(n)}\right\}. \tag{4.14}$$

In this representation, the system $\mathscr{S}^{\star}$ of closed filaments naturally appears as a reference system. Indeed, as described above, the evaluation of the collective part of each exchange factor $\mathscr{E}_{\Lambda}^{(n)}$ amounts to considering an inhomogeneous situation where n impurities (the opened filaments) are immersed in $\mathscr{S}^{\star}$.

Eventually, let us mention that another representation of the grand-partition function can be found [36,37] by starting also from the FK expression (4.3). Since any permutation of n objects is the product of p cycles, any set of n opened filaments $\mathscr{F}_{kl}^{\alpha}$ can be viewed as a collection of p loops. Each loop $\mathscr{L}^{(q)}$ is made of q opened filaments involved in a given cyclic permutation. For instance, the two opened filaments $\mathscr{F}_{12}^{\alpha}$ and $\mathscr{F}_{21}^{\alpha}$ constitute a single loop $\mathscr{L}^{(2)}$. Within this interpretation, the whole Slater expansion (3.1) of Ξ_{Λ} is identified to the grand-partition function of a mixture of classical loops $\mathscr{L}^{(q)}$ with $q=1,2,3,\ldots,\infty$. The loops $\mathscr{L}^{(1)}$ are the closed filaments $\mathscr{E}$ of $\mathscr{S}^{\star}$. The activities of the loops $\mathscr{L}^{(q)}$ for $q\geqslant 2$ incorporate self-energy terms arising from the two-body interactions between the q opened filaments which constitute $\mathscr{L}^{(q)}$, as well as permutation and spin factors which may be negative in the fermionic case. In this approach, the MB and exchange contributions are treated on an equal footing, at least at a formal level. In the following, we shall only use the perturbative representation (4.14).

V. DENSITY EXPANSIONS OF THE THERMODYNAMIC QUANTITIES

A. Slater expansion of the pressure

In the present approach, it is quite convenient to derive first the density expansion of the pressure P which is directly related to the grand-partition function via

$$\beta P=\lim_{\mathrm{TL}}\frac{1}{\Lambda}\ln\Xi_{\Lambda}. \tag{5.1}$$

Use of the representation (4.14) for Ξ_{Λ} in (5.1) provides a similar series for βP, i.e.,

$$\beta P=\beta P^{\mathrm{MB}}+\sum_{n=2}^{\infty}\beta P^{(n)}, \tag{5.2}$$

where $\beta P^{(n)}$ is the contribution of n exchanged particles. The MB pressure naturally comes out from the term

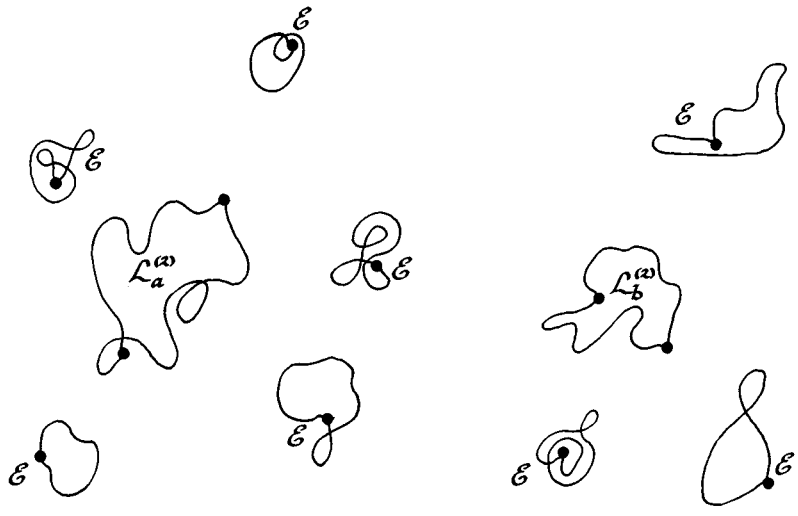

FIG. 2. Two loops $\mathscr{L}_{a}^{(2)}$ and $\mathscr{L}_{b}^{(2)}$ immersed in a bath of closed filaments $\mathscr{E}$. Each loop describes the exchange of two particles of the same species. The black circles and the curves have the same meaning as in Fig. 1.

$\Xi_\Lambda(\mathscr{S}^\star)=\Xi_\Lambda^{\rm MB}$ which is factored in (4.14). The other terms in (5.2) arise from the expansion

$$\ln\left[1+\sum_{n=2}^{\infty} E_\Lambda^{(n)}\right]=\sum_{p=1}^{\infty}\frac{(-1)^{p+1}}{p}\left[\sum_{n=2}^{\infty} E_\Lambda^{(n)}\right]^p. \quad (5.3)$$

Each $P^{(n)}$ corresponds to the sum of all the products $\Pi_{k=1}^q[E_\Lambda^{(n_k)}]^{p_k}$ with $\Sigma_{k=1}^q n_k p_k=n$ which appear in the right-hand side of (5.3). The first $P^{(n)}$'s obviously read

$$\beta P^{(2)}=\lim_{\rm TL}\frac{1}{\Lambda}E_\Lambda^{(2)}, \quad (5.4a)$$

$$\beta P^{(3)}=\lim_{\rm TL}\frac{1}{\Lambda}E_\Lambda^{(3)}, \quad (5.4b)$$

$$\beta P^{(4)}=\lim_{\rm TL}\frac{1}{\Lambda}\left(E_\Lambda^{(4)}-\frac{[E_\Lambda^{(2)}]^2}{2}\right). \quad (5.4c)$$

The general structure of the $P^{(n)}$'s is, of course, similar to that of the $E^{(n)}$'s studied is Sec. IV C. In each $P^{(n)}$, homogeneous monomials of degree n in the z's can be factored in front of integrals over n opened filaments with one of their extremities fixed. In particular, we easily infer from (4.11)

$$\beta P^{(2)}=\frac{1}{2!}\sum_\alpha(-1)^{2\sigma_\alpha}(2\sigma_\alpha+1)\frac{z_\alpha^2}{(2\pi\lambda_\alpha^2)^3}\int_\Lambda d\vec{r}_2\int\mathscr{D}(\vec{\xi}_1)\mathscr{D}(\vec{\xi}_2)\exp\left[\frac{-(\vec{r}_2-\vec{r}_1)^2}{\lambda_\alpha^2}-\beta e_\alpha^2 v(\mathscr{F}_{12}^\alpha,\mathscr{F}_{21}^\alpha)\right]$$
$$\times\exp\left\{-\beta\int_0^1 dg\int d\mathscr{E}'\rho_g(\mathscr{E}'|\mathscr{F}_{12}^\alpha,\mathscr{F}_{21}^\alpha)e_\alpha e_{\alpha'}[v(\mathscr{F}_{12}^\alpha,\mathscr{E}')+v(\mathscr{F}_{21}^\alpha,\mathscr{E}')]\right\}. \quad (5.5)$$

The convergence of the integrals involved in the $P^{(n)}$'s is ensured by the combination of two mechanisms. As quoted in Sec. IV D, each set of n opened filaments can be decomposed in p loops. The Gaussian measures in the ξ's, as well as the Gaussian factors $\exp[-r_{kl}^2/(2\lambda_\alpha^2)]$, control the integrability with respect to the sizes of the loops. In addition, the sufficiently fast decay with respect to the relative distances between the loops results from the truncated structure of the corresponding integrands and from screening. In particular, in the case of $P^{(4)}$, the contributions (4.13a), (4.13b) associated with the two loops $\mathscr{L}^{(2)}$ drawn in Fig. 2 and which arise from both $E_\Lambda^{(4)}$ and $-[E_\Lambda^{(2)}]^2/2$, do cancel in an integrable way for large separations of the $\mathscr{L}^{(2)}$'s (see Sec. V C).

B. The MB contribution

In the first two papers of the present series [1,13], we have studied the expansion of the MB pressure $\beta P^{\rm MB}$ with respect to the MB densities $\rho_\alpha^{\rm MB}$. These densities are those calculated from the MB grand-partition function for the fugacities z_α, i.e.,

$$\rho_\alpha^{\rm MB}=z_\alpha\lim_{\rm TL}\left.\frac{\delta\ln\Xi_\Lambda^{\rm MB}}{\delta z_\alpha(\vec{r})}\right|_{z_\alpha(\vec{r})=z_\alpha}. \quad (5.6)$$

They are, of course, different from the real densities ρ_α calculated from (2.4) for the same fugacities, because of the nonvanishing exchange contributions $\Xi_\Lambda^{\rm n}$ to Ξ_Λ. The density expansion of the pressure is obtained by starting from a diagrammatical representation of the filament correlations of the homogeneous system $\mathscr{S}^\star$ [1]. A scaling analysis with respect to $\kappa^{\rm MB}$ shows that $\beta P^{\rm MB}$ reduces to a double integer series with respect to $(\rho^{\rm MB})^{1/2}$ and $\ln\rho^{\rm MB}$.

C. Exchange contributions

For expanding the exchange contributions $\beta P^{(n)}$, we consider the expressions of the type (5.5). In the latter, the nontrivial density dependence is entirely contained in the filament density $\rho_g(\mathscr{E}'|\{\mathscr{F}\})$ of the inhomogeneous system $\mathscr{S}^\star$ in the presence of the external potential $g\Sigma_{\mathscr{F}}e_\alpha e_{\alpha'}v(\mathscr{F},\mathscr{E}')$. Such a quantity may be represented by a perturbative series in terms of the external potential

$$\phi_g(\mathscr{E}'|\{\mathscr{F}\})=g\sum_{\mathscr{F}} e_\alpha e_{\alpha'}v(\mathscr{F},\mathscr{E}').$$

The first terms read [38]

$$\rho_g(\mathscr{E}'|\{\mathscr{F}\})=\rho(\mathscr{E}') \quad (5.7a)$$

$$-\beta\int d\mathscr{E}''\phi_g(\mathscr{E}''|\{\mathscr{F}\})$$
$$\times[\rho_T(\mathscr{E}',\mathscr{E}'')+\rho(\mathscr{E}')\delta(\mathscr{E}''-\mathscr{E}')] \quad (5.7b)$$

$$+\cdots.$$

In (5.7), $\rho(\mathscr{E}')$ is the one-body density of the homogeneous system $\mathscr{S}^\star$ associated with the MB contributions, while $\rho_T(\mathscr{E}',\mathscr{E}'')$ is the corresponding truncated two-body density. Similarly, the terms of order ϕ_g^n ($n\geqslant 2$), which are not written explicitly in (5.7), involve combinations of the fully truncated p-body densities of the previous system with $2\leqslant p\leqslant n+1$. These combinations have the same structure as that of the $(n+1)$ point charge correlations for an ordinary Coulomb system with point charges [for instance, see the combination for $n=1$ in (5.7b)].

When inserting the perturbative series (5.7) into the many-body screening factor (4.13b), the contribution of (5.7a) reads (in the exponent)

$$-\beta\sum_{\mathscr{F}} e_\alpha \int_0^1 dg \int d\mathscr{E}' e_{\alpha'} \rho(\mathscr{E}') v(\mathscr{F},\mathscr{E}')$$

$$= 2\pi\beta \sum_{\mathscr{F}} e_\alpha \sum_{\alpha'} e_{\alpha'} \lambda_{\alpha'}^2 \int_0^1 ds \int \mathscr{D}(\vec{\xi}') \rho_{\alpha'}(\vec{\xi}') [\xi_\mu'(s)]^2, \tag{5.8}$$

where the Taylor expansion of $v(\mathscr{F},\mathscr{E}')$ with respect to $\lambda_{\alpha'}$, the rotational invariance of $\rho_{\alpha'}(\vec{\xi}')$, and Poisson's equation for $1/r$ have been used [notice that (5.8) does not depend on the shapes of the opened filaments $\mathscr{F}$]. The density expansion of (5.8) immediately follows from that of the translationally invariant density $\rho(\mathscr{E}')=\rho_\alpha(\vec{\xi}')$ derived in Ref. [1]. It takes the form of a double integer series in $(\rho^{\mathrm{MB}})^{1/2}$ and $\ln \rho^{\mathrm{MB}}$, similarly to the expansion of βP^{MB}.

For studying the contributions to (4.13b) of the next terms of order ϕ_g^n ($n \geqslant 1$) in (5.7), we replace all the correlations of the homogeneous system $\mathscr{S}^\star$ by series of prototype graphs similar to those which define the correlations between two filaments [1]. All these prototype graphs are built with the same resummed bonds F^{MB} as those introduced for the two-body correlations. The previous contributions are then rewritten as integrals over products of resummed bonds F^{MB} and potentials $v(\mathscr{F},\mathscr{E}')$. The behavior with respect to the MB densities of these integrals can be studied by techniques similar to those introduced in Ref. [13] for evaluating the purely MB contributions. Here, we do not reproduce the details of the analysis, but just mention the basic mechanisms which control the behaviors of interest. In the zero-density limit, the large-r divergencies arise from integer inverse powers of r. The many-body screening effects, which remove these divergencies, amount to scaling r with respect to the MB Debye length $(\kappa^{\mathrm{MB}})^{-1}$. Consequently, screening generates integer powers of κ^{MB} and $\ln \kappa^{\mathrm{MB}}$ (the logarithms are linked to the presence of $1/r^3$ tails which are at the borderline for integrability). The structure of the expansion of (4.13b) is then quite similar to that of the MB pressure itself. The former is not affected by the integration over the opened-filament degrees of freedom with the weighting self-factor (4.13a). Indeed, each piece of (4.13a) associated with a given loop is short ranged, while two of these pieces are linked by Coulomb-like interactions which are again ultimately screened on a range $(\kappa^{\mathrm{MB}})^{-1}$ [39]. It results that, apart from a trivial z^n prefactor, $\beta P^{(n)}$ reduces to a double integer series in $(\rho^{\mathrm{MB}})^{1/2}$ and $\ln \rho^{\mathrm{MB}}$, as βP^{MB}.

D. Elimination of the fugacities and of the MB densities

Once the above expansions of βP^{MB} and $\beta P^{(n)}$ have been performed, it still remains to eliminate the fugacities and the MB densities in favor of the real densities. The thermodynamical activity a_α of species α is defined through the thermodynamical relation

$$\ln a_\alpha = \frac{\partial}{\partial \rho_\alpha} \beta f\{\rho_\gamma\}|_\beta, \tag{5.9}$$

where $\beta f\{\rho_\gamma\}$ is the free energy per units of volume and $k_B T$. A straightforward manipulation of the relation (5.9) and of the standard formula

$$\beta P = \sum_\alpha \rho_\alpha \frac{\partial}{\partial \rho_\alpha} \beta f\{\rho_\gamma\}|_\beta - \beta f\{\rho_\gamma\} \tag{5.10}$$

then shows that

$$\rho_\alpha = a_\alpha \frac{\partial}{\partial a_\alpha} \beta P\{a_\gamma\}|_\beta. \tag{5.11}$$

Our method provides a perturbative representation of the pressure in terms of the activities a_γ and of the MB densities $\rho_\gamma^{\mathrm{MB}}$ which are such that

$$a_\alpha^{\mathrm{MB}}\{\rho_\gamma^{\mathrm{MB}}\} = a_\alpha. \tag{5.12}$$

Our knowledge of the MB thermodynamic quantities allows us to determine first the functions $a_\alpha^{\mathrm{MB}}\{\rho_\gamma^{\mathrm{MB}}\}$ from the definitions (5.9), and consequently to express $\rho_\alpha^{\mathrm{MB}}$ in terms of the a_γ's by inverting (5.12). Once the MB densities have been eliminated in favor of the a_α's in the Slater-like expansion (5.2), we are left with the function $P\{a_\gamma\}$. A simple inversion of (5.11) then gives the pressure in terms of the real densities ρ_α only, as required.

E. General structure of the density expansions

As shown in Secs. V B and V C, βP^{MB} is represented by a double integer series in $(\rho^{\mathrm{MB}})^{1/2}$ and $\ln \rho^{\mathrm{MB}}$, while $\beta P^{(n)}$ also reduces to similar series multiplied by prefactors a^n. This general structure, involving half-integer powers and logarithms, is conserved through the elimination of $\{\rho_\alpha^{\mathrm{MB}}\}$ and $\{a_\alpha\}$ in favor of $\{\rho_\alpha\}$, as a consequence of the low-density behaviors

$$\rho_\alpha \sim \rho_\alpha^{\mathrm{MB}} \sim \frac{(2\sigma_\alpha+1)}{(2\pi\lambda_\alpha^2)^{3/2}} a_\alpha, \tag{5.13}$$

when all the a_α's go to zero. Eventually, the density expansion of the pressure reads

$$\beta P = \sum_\alpha \rho_\alpha + \sum_{l,n,p} \mathscr{P}_l\{\rho_\alpha\} \left(4\pi\beta \sum_\alpha e_\alpha^2 \rho_\alpha \right)^{n/2} \times \ln^p \left(4\pi\beta \sum_\alpha e_\alpha^2 \rho_\alpha \right), \tag{5.14}$$

where $\mathscr{P}_l\{\rho_\alpha\}$ are homogeneous polynomials of degree l in the densities ρ_α with coefficients depending on the temperature while l,n,p are relative integers such that $l \geqslant 2$, $p \geqslant 0$, and $l + n/2 \geqslant \frac{3}{2}$ (n may take negative values).

Using (5.14) in the thermodynamic relation (5.10), we see that the expansion of the free energy must exhibit a structure similar to that of the pressure, i.e.,

$$\beta f=\sum_\alpha \rho_\alpha\left[\ln\left(\frac{(2\pi\lambda_\alpha^2)^{3/2}\rho_\alpha}{(2\sigma_\alpha+1)}\right)-1\right]+\sum_{l,n,p} Q_l\{\rho_\alpha\}$$
$$\times\left(4\pi\beta\sum_\alpha e_\alpha^2\rho_\alpha\right)^{n/2}\ln^p\left(4\pi\beta\sum_\alpha e_\alpha^2\rho_\alpha\right), \quad (5.15)$$

with the same constraints on l,n,p as above. Moreover, the homogeneous polynomials Q_l are easily computed in terms of the $\mathscr{P}_l$'s by an identification method. The expansions of all the other thermodynamic functions can be inferred from (5.14) or (5.15) by combining thermodynamic identities and relations between Jacobians. As in (5.14) and (5.15), their generic terms reduce to polynomials in the ρ_α's multiplied by integer powers of κ and $\ln\kappa$ with $\kappa=(4\pi\beta\Sigma_\alpha e_\alpha^2\rho_\alpha)^{1/2}$.

VI. EXPLICIT CALCULATIONS UP TO ORDER $\rho^{5/2}$

The general scheme described in the preceding section is now applied to the calculations of the virial coefficients up to order $\rho^{5/2}$. According to the low-density behaviors (5.13), this requires the evaluation of the MB pressure up to order $(\rho^{\mathrm{MB}})^{5/2}$. At the same time, only the two-body exchange contribution $\beta P^{(2)}$ has to be taken into account. All the other exchange contributions $\beta P^{(n)}$ with $n\geqslant 3$ are at least of order ρ^3 [40].

A. The MB pressure

The expansion in the $\rho_\alpha^{\mathrm{MB}}$'s of βP^{MB} has been calculated in Ref. [13] within the diagrammatical method briefly outlined in Sec. V B. We find

$$\beta P^{\mathrm{MB}}=\sum_\alpha \rho_\alpha^{\mathrm{MB}}-\frac{(\kappa^{\mathrm{MB}})^3}{24\pi}-\frac{\pi}{3}\left(C+\ln 3+\frac{1}{2}\right)\sum_{\alpha,\beta}\beta^3 e_\alpha^3 e_\beta^3\rho_\alpha^{\mathrm{MB}}\rho_\beta^{\mathrm{MB}}$$
$$-\frac{1}{2}\sum_{\alpha,\beta}\rho_\alpha^{\mathrm{MB}}\rho_\beta^{\mathrm{MB}}\lim_{R\to\infty}\left\{\int_{r<R}d\vec{r}\left[(2\pi\lambda_{\alpha\beta}^2)^{3/2}\langle\vec{r}|\exp(-\beta h_{\alpha\beta})|\vec{r}\rangle-1+\frac{\beta e_\alpha e_\beta}{r}-\frac{\beta^2 e_\alpha^2 e_\beta^2}{2r^2}\right]\right.$$
$$\left.+\frac{2\pi}{3}\beta^3 e_\alpha^3 e_\beta^3\ln(\kappa^{\mathrm{MB}}R)\right\}+\pi\left(\frac{1}{3}-\frac{C}{2}-\ln 2\right)\sum_{\alpha,\beta}\beta^4 e_\alpha^4 e_\beta^4\kappa^{\mathrm{MB}}\rho_\alpha^{\mathrm{MB}}\rho_\beta^{\mathrm{MB}}+C_1\sum_{\alpha,\beta,\gamma}\beta^5 e_\alpha^3 e_\beta^4 e_\gamma^3(\kappa^{\mathrm{MB}})^{-1}\rho_\alpha^{\mathrm{MB}}\rho_\beta^{\mathrm{MB}}\rho_\gamma^{\mathrm{MB}}$$
$$+C_2\sum_{\alpha,\beta,\gamma,\delta}\beta^6 e_\alpha^3 e_\beta^3 e_\gamma^3 e_\delta^3(\kappa^{\mathrm{MB}})^{-3}\rho_\alpha^{\mathrm{MB}}\rho_\beta^{\mathrm{MB}}\rho_\gamma^{\mathrm{MB}}\rho_\delta^{\mathrm{MB}}-\frac{3}{4}\sum_{\alpha,\beta}\beta e_\alpha e_\beta\kappa^{\mathrm{MB}}\rho_\alpha^{\mathrm{MB}}\rho_\beta^{\mathrm{MB}}$$
$$\times\lim_{R\to\infty}\left\{\int_{r<R}d\vec{r}\left[(2\pi\lambda_{\alpha\beta}^2)^{3/2}\langle\vec{r}|\exp(-\beta h_{\alpha\beta})|\vec{r}\rangle-1+\frac{\beta e_\alpha e_\beta}{r}-\frac{\beta^2 e_\alpha^2 e_\beta^2}{2r^2}\right]+\frac{2\pi}{3}\beta^3 e_\alpha^3 e_\beta^3\ln(\kappa^{\mathrm{MB}}R)\right\}$$
$$+\frac{1}{16}\sum_\alpha\frac{\beta^2\hbar^2 e_\alpha^2}{m_\alpha}(\kappa^{\mathrm{MB}})^3\rho_\alpha^{\mathrm{MB}}+O((\rho^{\mathrm{MB}})^3\ln\rho^{\mathrm{MB}}). \quad (6.1)$$

where the pure numerical constants C_1 and C_2 have been estimated as $C_1\sim 15.201\pm 0.001$ and $C_2\sim -14.734\pm 0.001$, while C is the Euler-Mascheroni constant, $C\sim 0.577\ldots$. Moreover, $h_{\alpha\beta}$ is the one-body Coulomb Hamiltonian of the relative particle with reduced mass $m_{\alpha\beta}=m_\alpha m_\beta/(m_\alpha+m_\beta)$ is the potential $e_\alpha e_\beta/r$, and $\lambda_{\alpha\beta}$ is the corresponding thermal de Broglie wavelength, $\lambda_{\alpha\beta}=(\beta\hbar^2/m_{\alpha\beta})^{1/2}$.

B. The two-body exchange contribution

The a_α^2 prefactors in $\beta P^{(2)}$ are at least of order ρ^2. Thus the many-body screening factor (4.13b) has to be evaluated up to order $(\rho^{\mathrm{MB}})^{1/2}$.

The contribution (5.8) to (4.13b) of (5.7a) is obviously of order ρ^{MB} since $\rho_\alpha(\vec{\xi}')$ reduces to $\rho_\alpha^{\mathrm{MB}}$ at lowest order [1]. The leading contribution to (4.13b) of (5.7b) arises from the simplest Debye prototype graph in the Π representation of $\rho_T(\mathscr{E}',\mathscr{E}'')$, i.e.,

$$\rho_{\alpha'}(\vec{\xi}')\rho_{\alpha''}(\vec{\xi}'')(-\beta e_{\alpha'}e_{\alpha''})\frac{\exp(-\kappa^{\mathrm{MB}}|\vec{r}''-\vec{r}'|)}{|\vec{r}''-\vec{r}'|}. \quad (6.2)$$

In addition, it is legitimate to replace each $\rho_\alpha(\vec{\xi})$ by $\rho_\alpha^{\mathrm{MB}}$ according to [1]

$$\rho_\alpha(\vec{\xi})=\rho_\alpha^{\mathrm{MB}}+O((\rho^{\mathrm{MB}})^2). \quad (6.3)$$

This gives for the previous contribution [in the exponent of (4.13b)]

$$\frac{\beta^2}{2}e_\alpha^2\sum_{i,j=1}^2\sum_{\alpha'}\int d\vec{r}'\,\mathscr{D}(\vec{\xi}')e_{\alpha'}v(\mathscr{F}_i,\mathscr{E}')\rho_{\alpha'}^{\mathrm{MB}}\int d\vec{r}''\,\mathscr{D}(\vec{\xi}'')\sum_{\alpha''}e_{\alpha''}v(\mathscr{F}_j,\mathscr{E}'')$$
$$\times\left[-\beta e_{\alpha'}e_{\alpha''}\rho_{\alpha''}^{\mathrm{MB}}\frac{\exp(-\kappa^{\mathrm{MB}}|\vec{r}''-\vec{r}'|)}{|\vec{r}''-\vec{r}'|}+\delta_{\alpha''\alpha'}\delta(\vec{r}''-\vec{r}')\delta(\vec{\xi}''-\vec{\xi}')\right], \quad (6.4)$$

with $\mathscr{F}_1 \equiv \mathscr{F}_{12}^{\alpha}$ and $\mathscr{F}_2 \equiv \mathscr{F}_{21}^{\alpha}$. In (6.4), the integral over finite distances r' is of order ρ^{MB} at least. The remaining integral over large distances $r' \sim (\kappa^{\mathrm{MB}})^{-1}$ may be estimated, at lowest order in ρ^{MB}, by replacing each potential $v(\mathscr{F}_i, \mathscr{E})$ by its monopole-monopole asymptotic form

$$v(\mathscr{F}_i, \mathscr{E}) = 1/r + O(1/r^2). \tag{6.5}$$

The integrals over the filament shapes $\vec{\xi}'(s)$ and $\vec{\xi}''(s)$ are then easily performed and the low-density limit form of (6.4) reduces to

$$2\beta^2 e_\alpha^2 \int d\vec{r}' \sum_{\alpha'} \rho_{\alpha'}^{\mathrm{MB}} \frac{e_{\alpha'}}{r'} \int d\vec{r}'' \sum_{\alpha''} \frac{e_{\alpha''}}{r''} \left[-\beta e_{\alpha'} e_{\alpha''} \rho_{\alpha''}^{\mathrm{MB}} \frac{\exp(-\kappa^{\mathrm{MB}} |\vec{r}'' - \vec{r}'|)}{|\vec{r}'' - \vec{r}'|} + \delta_{\alpha'' \alpha'} \delta(\vec{r}'' - \vec{r}') \right]$$

$$= 2\beta^2 e_\alpha^2 \int d\vec{r}' \sum_{\alpha'} \rho_{\alpha'}^{\mathrm{MB}} \frac{e_{\alpha'}^2}{r'} \frac{\exp(-\kappa^{\mathrm{MB}} r')}{r'}$$

$$= 2\beta e_\alpha^2 \kappa^{\mathrm{MB}}. \tag{6.6}$$

In deriving the second line of (6.6), we have used that $\int d\vec{r}''$... is nothing but the electrostatic potential at the origin created by a point charge $e_{\alpha'}$ at $\vec{r}'$ plus its Debye screening cloud, i.e., $e_{\alpha'} \exp(-\kappa^{\mathrm{MB}} r')/r'$.

The expression (6.6) constitutes the leading contribution of (5.7) to the exponent of (4.13b). The corrections to (6.6) are at least of order ρ^{MB} [41], as shown by a scaling analysis with respect to κ^{MB} similar to that of Ref. [13]. Thus the many-body screening factor (4.13b) reads

$$\exp\left[-\beta \int_0^1 dg \int d\mathscr{E}' \rho_g(\mathscr{E}' | \mathscr{F}_1, \mathscr{F}_2) \sum_{i=1}^{2} e_\alpha e_{\alpha'} v(\mathscr{F}_i, \mathscr{E}') \right] = 1 + 2\beta e_\alpha^2 \kappa^{\mathrm{MB}} + O(\rho^{\mathrm{MB}} \ln \rho^{\mathrm{MB}}). \tag{6.7}$$

This simple result, which does not depend on the shapes of the filaments $\mathscr{F}_1$ and $\mathscr{F}_2$, is easily recovered as follows. In the low-density limit, the characteristic sizes of the opened and closed filaments become small compared to the mean distance between these objects. As far as many-body effects on the two-body exchange are concerned, the physical picture which emerges is that of a classical point charge impurity $2e_\alpha$ immersed in a mixture of classical point charges $e_{\alpha'}$. The corresponding screening factor has the same structure as (4.13b) with the substitutions $\mathscr{E}' \to \vec{r}'$, $\rho_g(\mathscr{E}' | \mathscr{F}_1, \mathscr{F}_2) \to \rho_{2ge_\alpha}(\alpha', \vec{r}')$, $\Sigma_{i=1}^{2} e_\alpha e_{\alpha'} v(\mathscr{F}_i, \mathscr{E}') \to 2e_\alpha e_{\alpha'}/r'$. In addition, the inhomogeneous density $\rho_{2ge_\alpha}(\alpha', \vec{r}')$ of species α' in the presence of the impurity $2ge_\alpha$ fixed at the origin, is given at lowest order by Debye mean-field theory,

$$\rho_{2ge_\alpha}(\alpha', \vec{r}') = \rho_{\alpha'}^{\mathrm{MB}} - 2\beta g e_\alpha e_{\alpha'} \rho_{\alpha'}^{\mathrm{MB}} \frac{\exp(-\kappa^{\mathrm{MB}} r')}{r'}. \tag{6.8}$$

The first term in (6.8) does not contribute to the screening factor by virtue of the neutrality condition. The contribution of the second term is identical to (6.6) and we indeed recover (6.7).

Inserting the expansion (6.7) in (5.5), we find

$$\beta P^{(2)} = \frac{1}{2} \sum_{\alpha} (-1)^{2\sigma_\alpha} (2\sigma_\alpha + 1) \frac{a_\alpha^2}{(2\pi\lambda_\alpha^2)^3} \int d\vec{r}_2 \int \mathscr{D}(\vec{\xi}_1) \int \mathscr{D}(\vec{\xi}_2) \exp\left[-\frac{(\vec{r}_2 - \vec{r}_1)^2}{\lambda_\alpha^2} - \beta e_\alpha^2 v(\mathscr{F}_1, \mathscr{F}_2) \right]$$
$$\times \{1 + 2\beta e_\alpha^2 \kappa^{\mathrm{MB}} + O(\rho^{\mathrm{MB}} \ln^{\mathrm{MB}})\}$$

$$= \frac{1}{2} \sum_{\alpha} (-1)^{2\sigma_\alpha} (2\sigma_\alpha + 1) a_\alpha^2 \int d\vec{r}_2 \left\langle \vec{r}_2 \vec{r}_1 \right| \exp\left\{ -\beta \left[-\frac{\hbar^2}{2m_\alpha} \Delta_1 - \frac{\hbar^2}{2m_\alpha} \Delta_2 + \frac{e_\alpha^2}{|\vec{r}_2 - \vec{r}_1|} \right] \right\} \left| \vec{r}_1 \vec{r}_2 \right\rangle$$
$$\times \{1 + 2\beta e_\alpha^2 \kappa^{\mathrm{MB}} + O(\rho^{\mathrm{MB}} \ln \rho^{\mathrm{MB}})\}$$

$$= \frac{1}{2} \sum_{\alpha} (-1)^{2\sigma_\alpha} (2\sigma_\alpha + 1) \frac{a_\alpha^2}{(\pi\lambda_\alpha^2)^{3/2}} [1 + 2\beta e_\alpha^2 \kappa^{\mathrm{MB}}] \int d\vec{r} \langle -\vec{r} | \exp(-\beta h_{\alpha\alpha}) | \vec{r} \rangle + O(\rho^3 \ln \rho). \tag{6.9}$$

The second line of (6.9) follows by applying backwards the FK formula (4.3) with $N=2$, $|\vec{R}_2\rangle=|\vec{r}_1\vec{r}_2\rangle$, and $\langle\vec{R}_2'|=\langle\vec{r}_2\vec{r}_1|$, while in the final result, the trivial kinetic contribution of the center of mass of the two particles α is factored out.

C. Activities and MB densities

Now we express the activities a_γ and the MB densities $\rho_\gamma^{\mathrm{MB}}$ in terms of the real densities ρ_α, according to the prescriptions derived in Sec. V D. At the present order $\rho^{5/2}$, only the terms βP^{MB} and $\beta P^{(2)}$ have to be retained in the series (5.2), i.e.,

$$\beta P=\beta P^{\mathrm{MB}}+\beta P^{(2)}+O(\rho^3). \tag{6.10}$$

Using (6.10) in (5.11), we find

$$\begin{aligned}\rho_\alpha&=a_\alpha\frac{\partial}{\partial a_\alpha}\beta P^{\mathrm{MB}}+a_\alpha\frac{\partial}{\partial a_\alpha}\beta P^{(2)}+O(\rho^3)\\&=\rho_\alpha^{\mathrm{MB}}+a_\alpha\frac{\partial}{\partial a_\alpha}\beta P^{(2)}+O(\rho^3),\end{aligned} \tag{6.11}$$

where the second line results from the combination of (5.11) and (5.12) (for the MB quantities). The relation (6.11) shows that ρ_α differs from $\rho_\alpha^{\mathrm{MB}}$ by terms which are of order ρ^2 at least. This general feature (not specific to Coulomb systems) allows further simplifications in the elimination process.

The MB activities a_α^{MB} are readily obtained in terms of the MB densities $\rho_\gamma^{\mathrm{MB}}$ by inserting into the definitions (5.9) the expansion of the MB free energy which is explicitly known up to order $(\rho^{\mathrm{MB}})^{5/2}$ [13]. In the corresponding relation, we may substitute a_α for a_α^{MB} by virtue of (5.12). It is also legitimate, up to order $\rho^{3/2}$, to replace $\rho_\alpha^{\mathrm{MB}}$ by ρ_α because the difference $(\rho_\alpha-\rho_\alpha^{\mathrm{MB}})$ is of order ρ^2 at least. This gives

$$a_\alpha=\frac{(2\pi\lambda_\alpha^2)^{3/2}}{(2\sigma_\alpha+1)}\rho_\alpha-\frac{(2\pi\lambda_\alpha^2)^{3/2}}{2(2\sigma_\alpha+1)}\beta e_\alpha^2\kappa\rho_\alpha+O(\rho^2\ln\rho), \tag{6.12}$$

which is sufficient for our purpose.

When using the expression (6.9) of $\beta P^{(2)}$ in (6.11), we can replace κ^{MB} by $\kappa_a=\{4\pi\beta\Sigma_\alpha e_\alpha^2[(2\sigma_\alpha+1)/(2\pi\lambda_\alpha^2)^{3/2}]a_\alpha\}^{1/2}$ with the result

$$\begin{aligned}\rho_\alpha=\rho_\alpha^{\mathrm{MB}}&+(-1)^{2\sigma_\alpha}\frac{(2\sigma_\alpha+1)}{(\pi\lambda_\alpha^2)^{3/2}}a_\alpha^2(1+2\beta e_\alpha^2\kappa_a)\int d\vec{r}\langle-\vec{r}|e^{-\beta h_{\alpha\alpha}}|\vec{r}\rangle\\&+\frac{1}{2}\sum_\gamma(-1)^{2\sigma_\gamma}\frac{(2\sigma_\gamma+1)}{(\pi\lambda_\gamma^2)^{3/2}}a_\gamma^2\beta e_\gamma^2\left(\frac{4\pi\beta e_\alpha^2(2\sigma_\alpha+1)}{(2\pi\lambda_\alpha^2)^{3/2}\kappa_a}a_\alpha\right)\int d\vec{r}\langle-\vec{r}|e^{-\beta h_{\gamma\gamma}}|\vec{r}\rangle+O(\rho^3\ln\rho).\end{aligned} \tag{6.13}$$

Use of (6.12) in (6.13) leads to the required expression of $\rho_\alpha^{\mathrm{MB}}$,

$$\begin{aligned}\rho_\alpha^{\mathrm{MB}}=\rho_\alpha&+\frac{(-1)^{2\sigma_\alpha+1}}{(2\sigma_\alpha+1)}(2\pi\lambda_{\alpha\alpha}^2)^{3/2}\rho_\alpha^2(1+2\beta e_\alpha^2\kappa)\int d\vec{r}\langle-\vec{r}|e^{-\beta h_{\alpha\alpha}}|\vec{r}\rangle\\&+\frac{1}{2}\sum_\gamma\frac{(-1)^{2\sigma_\gamma+1}}{(2\sigma_\gamma+1)}(2\pi\lambda_{\gamma\gamma}^2)^{3/2}\rho_\gamma^2\beta e_\gamma^2\frac{4\pi\beta e_\alpha^2}{\kappa}\rho_\alpha\int d\vec{r}\langle-\vec{r}|e^{-\beta h_{\gamma\gamma}}|\vec{r}\rangle+O(\rho^3\ln\rho).\end{aligned} \tag{6.14}$$

D. Final form of the virial expansions

The final expression of the pressure is obtained from (6.10) where βP^{MB} and $\beta P^{(2)}$ are replaced by (6.1) and (6.9), respectively, while at the same time the a_α's and $\rho_\alpha^{\mathrm{MB}}$'s are eliminated in favor of the ρ_α's according to (6.12) and (6.14). A straightforward calculation gives

$$\begin{aligned}\beta P=&\sum_\alpha\rho_\alpha-\frac{\kappa^3}{24\pi}-\frac{1}{2}\sum_{\alpha,\beta}\rho_\alpha\rho_\beta\lim_{R\to\infty}\left\{\int_{r<R}d\vec{r}\left[(2\pi\lambda_{\alpha\beta}^2)^{3/2}\langle\vec{r}|\exp(-\beta h_{\alpha\beta})|\vec{r}\rangle-1+\frac{\beta e_\alpha e_\beta}{r}-\frac{\beta^2e_\alpha^2e_\beta^2}{2r^2}\right]\right.\\&\left.+\frac{2\pi}{3}\beta^3e_\alpha^3e_\beta^3\ln(\kappa R)\right\}+\frac{1}{2}\sum_\alpha\frac{(-1)^{2\sigma_\alpha+1}}{(2\sigma_\alpha+1)}(2\pi\lambda_{\alpha\alpha}^2)^{3/2}\rho_\alpha^2\int d\vec{r}\langle-\vec{r}|\exp(-\beta h_{\alpha\alpha})|\vec{r}\rangle\\&-\frac{\pi}{3}\left(C+\ln3+\frac{1}{2}\right)\sum_{\alpha,\beta}\beta^3e_\alpha^3e_\beta^3\rho_\alpha\rho_\beta-\frac{3}{4}\sum_{\alpha,\beta}\beta e_\alpha e_\beta\kappa\rho_\alpha\rho_\beta\lim_{R\to\infty}\{\cdots\}+\frac{1}{16}\sum_\alpha\frac{\beta^2\hbar^2e_\alpha^2}{m_\alpha}\kappa^3\rho_\alpha\end{aligned}$$

$$+\frac{3}{4}\sum_{\alpha}\frac{(-1)^{2\sigma_\alpha+1}}{(2\sigma_\alpha+1)}(2\pi\lambda_{\alpha\alpha}^2)^{3/2}\beta e_\alpha^2\kappa\rho_\alpha^2\int d\vec{r}\langle-\vec{r}|\exp(-\beta h_{\alpha\alpha})|\vec{r}\rangle+\pi\left(\frac{1}{3}-\frac{C}{2}-\ln 2\right)\sum_{\alpha,\beta}\beta^4e_\alpha^4e_\beta^4\kappa\rho_\alpha\rho_\beta$$

$$+C_1\sum_{\alpha,\beta,\gamma}\beta^5e_\alpha^3e_\beta^4e_\gamma^3\kappa^{-1}\rho_\alpha\rho_\beta\rho_\gamma+C_2\sum_{\alpha,\beta,\gamma,\delta}\beta^6e_\alpha^3e_\beta^3e_\gamma^3e_\delta^3\kappa^{-3}\rho_\alpha\rho_\beta\rho_\gamma\rho_\delta+O(\rho^3\ln\rho). \tag{6.15}$$

The structure of the expansion (6.15) is indeed that of (5.14) predicted on the basis of the general scaling arguments. The expansions of the other thermodynamic functions are easily inferred from (6.15) as explained in Sec. V E.

VII. COMMENTS AND COMPARISONS

For the present discussion, it is sufficient to consider a given thermodynamic quantity, for instance, the free energy. Moreover, it is useful to rewrite the truncated trace $\lim_{R\to\infty}\int_{r<R}d\vec{r}\ldots$ appearing in the density expansion (6.15) in terms of the so-called quantum second-virial coefficient introduced by Ebeling,

$$Q(x_{\alpha\beta})=\frac{1}{(\sqrt{2}\pi\lambda_{\alpha\beta}^3)}\lim_{R\to\infty}\left\{\int_{r<R}d\vec{r}\left[(2\pi\lambda_{\alpha\beta}^2)^{3/2}\langle\vec{r}|e^{-\beta h_{\alpha\beta}}|\vec{r}\rangle-1+\frac{\beta e_\alpha e_\beta}{r}-\frac{\beta^2e_\alpha^2e_\beta^2}{2r^2}\right]+\frac{2\pi}{3}\beta^3e_\alpha^3e_\beta^3\left[\ln\left(\frac{3\sqrt{2}R}{\lambda_{\alpha\beta}}\right)+C\right]\right\}, \tag{7.1}$$

with $x_{\alpha\beta}=-\sqrt{2}l_{\alpha\beta}/\lambda_{\alpha\beta}$ and $l_{\alpha\beta}=\beta e_\alpha e_\beta$ (this quantity is the analog of the usual second-virial coefficient for quantum systems with short-range forces). The dimensionless function Q defined by (7.1) depends on the temperature and on the charges and masses of the particles via the sole dimensionless parameter $x_{\alpha\beta}$. Similarly, it is also useful to introduce the dimensionless exchange integral

$$E(x_{\alpha\alpha})=(2\sqrt{\pi})\int d\vec{r}\langle-\vec{r}|e^{-\beta h_{\alpha\alpha}}|\vec{r}\rangle, \tag{7.2}$$

which only depends on $x_{\alpha\alpha}=-\sqrt{2}l_{\alpha\alpha}/\lambda_{\alpha\alpha}$. We write the virial expansion of the free energy as

$$\beta f=\sum_\alpha\rho_\alpha\left[\ln\left(\frac{(2\pi\lambda_\alpha^2)^{3/2}\rho_\alpha}{(2\sigma_\alpha+1)}\right)-1\right]-\frac{\kappa^3}{12\pi}+\frac{\pi}{6}\ln 2\sum_{\alpha,\beta}\beta^3e_\alpha^3e_\beta^3\rho_\alpha\rho_\beta-\frac{\pi}{\sqrt{2}}\sum_{\alpha,\beta}\rho_\alpha\rho_\beta\lambda_{\alpha\beta}^3Q(x_{\alpha\beta})$$

$$-\frac{\pi}{3}\beta^3\sum_{\alpha,\beta}\rho_\alpha\rho_\beta e_\alpha^3e_\beta^3\ln(\kappa\lambda_{\alpha\beta})+\frac{\pi}{\sqrt{2}}\sum_\alpha\frac{(-1)^{2\sigma_\alpha+1}}{(2\sigma_\alpha+1)}\rho_\alpha^2\lambda_{\alpha\alpha}^3E(x_{\alpha\alpha})+\pi\left(\frac{1}{3}-\frac{1}{2}\ln 2+\frac{1}{3}\ln 3\right)\sum_{\alpha,\beta}\beta^4e_\alpha^4e_\beta^4\kappa\rho_\alpha\rho_\beta$$

$$+\frac{2}{3}C_1\sum_{\alpha,\beta,\gamma}\beta^5e_\alpha^3e_\beta^4e_\gamma^3\kappa^{-1}\rho_\alpha\rho_\beta\rho_\gamma+\frac{2}{3}C_2\sum_{\alpha,\beta,\gamma,\delta}\beta^6e_\alpha^3e_\beta^3e_\gamma^3e_\delta^3\kappa^{-3}\rho_\alpha\rho_\beta\rho_\gamma\rho_\delta-\frac{\pi}{\sqrt{2}}\sum_{\alpha,\beta}\beta e_\alpha e_\beta\kappa\rho_\alpha\rho_\beta\lambda_{\alpha\beta}^3Q(x_{\alpha\beta})$$

$$-\frac{\pi}{3}\sum_{\alpha,\beta}\beta^4e_\alpha^4e_\beta^4\kappa\rho_\alpha\rho_\beta\ln(\kappa\lambda_{\alpha\beta})+\frac{\pi}{\sqrt{2}}\sum_\alpha\frac{(-1)^{2\sigma_\alpha+1}}{(2\sigma_\alpha+1)}\beta e_\alpha^2\kappa\rho_\alpha^2\lambda_{\alpha\alpha}^3E(x_{\alpha\alpha})+\frac{1}{24}\sum_\alpha\frac{\beta^2\hbar^2e_\alpha^2}{m_\alpha}\kappa^3\rho_\alpha+O(\rho^3\ln\rho). \tag{7.3}$$

Most virial coefficients in (7.3) are explicitly computed and exhibit simple power-law dependences with respect to the inverse temperature $\beta=1/k_BT$. The functions $Q(x)$ and $E(x)$ can be determined with a good numerical accuracy [20]. The small- and large-x expansions of these functions have also been derived in the literature [20], while a simple integral representation of $E(x)$ is given in Ref. [42] [similar useful representations of $Q(x)$ might be found by exploiting recent exact results on the two-body Coulomb density matrix [43]].

The expression (7.3) is valid for any multicomponent system made of mobile point particles, where at least two species with positive and negative charges are present in order to satisfy charge neutrality. For our purpose, it is useful to write the specific form of the virial expansions for the one-component plasma (OCP). This model is made of identical particles with charge e moving in a neutralizing rigid background with charge density $-e\rho$ if ρ is the density of particles. The expansion of $\beta f^{\rm OCP}$ is

$$\beta f^{\rm OCP}=\rho\left[\ln\left(\frac{(2\pi\lambda^2)^{3/2}\rho}{(2\sigma+1)}\right)-1\right]-\frac{\kappa^3}{12\pi}-2\pi\rho^2\lambda^3Q(-\beta e^2/\lambda)-\frac{\pi}{3}\beta^3e^6\rho^2\ln(\kappa\lambda)+2\pi\frac{(-1)^{2\sigma+1}}{(2\sigma+1)}\rho^2\lambda^3E(-\beta e^2/\lambda)$$

$$+\frac{\pi\beta^2\hbar^2e^2\rho^2}{3m}-2\pi\beta e^2\kappa\rho^2\lambda^3Q(-\beta e^2/\lambda)-\frac{\pi}{3}\beta^4e^8\kappa\rho^2\ln(\kappa\lambda)+2\pi\frac{(-1)^{2\sigma+1}}{(2\sigma+1)}\beta e^2\kappa\rho^2\lambda^3E(-\beta e^2/\lambda)$$

$$+\frac{\pi\beta^3\hbar^2e^4\kappa\rho^2}{6m}+\left[\frac{\pi}{3}(1-2\ln 2+\ln 3)+\frac{C_1}{6\pi}+\frac{C_2}{24\pi^2}\right]\beta^4e^8\kappa\rho^2+O(\rho^3\ln\rho), \tag{7.4}$$

with $\lambda=(\beta\hbar^2/m)^{1/2}$ and $\kappa=(4\pi\beta e^2\rho)^{1/2}$.

As already mentioned in Ref. [16], all the terms in the expansion (7.3) coincide with those calculated by Ebeling and co-workers [20] via the effective-potential method, except the diffraction term of order $\rho^{5/2}$ proportional to $\hbar^2$ which is missing in their expressions. This discrepancy, as well as other checkings against known results in some particular limits, are discussed in the following. We consider successively the four kinds of terms which arise from classical screening, quantum diffraction, recombination or scattering, and exchange. At the end of the section, we also discuss the high-temperature expressions which can be readily derived from (7.3) as a by-product.

A. Classical terms

First, in (7.3), there appears a class of terms which do not depend on Planck's constant. These purely classical terms arise from large distance configurations for which the Coulomb interactions are screened on a range κ^{-1}. These terms are also present in the expression (7.4) specific to the OCP. The result of Cohen and Murphy [23] for the classical OCP [44] is exactly recovered by taking the limit $\hbar \to 0$ (all other parameters being kept fixed).

B. Quantum diffraction

For the general multicomponent system, the contribution of quantum diffraction appears only at order $\rho^{5/2}$ and reduces to

$$\frac{1}{24} \sum_{\alpha} \frac{\beta^2 \hbar^2 e_\alpha^2}{m_\alpha} \kappa^3 \rho_\alpha . \tag{7.5}$$

This term is linked to the quantum fluctuations of the particles which cannot be entirely neglected at large distances. These fluctuations induce multipolelike interactions (in the FK representation), the amplitudes of which are controlled by λ_α while the corresponding nonintegrable parts are screened on a range κ^{-1}.

Like the classical contributions, the diffraction terms may be tested in the particular case of the OCP. In that case, the quantum corrections to the classical virial coefficients can be calculated by inserting into (7.4) the asymptotic behaviors of $Q(x)$ and $E(x)$ when $x \to -\infty$ [20]. The $\hbar^2$ correction to the classical virial coefficient of order ρ^2 in $\beta f_{\text{class}}^{\text{OCP}}$ reads

$$\frac{\pi \beta^2 e^2 \rho^2 \hbar^2}{6m}, \tag{7.6}$$

which is identical to the full $\hbar^2$ correction to $\beta f_{\text{class}}^{\text{OCP}}$ calculated by Pollock and Hansen [22] within the Wigner-Kirkwood method. Since the result of these authors is valid for any density, all the $\hbar^2$ corrections in the virial coefficients of order higher than ρ^2 must vanish. This remarkable property is indeed satisfied by the $\rho^{5/2}$ term in (7.4) because both $\hbar^2$ contributions of

$$-2\pi\beta e^2 \kappa \rho^2 \lambda^3 Q(x) \tag{7.7a}$$

and

$$\frac{\pi \beta^3 e^4 \kappa \rho^2 \hbar^2}{6m} \tag{7.7b}$$

cancel out. We stress that the presence of the purely diffraction term (7.7b), which is the strict analog of (7.5), is crucial in this checking.

C. Recombination and scattering

The ρ^2 term

$$-\frac{\pi}{\sqrt{2}} \rho_\alpha \rho_\beta \lambda_{\alpha\beta}^3 Q(x_{\alpha\beta}) \tag{7.8}$$

is the total contribution from both bound and scattering states of two charges e_α and e_β. The truncation of $\langle \vec{r} | \exp(-\beta h_{\alpha\beta}) | \vec{r} \rangle$ in the integral (7.1) defining $Q(x_{\alpha\beta})$ ensures that this contribution is finite. This regularization is not an arbitrary mathematical artifact and is directly related to the truncated structure of the bond f_T which is introduced in the MB diagrammatics [1,13]. It reflects the screening of the Coulomb interaction at large distances.

For opposite charges such that $e_\alpha e_\beta < 0$, one may extract from $Q(x_{\alpha\beta})$ a contribution of the bound states which reduces to the familiar Planck-Brillouin-Larkin (PBL) sum

$$\sum_{n=1}^{\infty} n^2 [\exp(-\beta \epsilon_n^{\alpha\beta}) - 1 + \beta \epsilon_n^{\alpha\beta}], \tag{7.9}$$

where $\epsilon_n^{\alpha\beta} = -e_\alpha^2 e_\beta^2 m_{\alpha\beta}/(2\hbar^2 n^2)$ are the energy levels of the hydrogenoid atom with Hamiltonian $h_{\alpha\beta}$. However, other definitions of the bound state contributions can be introduced from (7.1) by using the basic properties of the trace. For instance, as shown by Bollé [45], there exists an infinite set of arbitrary decompositions in terms of bound and scattering contributions of the PBL sum itself. So, as far as thermodynamic quantities are concerned, only the total contribution of both bound and scattering states is an unambiguous quantity.

D. Exchange

The contribution

$$\frac{\pi}{\sqrt{2}} \frac{(-1)^{2\sigma_\alpha + 1}}{(2\sigma_\alpha + 1)} \rho_\alpha^2 \lambda_{\alpha\alpha}^3 E(x_{\alpha\alpha}) \tag{7.10}$$

arises from the exchange of two charges e_α in the vacuum. It is finite, independently of any screening effect, because the off-diagonal matrix elements $\langle -\vec{r} | \exp(-\beta h_{\alpha\alpha}) | \vec{r} \rangle$ are short ranged. The magnitude of this contribution is smaller than that of free particles because the repulsive potential e_α^2/r inhibits the exchange.

Similarly to what happens for the contributions of bound and scattering states, at the order $\rho^{5/2}$, the many-body effects on the two-particle exchange lower the repulsive barrier e_α^2/r by the constant $-e_\alpha^2 \kappa$. In the OCP case, the total exchange contribution up to order $\rho^{5/2}$ does coincide with the

expression derived by Jancovici [42]. Moreover, in the classical limit $\hbar \to 0$, this contribution vanishes as $\exp(-\text{const}/\hbar^{2/3})$ [42].

E. High-temperature expansions

Eventually, high-temperature series can be deduced from (7.3) by expanding the virial coefficients in powers of β. Since the dimensionless parameters $x_{\alpha\beta}$ are proportional to $\beta^{1/2}$, the β expansions of $Q(x_{\alpha\beta})$ and $E(x_{\alpha\alpha})$ coincide with their Taylor series in powers of x [20],

$$Q(x_{\alpha\beta}) = -\frac{x_{\alpha\beta}}{6} - \frac{\sqrt{\pi}}{8} x_{\alpha\beta}^2 + O(x_{\alpha\beta}^3) \tag{7.11}$$

and

$$E(x_{\alpha\alpha}) = \frac{\sqrt{\pi}}{4} + \frac{x_{\alpha\alpha}}{2} + \frac{\sqrt{\pi}\,\ln 2}{4} x_{\alpha\alpha}^2 + O(x_{\alpha\alpha}^3). \tag{7.12}$$

Inserting (7.11) and (7.12) into (7.3), we find a series representation of the free energy in powers of the inverse temperature β, the densities ρ, and the charges e [46]. The terms which do not depend on the charges correspond to the expansion of the ideal part of βf. The remaining terms define the excess part which reads

$$\begin{aligned}
\beta f_{\text{exc}} = \beta f - \beta f_{\text{id}} = & -\frac{\kappa^3}{12\pi} - \frac{\pi}{2} \sum_{\alpha} \frac{(-1)^{2\sigma_\alpha+1}}{(2\sigma_\alpha+1)} \rho_\alpha^2 \beta e_\alpha^2 \lambda_{\alpha\alpha}^2 \\
& + \frac{\pi^{3/2}\sqrt{2}}{8} \sum_{\alpha,\beta} \rho_\alpha \rho_\beta \beta^2 e_\alpha^2 e_\beta^2 \lambda_{\alpha\beta} + \frac{\pi^{3/2}\sqrt{2}}{4} \\
& \times \ln 2 \sum_{\alpha} \frac{(-1)^{2\sigma_\alpha+1}}{(2\sigma_\alpha+1)} \rho_\alpha^2 \beta^2 e_\alpha^4 \lambda_{\alpha\alpha} + \frac{\pi^{3/2}\sqrt{2}}{8} \\
& \times \sum_{\alpha} \frac{(-1)^{2\sigma_\alpha+1}}{(2\sigma_\alpha+1)} \rho_\alpha^2 \beta e_\alpha^2 \kappa \lambda_{\alpha\alpha}^3 \\
& - \frac{\pi}{12} \sum_{\alpha,\beta} \rho_\alpha \rho_\beta \beta^2 e_\alpha^2 e_\beta^2 \kappa \lambda_{\alpha\beta}^2 \\
& - \frac{\pi}{2} \sum_{\alpha} \frac{(-1)^{(2\sigma_\alpha+1)}}{(2\sigma_\alpha+1)} \rho_\alpha^2 \beta^2 e_\alpha^4 \kappa \lambda_{\alpha\alpha}^2 + \cdots .
\end{aligned} \tag{7.13}$$

All the terms which are omitted in (7.13) have orders which are higher than $\beta^{7/2}$, $\rho^{5/2}$, or e^5. A similar expansion for $\beta f_{\text{exc}}^{\text{OCP}}$ is easily derived from (7.4),

$$\begin{aligned}
\beta f_{\text{exc}}^{\text{OCP}} = & -\frac{\kappa^3}{12\pi} - \pi \frac{(-1)^{2\sigma+1}}{(2\sigma+1)} \rho^2 \beta e^2 \lambda^2 + \frac{\pi^{3/2}}{4} \rho^2 \beta^2 e^4 \lambda \\
& + \frac{\pi^{3/2}}{2} (\ln 2) \frac{(-1)^{2\sigma+1}}{(2\sigma+1)} \rho^2 \beta^2 e^4 \lambda \\
& + \frac{\pi^{3/2}}{2} \frac{(-1)^{2\sigma+1}}{(2\sigma+1)} \rho^2 \beta e^2 \kappa \lambda^3 - \frac{\pi}{6} \rho^2 \beta^2 e^4 \kappa \lambda^2 \\
& - \pi \frac{(-1)^{2\sigma+1}}{(2\sigma+1)} \rho^2 \beta^2 e^4 \kappa \lambda^2 + \cdots .
\end{aligned} \tag{7.14}$$

Notice that the OCP expansion (7.14) coincides exactly with the pure contribution of one given species to the multicomponent expression (7.13) [in other words, (7.14) is the particular form taken by (7.13) when the species summations are restricted to only one species].

Since the high-temperature series involve increasing powers of the charges, they may also be directly obtained from the standard many-body perturbation theory where these charges constitute the natural expansion parameter. The first calculations in this spirit have been done by DeWitt [27,28], who retained contributions arising from the ring and e^2-exchange graphs only. These results have been completed recently by DeWitt *et al.* [29], who included higher-order contributions, in particular those from the e^4-exchange graph. Their expression for the OCP excess pressure is identical to that derived from our expansion (7.14) of the OCP excess free energy,

$$\begin{aligned}
\beta P_{\text{exc}}^{\text{OCP}} = \beta P^{\text{OCP}} - \beta P_{\text{id}}^{\text{OCP}} = & \rho \frac{\partial}{\partial \rho} \beta f_{\text{exc}}^{\text{OCP}} - \beta f_{\text{exc}}^{\text{OCP}} \\
= & -\frac{\kappa^3}{24\pi} - \pi \frac{(-1)^{2\sigma+1}}{(2\sigma+1)} \rho^2 \beta e^2 \lambda^2 + \frac{\pi^{3/2}}{4} \\
& \times \left[1 + 2(\ln 2) \frac{(-1)^{2\sigma+1}}{(2\sigma+1)} \right] \rho^2 \beta^2 e^4 \lambda \\
& + \frac{3\pi^{3/2}}{4} \frac{(-1)^{2\sigma+1}}{(2\sigma+1)} \rho^2 \beta e^2 \kappa \lambda^3 - \frac{\pi}{4} \\
& \times \left[1 + 6 \frac{(-1)^{2\sigma+1}}{(2\sigma+1)} \right] \rho^2 \beta^2 e^4 \kappa \lambda^2 + \cdots .
\end{aligned} \tag{7.15}$$

This perfect agreement between independent calculations based on completely different formalisms is a quite satisfactory test for the reliability of the results.

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[40] Since the three opened filaments $\mathscr{F}$ which appear in the FK representation of $\beta P^{(3)}$ constitute a single loop $\mathscr{L}^{(3)}$, the leading order of $\beta P^{(3)}$ obviously is ρ^3. For $\beta P^{(n)}$ with $n \geqslant 4$, the screening of the interactions between different loops generates inverse powers of κ. In the case of $\beta P^{(4)}$, the integration over $\vec{R}_{ab}$ of the screened contribution of $\mathscr{L}_a^{(2)}$ and $\mathscr{L}_b^{(2)}$ to $[E^{(4)}-(E^{(2)})^2/2]$ makes a factor $(\kappa^{\mathrm{MB}})^{-2}$ appear. The leading term in the expansion of $\beta P^{(4)}$ then is of order ρ^3. In general, for $n>4$, $\beta P^{(n)}$ behaves as ρ^{p_n} with $p_n=(n+2)/2$ for n even and $p_n=(n+3)/2$ for n odd (these powers are readily obtained from a simple scaling analysis).
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