Virial expansions for quantum plasmas: Maxwell-Boltzmann statistics

Angel Alastuey, Françoise Cornu, and Asher Perez

1Laboratoire de Physique, Unité de Recherche Associée No. 1325 au Centre National de la Recherche Scientifique, Ecole Normale Supérieure de Lyon, 46 allée d'Italie, 69364 Lyon Cedex 07, France
2Laboratoire de Physique Théorique–ENSLAPP, Unité de Recherche Associée No. 1436 au Centre National de la Recherche Scientifique, Ecole Normale Supérieure de Lyon, 46 allée d'Italie, 69364 Lyon Cedex 07, France

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This paper is devoted to the calculation of the density expansions (at fixed temperature) of the Maxwell-Boltzmann thermodynamic functions for a quantum plasma. We start from a standard identity that relates the free energy to the particle correlations. These correlations are represented by diagrammatic series, which have been introduced in a previous paper. In the corresponding graphs, the ordinary points are replaced by extended objects, the filaments, which are linked by resummed bonds depending on the particle densities \( \rho \). A scaling analysis of the spatial integrals involved in the graphs shows that the free energy can be represented by a double integer series in \( \rho^{1/2} \) and \( \ln \rho \). Furthermore, we derive simple rules that give the leading order in \( \rho \) of the contribution from every previous graph. The exact density expansion of the free energy is explicitly calculated up to order \( \rho^{5/2} \). In the corresponding expression, the contributions of various physical effects, such as screening, diffraction, or recombination, are clearly identified. At the order \( \rho^3 \), we recover the expansion obtained via the effective-potential method. Our present terms of order \( \rho^{5/2} \) correctly reproduce results that are known in some particular limits.

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I. INTRODUCTION

This paper is the second of a series devoted to the study of the density expansions of the thermodynamic quantities for quantum plasmas. We consider a multicomponent system \( \mathcal{S} \) made of electrons and nuclei that are assumed to be point particles. Each particle has a mass \( m_\alpha \) and carries a charge \( e_\alpha \) and a spin \( \sigma_\alpha \) where \( \alpha \) is a species index that specifies the nature of the particle. The Hamiltonian of \( \mathcal{S} \) 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. Beside 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 an earlier paper [1] (hereafter referred to as paper I), we derived a diagrammatic representation for the particle correlations of \( \mathcal{S} \) 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 \( \mathcal{S}^* \) made of closed filaments. Since the filaments interact via two-body forces, all the familiar diagrammatic methods [4] can be applied to \( \mathcal{S}^* \). However, the corresponding Mayer-like graphs diverge because of the long-range Coulombic nature of the interaction potential between two filaments. These long-range divergences are removed via the chain resummations first 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 \( \mathcal{S}^* \) can be transformed exactly into a new set of prototype graphs \( \Pi \) built with resummed bonds. This provides a well-behaved diagrammatic representation for the particle correlations of \( \mathcal{S} \), 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 [9,10].

In the present paper, the above diagrammatic representation is used for studying the density expansions of the Maxwell-Boltzmann thermodynamic functions (at fixed inverse temperature \( \beta \)) in a systematic way. On the basis of simple scaling arguments, we show 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 first conjectured by Friedman [11].) We also give detailed prescriptions for selecting the graphs (in finite number) that contribute to a given order in \( \rho \) where \( \rho \) is a generic notation for the particle densities. This allows us to recover the known results up to order \( \rho^2 \), and to calculate exactly the next term of order \( \rho^{5/2} \).

As announced previously [1], the above expansions are term-to-term well defined despite the macroscopic collapse of the Maxwell-Boltzmann (MB) system [12]. In future papers, the exchange contributions due to Fermi or Bose statistics will be evaluated via a perturbative
scheme, in which the MB quantities are the reference ingredients. A brief description of this scheme has been already given [13], as well as the complete form of the virial expansion up to order $\rho^{3/2}$.

The present paper is organized as follows. In Sec. II, we recall the form of the diagrammatic representation for the particle correlations. The topological rules, statistical weights, and resummed bonds defining the II graphs are explicit.

In Sec. III, we study the general structure of the density expansion of the free energy. We start from a standard identity, which expresses the free energy in terms of the particle correlations via an integral over a coupling parameter. Inserting the above II representation into this identity, we rewrite the free energy as a sum of II contributions. Simple arguments suggest that the contribution of each graph can be expanded in a double integer series in $\rho^{3/2}$ and $\ln \rho$. This nonanalytic structure reflects the screening of the bare Coulomb potential. The half powers of $\rho$ are linked to partial scaling of the resummed bonds with respect to the Debye length $\kappa^{-1}=(4\pi\beta \sum_\alpha \varepsilon_\alpha P_\alpha)^{-1/2}$. The logarithms arise from the presence of $1/r^3$ tails in some bonds. We give simple rules for evaluating the order in the density of the leading contribution of any graph. Roughly speaking, the latter increases with the number of points and the number of resummed bonds. Only a finite number of graphs then contributes to a given term in the density expansion of the free energy.

The explicit calculations are carried out up to order $\rho^{5/2}$ in Sec. IV. The contributions of the various physical effects mentioned in paper I, can be clearly identified. There are purely classical terms that arise from Debye screening at large distances. The short-range quantum effects associated to bound and scattering states enter in suitably truncated traces of the quantum Gibbs factors for a finite number of charges. Eventually, there are diffraction terms that appear as quantum corrections to a classical treatment of the long-range part of the interactions. All these physical effects should be coupled together at higher orders in the density. Comparisons to previous results and checkings are briefly described.

The other thermodynamic functions are considered in Sec. V. Their density expansions can be obtained from that of the free energy via partial differentiations with respect to the temperature or the densities. In particular, we calculate the pressure up to order $\rho^{3/2}$.

Of course, the virial expansions can be also studied by using other first-principles formalisms. First, the effective-potential method formulated by Morita [14] for quantum systems with two-body interactions, has been applied to the present Coulomb case by Ebeling [15]. This method consists in introducing classical equivalent systems made of point objects with two-, three-, and higher-order many-body effective interactions. In practice, only two-body effective potentials have been retained [15–17]. 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 [16,17] provide the exact form of the virial expansions up to order $\rho^2$, which is indeed recovered by our formalism [13]. However, the expressions proposed for the $\rho^{3/2}$ term [17] are not complete because the three-body effective potentials do contribute at this order [18]. 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 [19] to the classical quantities for the one-component plasma. In this way, we also recover the virial expansion for the classical one-component plasma calculated by Cohen and Murphy [20].

Another possible approach is based on the standard many-body perturbative expansions with respect to the Coulomb interaction potential $v_\epsilon(r)=1/r$ in the framework of the grand-canonical ensemble. These expansions can be written in terms of graphs similar to those that 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 $v_\epsilon$ [21]. The long-range Coulomb divergencies are eliminated via the well-known ring resummations [22,23]. To our knowledge, analytic evaluations of the corresponding Feynman graphs have been restricted to the high-density regime at zero temperature [22], and to the high-temperature limit [24]. Explicit calculations of the virial coefficients at finite nonzero temperature should be also possible by following Rogers's idea [25]. 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 [26] (i.e., at moderately high densities where complex entities made of several charges may be formed). At the moment, we have checked that the high-temperature expansions up to order $\beta^{-2/2}$ of our virial coefficients do coincide with the terms found by DeWitt [24].

II. THE PARTICLE CORRELATIONS

In paper I, we have shown that the two-particle correlations $\rho_T(\alpha_\alpha r_\alpha, \alpha_\beta r_\beta)$ of $\delta^*$ can be represented by the diagrammatic series

$$\rho_T(\alpha_\alpha r_\alpha, \alpha_\beta r_\beta) = \sum_{\Pi} \frac{1}{S_{\Pi}} \int D(\xi_\alpha) D(\xi_\beta) p(\xi_\alpha)p(\xi_\beta)$$

$$\times \int \prod_{n=1}^{N} d\mathcal{P}_n(\mathcal{P}_n) \left[ \Pi F \right]_{\Pi},$$

(2.1)

where the ordinary points are replaced by filaments. Each graph $\Pi$ is made of the two root filaments $\xi_\alpha$ and $\xi_\beta$, and of $N$ internal filaments $\mathcal{P}_n$ $(N=0, \ldots, \infty)$. The state of each filament is characterized by its species index $\alpha$, its position $r$, and its shape. The latter is parametrized
by \( \lambda_\alpha \xi(s) \) (0 \( \leq s \leq 1 \)) where \( \lambda_\alpha = (\beta \hbar^2 / m_\alpha)^{1/2} \) is the de Broglie wavelength of species \( \alpha \) and \( \xi(s) \) is a Brownian bridge subjected to the constraint \( \xi(0) = \xi(1) = 0 \). The phase-space measure \( d\mathcal{P} \) means a discrete summation over \( \alpha \) combined to a spatial integration over \( r \), and a functional integration over \( \xi(s) \) with the normalized Gaussian measure \( \mathcal{D}(\xi) \) defined by its covariance

\[
\int \mathcal{D}(\xi) \xi_\alpha(s) \xi_\alpha(t) = \delta_{\alpha} \times \begin{cases} \sigma(1-t), & s \leq t \\ \sigma(t-1), & t \leq s. \end{cases}
\]

(\( \xi_\alpha \) is the component of \( \xi \) along the \( \mu \) axis.)

The topological prescriptions that define the graphs II are similar to that of the familiar Mayer graphs. Each graph II is connected and contains no articulation filament. Two filaments are linked by at most one resummed \( F \) bond. \( \prod \mathcal{F} \) is the product of \( F \) bonds in the graph II and \( S_\Pi \) is its symmetry factor, i.e., the number of permutations of the internal filaments \( \mathcal{P}_\alpha \), which do not change this product. The sum (2.1) runs over all the unlabeled topologically different graphs II.

There are four kinds of resummed bonds \( F \). Two of them are short ranged and proportional to the screened charge-charge and screened dipole-charge potential between the filaments \( \mathcal{P}_i \) and \( \mathcal{P}_j \), i.e.,

\[
F_{cc}(\mathcal{P}_i, \mathcal{P}_j) = -\beta e_a e_a \phi_D(|r_i - r_j|)
\]

and

\[
F_{dc}(\mathcal{P}_i, \mathcal{P}_j) = -\beta e_a e_a \int_0^1 ds \lambda_\alpha \xi_\alpha(s) \cdot \nabla_i \phi_D(|r_i - r_j|).
\]

In (2.3) and (2.4), \( \phi_D(r) \) is the usual Debye potential

\[
\phi_D(r) = \frac{\exp(-kr)}{r}.
\]

The other two resummed bonds reduce to

\[
f_{\text{dip}}(\mathcal{P}_i, \mathcal{P}_j) = -\beta e_a e_a \int_0^1 ds \int_0^1 ds' \lambda_\alpha \xi_\alpha(s) \cdot \nabla_i \lambda_\alpha \xi_\alpha(s') \cdot \nabla_j \phi_D - v_c(r_i)
\]

and decay only as \( 1/r_i \) when \( r_i \to \infty \). Each of the resummed bonds may link any pair of filaments with the sole restriction that the convolution structures \( F_{cc} \circ F_{cc}, F_{dc} \circ F_{cc}, F_{cc} \circ F_{cd}, \) and \( F_{dc} \circ F_{cd} \) are excluded (this avoids double counting).

The statistical weights of the filaments in the graphs II are the filament densities \( \rho(\mathcal{C}) \), which are complicated functionals of the shapes of the filaments, i.e., \( \rho(\mathcal{C}) = \rho_\alpha(\xi) \). These functionals are determined from their expansions with respect to the particle densities, which reduce to double integer series in \( \rho^{1/2} \) and \( \ln \rho \). The first two terms of these series read

\[
\rho_\alpha(\xi) = \rho_\alpha + \sum_B \rho_\alpha \rho_B \int dr \int \mathcal{D}(\xi_1) \left[ \exp \left[ -\beta e_a e_B \int_0^1 ds v_c(|r + \lambda_\beta \xi_1(s) - \lambda_\alpha \xi(s)|) \right] - \int \mathcal{D}(\xi_1) \exp \left[ -\beta e_a e_B \int_0^1 ds v_c(|r + \lambda_\beta \xi_1(s) - \lambda_\alpha \xi(s)|) \right] \right] + \mathcal{O}(\rho^{3/2}).
\]
be calculated by inserting the II representation (2.1) of
\( \rho_{Tg} \) in the right-hand side of (3.1). The corresponding
contribution of a given prototype diagram II reads (with
obvious notations)
\[
\frac{1}{2} \beta e_a e_{a'} \int_0^1 dg \int d\tau \frac{1}{r} \Pi_g(r),
\]
(3.2)
with
\[
\Pi_g(r) = \int D(\xi_a) D(\xi_{a'}) \rho_g(\xi_a) \rho_{g}(\xi_{a'}) \Pi_{g}(r, \xi_a, \xi_{a'}). \quad \text{(3.3)}
\]
The subscript \( g \) means that the resummed bonds in II are
calculated with the coupling constant \( \epsilon_a \epsilon_j \) instead of \( \epsilon_a \epsilon_j \)
(consistently, \( \kappa \) is changed into \( \sqrt{g} \kappa \)) like the statistical
weights \( \rho_g(\xi) \). Each contribution (3.2) can be itself expanded
in powers of the particle densities because of the following two mechanisms.
First, as noted in Sec. II, the functions \( \rho_g(\xi) \) have to be replaced by
double integer series in \( \rho_{1/2} \) and \( \ln \rho \). Second, the distance dependence
of some resummed bonds is scaled by the Debye length \( \sqrt{g} \kappa \sim (4\pi g \kappa)^{-1} = (4\pi g \kappa \sum_a \epsilon_a^2 \rho_a)^{-1/2} \). Thus, as shown
in the Sec. III B, the space integrations in II provide series in \( \kappa \), whose structure is independent of the precise
form of the functional \( \rho_g(\xi) \). This allows us to determine
the general form of the contribution (3.2).

\section{III. THE FREE ENERGY}

\subsection{A. Principle of the method}

The free energy \( \beta F / \Lambda \) per unit of volume and in
units of \( k_B T \), is related to the particle correlations via
\[
\frac{\beta F}{\Lambda} = \frac{\beta F_{id}}{\Lambda} + \frac{1}{2} \sum_{\alpha_a \alpha_{a'}} \beta e_a e_{a'} \int_0^1 dg \int d\tau \rho_{Tg} \rho_a \rho_{a'} \frac{1}{r}. \quad \text{(3.1)}
\]
In this identity, \( g \) is a dimensionless coupling parameter,
while \( \rho_{Tg}(\alpha_a 0, \alpha_{a'} r) \) is the two-point correlation of the
system \( \delta_g \) where the coupling between two charges \( e_a \)
and \( e_{a'} \) is multiplied by \( g \) and becomes \( ge_a e_{a'} \) (\( F_{id} \) is the
free energy of the ideal system \( \delta_{g=0} \)). Furthermore, the
temperature and the particle densities of the systems \( \delta_g \)
are identical to those of the genuine system \( \delta \) corresponding to \( g = 1 \).

The required density expansion of the free energy will

\begin{equation}
\begin{aligned}
 f_D &= -\kappa \beta_{ij} \frac{e^{-x}}{x}, \\
 \lambda_{a_i} \xi_i \cdot \nabla f_D &= \kappa^2 \beta_{ij} \lambda_{a_i} \int_0^1 ds (\xi_i(s) \cdot \hat{r}) \left[ \frac{e^{-x}}{x} + \frac{e^{-x}}{x^2} \right], \\
 f_{dip} &= \kappa^2 \beta_{ij} \lambda_{a_i} \int_0^1 ds \int_0^1 ds' \left[ (\xi_i(s) \cdot \xi_i(s')) \frac{1-e^{-x-xe^{-x}}}{x^3} - (\xi_i(s) \cdot \hat{r})(\xi_i(s') \cdot \hat{r}) \frac{3(3-3e^{-x}-3xe^{-x}-xe^{-x})}{x^3} \right].
\end{aligned}
\end{equation}
(3.4)
with $x = \kappa(r_i - r_j)$ and $\beta_{ij} = \beta e r_{ij}$. However, the bond $f_R$ is not entirely scaled by $\kappa^{-1}$ since it is not proportional to a dimensionless integrable function of $x$. Otherwise, the present analysis would be immediately performed by making the variable changes $r_i \rightarrow x_i = \kappa r_i$ in $\Pi$. In fact, the spatial behavior of $f_R$ is also controlled by the Landau lengths $l_{ab} = \beta e r_{ab}$ and the de Broglie wavelengths $\lambda_{\alpha}$. These lengths only depend on the temperature and remain fixed in the zero-density limit. In order to disentangle the various scales associated to $\kappa^{-1}$, $\beta e r_{ab}$, and $\lambda_{\alpha}$, it is convenient to rewrite $f_R$ as $f_R = f_T(x, \xi_i, \xi_j) + f_T(x, \xi_i, \xi_j) \sum_{n=1}^{\infty} \kappa^n H_n(x, \xi_i, \xi_j) + \sum_{n=2}^{\infty} \kappa^n g_n(x, \xi_i, \xi_j)$, (3.7)

$$f_T(x, \xi_i, \xi_j) = \exp \left\{ -\beta_{ij} \int_0^1 ds v_i(|s + \lambda_i \xi_i(s) - \lambda_j \xi_j(s)|) \right\}$$

$$- 1 + \frac{\beta_{ij}}{r} - \frac{\beta_{ij}^2}{2r^2}$$

$$+ \beta_{ij} \int_0^1 ds (\lambda_{\alpha} \xi_i(s) \cdot \nabla - \lambda_{\alpha} \xi_j(s) \cdot \nabla) \frac{1}{r} ,$$

while the $\kappa$-scaled functions $H_n$ and $G_n$ can be calculated from (2.7). For instance, we find

$$H_1(x, \xi_i, \xi_j) = H_1(x) = -\beta_{ij} \frac{e^{-x} - 1}{x} ,$$

(3.9)

$$G_2(x, \xi_i, \xi_j) = G_2(x) = \frac{\beta_{ij}^2 e^{-2x}}{2} ,$$

(3.10)

$$G_3(x, \xi_i, \xi_j) = \frac{\beta_{ij}^3}{6} \frac{1 - e^{-3x}}{x^3}$$

$$+ \beta_{ij} \int_0^1 ds (\lambda_{\alpha} \xi_i(s) \cdot \hat{x} - \lambda_{\alpha} \xi_j(s) \cdot \hat{x}) \times \frac{1 - (1 + x)e^{-2x}}{x^3} .$$

(3.11)

The functions $G_n$ are integrable at large distances as the functions $H_n$ for $n \geq 4$ since they decay at most as $1/x^n$ for $x$ large. The truncated bond $f_T$ does not depend on $\kappa^{-1}$, and is scaled by the above temperature-dependent lengths.

The decompositions (3.4)–(3.7) with respect to the various scales are quite useful for our purpose, because they provide a series representation of any graph $\Pi$ in terms of graphs where all bonds are scaled either by $\kappa^{-1}$ or by the fixed lengths $\beta e r_{ab}$ and $\lambda_{\alpha}$. These graphs are called scaling-decomposed graphs and noted $G_{\Pi}^{\text{scaled}}$. Each prototype diagram $\Pi$ with one or more bonds $f_R$ generates an infinite set of graphs $G_{\Pi}^{\text{scaled}}$. If $\Pi$ is made with only $\kappa$-scaled bonds, there is only one graph $G_{\Pi}^{\text{scaled}}$, identical to $\Pi$ of course. In Fig. 2, we show four graphs $G_{\Pi}^{\text{scaled}}$ arising in the scaling decomposition of the diagram II drawn in Fig. 1.

In each graph $G_{\Pi}^{\text{scaled}}$, the long-range Coulomb divergences are removed because all the terms in the decompositions (3.4)–(3.7) decay at least as $1/r^3$ at large distances. However, there may appear spurious nonintegrable singularities at short distances because some of these terms diverge at the origin. These unphysical divergencies, also present in the classical Abe-Meeron graphs [27], are eliminated by suitably collecting together the dangerous contributions (see Sec. IV C for an example). The corresponding procedure is a pure mathematical artifact and does not reflect any density-dependent many-body effect. Consequently, the structure of the $\kappa$ expansion of the spatial integrals in each $G_{\Pi}^{\text{scaled}}$ can be determined without any explicit consideration of the previous short-range divergencies. The analysis is carried out in Fourier space with the help of the generalized Plancherel identity. The spatial contribution of each $G_{\Pi}^{\text{scaled}}$, and consequently of any graph $\Pi$, reduces to a double integer series in $\kappa$ and $\ln \kappa$. Only integer powers of $\kappa$ appear because both large-$r$ expansion of $f_T$ and small-$r$ expansions of $G_n$ and $H_n$ involve only integer powers of $r$. Moreover, the logarithms arise in part from the $1/r^3$ tail in $f_T$.

Now, we turn to the functional integrations over the shapes of the filaments of the spatial contribution to (3.2). As argued in paper I, the general term in the density ex-

![FIG. 2. Four graphs $G_{\Pi}^{\text{scaled}}$, which arise in the scaling decomposition of the graph $\Pi$ shown in Fig. 1. The double solid lines (bubbles) represent bonds $f_R/2$ while the dashed lines are bonds $f_T$.](image)
pansion of the functional $\rho_{\xi}(\xi')$ around $\rho_{\xi}$ is a product of integer powers of $\rho_{\xi}$, $\kappa$, and $\ln \kappa$, by functionals of $\xi_i$, which only depend on the temperature (and on the coupling parameter $g$ of course). The structure of the density expansion of the previous spatial contribution is identical, because the $\xi_i$ dependence of the functions $H_{\alpha}$ and $G_{\alpha}$ only enters as polynomials in $\xi_i$, which multiply functions of $x$. (The $\xi$ dependence of the function $f_T$ is more complicated but does not play any role since $f_T$ does not depend on the density.) Therefore, the functional integrations over the $\xi_i$’s weighted by $\rho_{\xi}(\xi_i)$ may be factored in each term of order $\rho^k \ln^k \kappa$ (with $l,n,p$ integers) and does not change the structure of the density expansion [some terms may disappear because of the parity of the measure $D(\xi) \rho_{\xi}(\xi)$]. Since $\kappa$ is proportional to $g^{1/2}$, the integration over the coupling parameter $g$ in (3.2) is also factored out in each term of order $\rho^k \ln^k \kappa$, while the discrete summations over the species may only kill some terms because of the neutrality condition $\sum_{\alpha} e_{\alpha} \rho_{\alpha} = 0$. The density expansion of the excess free energy (3.1) finally reads

$$\frac{\beta F}{\lambda} - \frac{\beta F_{\text{id}}}{\lambda} = \sum_{l,n,p} P_l[\rho_{\alpha}] \left[ \frac{4\pi \beta}{4\pi \beta} \sum_{\alpha} e_{\alpha}^2 \rho_{\alpha} \right]^{n/2} \times \ln^2 \left[ \text{const} \times 4\pi \beta \sum_{\alpha} e_{\alpha}^2 \rho_{\alpha} \right],$$

(3.12)

where $P_l[\rho_{\alpha}]$ are homogeneous polynomials of degree $l$ in the densities $\rho_{\alpha}$ with coefficients depending on the temperature, while the “constants” in the logarithmic terms are built with the temperature-dependent lengths $\beta e_{\alpha} \rho_{\alpha}$ and $\lambda_{\alpha}$.

C. Leading II contribution

Now we turn to the evaluation of the leading contribution of a given prototype graph $\Pi$. In fact, we just sketch the main arguments that allow such an evaluation in the most general case. The precise order of this leading contribution is estimated only in a few simple cases. Like in Sec. III B, the central part of the analysis relies in the determination of the density dependence of the spatial integrals over the filament positions involved in (3.2). Consequently, in the meantime, the dependences with respect to the filament shapes, the species indexes, and the coupling parameter $g$ are not explicitly taken into account. In particular, the filaments are assimilated to points. The effects of the integrations and summations over the omitted variables will be briefly mentioned at the end of the method. All the eventual logarithmic terms are considered to be of order $\rho^2 = 1$.

For the present analysis, it is convenient to introduce the following numbers: $N$ (internal points), $M_R$ (bonds $f_R$), $M_D$ (bonds $f_D$), $M_\alpha$ (bonds $\lambda_{\alpha} \xi_i \cdot \nabla, f_D$), $M''_D$ (bonds $f_{dip}$), and $M = M_R + M_D + M_\alpha + M''_D$ ($F$ bonds). Since each $\rho_{\xi}(\xi_i)$ is at least of order $\rho$, according to the expansion (2.8), the product of the statistical weights in a graph $\Pi$ is at least of order $\rho^{N+2}$. The scaling decomposition (3.7) shows that the lowest order contributions arise from $\kappa^2 G_2(x) = f^2_B / 2$ and $f_T$ because $f_T$ is integrable [except for possible logarithmic singularities, which ultimately give $\ln(\text{const} \times \kappa)$ terms]. Indeed, all the other $\kappa$-scaled terms in (3.7) are at least of order $\kappa^3$, while the mixed functions $\kappa^2 H_\alpha f_T$ with $n \geq 1$ introduce $\kappa^4$ multiplicative factor to the bare contribution of $f_T$. Therefore, the lowest-order contribution to (3.2) is given by one of the decomposed graphs $G^{\text{II},\text{min}}_{\alpha} = M_R$ bonds $f_T$ and $(M_R - M_T)$ bonds $\kappa^2 G_2(x)$. For instance, in the case of the graph $\Pi$ ($N = 2, M_R = 2, M_D = 2, M_\alpha = 0, M''_D = 0$) shown in Fig. 1, the lowest-order $G^{\text{scaled}}_{\Pi,\text{II},\text{min}}$ graphs are those drawn in Fig. 2.

Since $f_T$ is integrable and entirely controlled by the lengths $\beta e_{\alpha} \rho_{\alpha}$ and $\lambda_\alpha$ which do not depend on the density, the dominant space configurations in $G^{\text{II},\text{min}}_{\alpha}$ are such that each pair $(i,j)$ connected by a $f_T$ bond is contained in a “contraction” disk with a finite radius $\sigma$, which only depends on the temperature. In the low-density limit, $\kappa^{-1}$ is large compared to $\sigma$ and the $\kappa$-scaled bonds $f_D$, $f^2_B / 2$, $\lambda_{\alpha} \xi_i \cdot \nabla, f_D$, and $f_{dip}$, which connect part of the points belonging to the same contraction disk, can be replaced by their respective short-distance forms $-\beta_{ij}/\sigma$, $-\beta_{ij}/(2\sigma^2)$, $-\beta_{ij} \lambda_\alpha \xi_i \cdot \nabla, (1/\sigma)$, and $-\beta_{ij} \kappa^2 (\lambda_{\alpha} \xi_i \cdot \nabla, (1/\sigma) \sigma^2 / 2$. Therefore, the order of the contribution of $G^{\text{scaled}}_{\Pi,\text{II},\text{min}}$ is directly related to the one of the contracted graph made with disks of radius $\sigma$ located at $R_{\alpha}$ and connected by the remaining $\kappa$-scaled bonds. For the graphs $G^{\text{scaled}}_{\Pi,\text{II},\text{min}}$ shown in Fig. 2, this first step of the contraction process leads to the graphs represented in Fig. 3. (The points that do not enter in the contraction

FIG. 3. The four contracted graphs, which are obtained from the graphs shown in Fig. 2 after the first step of the contraction process. The big hatched circles are contraction disks. Each solid line represents a bond $f_D$. 
procedure can be also replaced by disks.

At this level, in a contracted graph derived from a $G_{\text{II, min}}^{\text{scaled}}$, some disks may be connected by products of $k$-scaled bonds involving at least either three $f_D$ bonds; two $f_D$ bonds and one $f_{\text{dip}}$ bond; one $f_B$ bond and two $f_{\text{dip}}$ bonds; one $f_D$ bond and one $\lambda e \cdot \nabla f_D$ bond; three $f_{\text{dip}}$ bonds; two $f_{\text{dip}}$ bonds and one $\lambda e \cdot \nabla f_{\text{dip}}$ bond; one $f_{\text{dip}}$ bond and one $\lambda e \cdot \nabla f_D$ bond; or two $\lambda e \cdot \nabla f_D$ bonds. All these products decay at least as $1/r^3$ over a length scale $\sigma \ll \kappa^{-1}$, which does not depend on the density, so the corresponding disks can be themselves contracted into a single one. We point out that $f_{\text{dip}}$ behaves as $k^2/r$ for $r \sim \sigma$, while $f_{\text{dip}}$ decays as $1/r^3$ for $r$ large compared to $\kappa^{-1}$. For instance, Figs. 3(b) and 3(c) are transformed into Fig. 3(d), while 3(a) and 3(d) remain unchanged in the second step of the contraction. At the end of this contraction process, the contracted disks that are left over are connected either by a single $f_D$ bond, two $f_D$ bonds, one $f_D$ bond and one $f_{\text{dip}}$ bond, a single $f_{\text{dip}}$ bond, two $f_{\text{dip}}$ bonds, or a single $\lambda e \cdot \nabla f_D$ bond.

If $M_f < N + 1$, the contracted graph resulting from $G_{\text{II, min}}^{\text{scaled}}$ contains $N_d$ disks with $N_d \leq N + 2 - M_f$, $M_f^{\text{cont}}$ $f_D$ bonds with $0 \leq M_f^{\text{cont}} \leq M_f + 2(M_f - M_f^T)$, $M_f^{\text{cont}}$ $\lambda e \cdot \nabla f_D$ bonds with $0 \leq M_f^{\text{cont}} \leq M_f$, and $M_f^{\text{cont}}$ $f_{\text{dip}}$ bonds with $0 \leq M_f^{\text{cont}} \leq M_f$. In the contraction procedure, the order of the contribution of $G_{\text{II, min}}^{\text{scaled}}$ remains unchanged when $f_D$ bonds and $\lambda e \cdot \nabla f_D$ bonds are absorbed because their respective short-range behaviors at distances $r \sim \sigma$ do not depend on the density. On the contrary, each absorption of one $f_{\text{dip}}$ bond introduces a multiplicative factor $k^2$. Therefore, the order of the contribution of $G_{\text{II, min}}^{\text{scaled}}$ is equal to the one of the contracted graph multiplied by $k^{(M_f^{\text{cont}} - M_f^{\text{cont}})}$. The order of the remaining integrals over the $(N_d - 1)$ positions of $R_i$ of the contraction disks, which are integrated over in (3.2), is easily determined by the variable change $X_i = \kappa R_i$. In this simple scaling transformation, each integration volume $dR_i$ gives a factor $\kappa^{-3}$, while, according to (3.4)–(3.6), each of the bonds $f_D$, $\lambda e \cdot \nabla f_D$, and $f_{\text{dip}}$ gives factors $\kappa$, $k^2$, and $k^3$, respectively. Moreover, the potential term $1/r$ in (3.2) gives a factor $k^{\varepsilon^{cont}}$ with $\varepsilon^{cont} = 1$ if $a$ and $b$ are not contracted into the same disk and $\varepsilon^{cont} = 0$, otherwise. So, when all the factors arising from the density weights, the absorption of $f_{\text{dip}}$ bonds, and the previous scaling transformation are taken into account, the order of the contribution of $G_{\text{II, min}}^{\text{scaled}}$ to (3.2) reduces to $\rho^{\kappa} \rho^{n_0}$ with

$$n_0 = N + 2 + M_f^T - M_f^{\text{cont}} - \frac{1}{2}(N_d - 1)$$

$$+ \frac{1}{2} M_f^{\text{cont}} + M_f^T + \frac{3}{2} M_f^{\text{cont}} + \frac{1}{2} \varepsilon^{\text{cont}}.$$  \hfill (3.13)

If $M_f > N + 1$, the contraction procedure leads to the collapse of all the points of $G_{\text{II, min}}^{\text{scaled}}$ into a single disk. The order of the contribution of $G_{\text{II, min}}^{\text{scaled}}$ to (3.2) reduces then to the one of the weighting prefactor multiplied by $k^{2M_f^T}$, i.e., to $\rho^{m_0}$ with

$$m_0 = N + 2 + M_f^T.$$  \hfill (3.14)

Notice that in the case of short-range forces, the leading order of the Mayer graphs is always $\rho^{N+2}$.

For similar reasons as those exposed in Sec. III B, the integration over $g$ does not change the above orders, while the functional integrals over the $\xi$'s and the summation over the $\alpha$'s may only kill some contributions. Therefore, strictly speaking, the powers (3.13) and (3.14) should be understood in fact as lower bounds in the present study.

In principle, the order of the leading contribution of any graph II might be determined by taking either the infimum of the $n_G$'s if $M_f < N + 1$, or the infimum of the $n_G$'s and $m_G$'s, otherwise. For instance in the case of the graph II $(N = 2, M_f = 2, M_D = 2, M_D^T = 0, M_D^{\text{cont}} = 0)$ shown in Fig. 1, the order in $\rho$ of the corresponding four graphs $G_{\text{II, min}}^{\text{scaled}}$ shown in Fig. 2 are, according to (3.13), $n_G^{(a)} = 3$, $n_G^{(b)} = 6$, $\varepsilon^{\text{cont}} = 1$ and $n_G^{(c)} = n_G^{(d)} = 2$, $N_d = 2, M_D^{\text{cont}} = 1, \varepsilon^{\text{cont}} = 1$. The leading contribution of this graph II obviously is of order $\rho^{3}$. However, such quantitative evaluations are not easy to carry out, in general, because the determination of the numbers $N_d, M_f^{\text{cont}}, M_D^{\text{cont}}, M_D^{\text{cont}}$, and $\varepsilon^{\text{cont}}$ requires a careful analysis of the topological structure of the considered graph II. When the graph is highly connected (as it is the case for the bridges), many points may be contracted in the same disk through cascade mechanisms, the control of which is far beyond the scope of the present paper. In the simple case $M_f = 0$, there is no contraction, these numbers obviously reduce to $N + 2, M_f, M_D, M_D^{\text{cont}}, \varepsilon^{\text{cont}} = 1$, and the contribution of II is exactly of order $\rho^3$.

$$1 + \frac{(M - N)}{2} + M_f^T + \frac{M_D^{\text{cont}}}{2} + M_D^{\text{cont}}.$$  \hfill (3.15)

It is quite reasonable to assume that the order of the leading contribution of II is, roughly speaking, an increasing function with respect to the number $N$ of internal points and the number $M$ of $F$ bonds. This assumption is supported by the following simple qualitative arguments. If II contains a few bonds $f_B$, the numbers $M$ or $M_D^{\text{cont}}$ and $M_D^{\text{cont}}$ are large enough since II must obey the excluded-convolution rule. In particular, the power (3.15) relative to graphs without any bond $f_D$ do increase with $N$, because the chain graphs made only with bonds $f_D (M - N = 1, M_D^T = 0, M_D^{\text{cont}} = 0)$ are not allowed. When II contains many bonds $f_B$, the order of the graph $G_{\text{II, min}}^{\text{scaled}}$ with a few functions $f_B$ should be analogous to (3.15) while it reduces to (3.14) if $M_f > N + 1$: both quantities do exhibit the above monotonicity. Consequently, there is a finite number of graphs that contribute to a given order in the density expansion (3.12) and the minimal power $(1 + n/2)$ in (3.12) is $\frac{1}{2}$.

IV. EXPLICIT CALCULATIONS AT THE ORDER $\rho^{3/2}$

According to the general power-counting rules derived in Sec. III C, the graphs II contributing to the expansion (3.12) up to the order $\rho^{3/2}$ are found to have at most two

$$E_a \quad \cdots \quad E_b$$

FIG. 4. The simplest Debye graph II $(N = 0, M_D = 1)$. 
bonds $f_R$ (simple examples strongly suggest that all the remaining graphs with three or more bonds $f_R$ are at least of order $\rho^3$). Taking into account the excluded-convolution rule as well as the parity of the measure $D(\xi)\rho(\xi)$, which makes some contributions vanish, the graphs of interest can be listed as follows.

A. Debye graphs ($M_R = 0, M_D = 0, M_D' = 0$)

There are five graphs $\Pi_D$ built only with bonds $f_D$ that contribute: the simplest graph $\Pi_D(N = 0, M_D = 1)$ (see Fig. 4) and the bridge graphs shown in Figs. 5 and 6 (the bridges in Fig. 6 are built by convoluting the bridge in Fig. 5 with one or two bonds $f_D$).

Their contributions read

$$
\frac{1}{2} \sum_{a,b} \beta_{ab} \int_0^1 \int \mathcal{D}(\xi_a) \mathcal{D}(\xi_b) \rho(\xi_a) \rho(\xi_b) \int dr \left[ -g \beta_{ab} \frac{\exp(-g^{1/2}kr)}{r} \right] = -\frac{1}{2} \sum_{a,b} \beta_{ab} \int_0^1 \int \rho(\xi_a) \rho(\xi_b) 4\pi \beta_{ab} \kappa^{-1} g^{1/2}
$$

$$
= -\frac{\kappa^3}{12\pi}
$$

(4.1)

for the familiar Debye graph,

$$
\frac{1}{2} \sum_{a_1, a_2, a_1, a_2} \beta_{ab} \int_0^1 \int \mathcal{D}(\xi_a) \mathcal{D}(\xi_b) \mathcal{D}(\xi_a) \mathcal{D}(\xi_b) \rho(\xi_a) \rho(\xi_b) \rho(\xi_a) \rho(\xi_b)
$$

$$
\times \left[ -g \beta_{a_1} \frac{\exp(-g^{1/2}kr_1)}{r_1} \right] \left[ -g \beta_{a_2} \frac{\exp(-g^{1/2}kr_2)}{r_2} \right] \left[ -g \beta_{b_1} \frac{\exp(-g^{1/2}kr_{1b})}{r_{1b}} \right] \left[ -g \beta_{b_2} \frac{\exp(-g^{1/2}kr_{2b})}{r_{2b}} \right] \left[ -g \beta_{b_1} \frac{\exp(-g^{1/2}kr_{12})}{r_{12}} \right]
$$

$$
= -\frac{1}{2} \int d\mathbf{x} d\mathbf{x}_1 d\mathbf{x}_2 \frac{e^{-\mathbf{x}}}{\mathbf{x}_1} \frac{e^{-\mathbf{x}_1}}{\mathbf{x}_1} \frac{e^{-\mathbf{x}_2}}{\mathbf{x}_2} \frac{e^{-\mathbf{x}_2}}{\mathbf{x}_2} \frac{e^{-\mathbf{x}_1}}{\mathbf{x}_1} \frac{e^{-\mathbf{x}_2}}{\mathbf{x}_2} \sum_{a_1 a_2 b_1 b_2} \beta_{a_1}^* \beta_{a_2}^* \beta_{b_1} \beta_{b_2} \kappa^{-3} \rho(\mathbf{a}) \rho(\mathbf{b}) (4.2)
$$

for the bare bridge graph, and

$$
-\frac{1}{2} \int d\mathbf{x} d\mathbf{x}_1 d\mathbf{x}_2 \left[ \frac{e^{-\mathbf{x}}}{\mathbf{x}} - \frac{1}{2} \frac{e^{-\mathbf{x}}}{\mathbf{x}} \right] \frac{e^{-\mathbf{x}_1}}{\mathbf{x}_1} \frac{e^{-\mathbf{x}_1}}{\mathbf{x}_1} \frac{e^{-\mathbf{x}_2}}{\mathbf{x}_2} \frac{e^{-\mathbf{x}_2}}{\mathbf{x}_2} \frac{e^{-\mathbf{x}_2}}{\mathbf{x}_2} \sum_{a_1 a_2 b_1 b_2} \beta_{a_1}^* \beta_{a_2}^* \beta_{b_1} \beta_{b_2} \kappa^{-3} \rho(\mathbf{a}) \rho(\mathbf{b}) (4.3)
$$

FIG. 6. The three graphs obtained by convoluting the bridge graph shown in Fig. 5 with one or two bonds $f_D$. 

FIG. 5. The bare bridge graph $\Pi_D (N = 2, M_D = 5)$. 

\[ \text{FIG. 5. The bare bridge graph } \Pi_D (N = 2, M_D = 5). \]
for the convoluted bridges. The contribution (4.1) of the simplest graph is nothing but the well-known classical Debye-Hückel term. In (4.2) and (4.3), the dimensionless integrals can be evaluated numerically by Legendre polynomial expansion. We stress that the contributions (4.1)-(4.3) are exactly proportional to half-integer powers of $\rho$. This is due to the fact that the functional integrations over the filament shapes exactly amount to replace each $\rho g(\mathcal{E}_1)$ by the corresponding particle density $\rho_a$. This property holds for any Debye graph $\Pi_D$ with only bonds $f_{DP}$.

B. Diffraction graphs $(M_R = 0, M''_F = 0, \text{or/and } M''_D = 0)$

The sole contributing diffraction graph $\Pi_{\text{diff}} (N = 1, M_D = 0, M''_F = 2, M''_D = 0)$ has one internal point $\mathcal{E}_1$ linked to $\mathcal{E}_a$ and $\mathcal{E}_b$ by the bonds $\lambda_a \xi_a \cdot \nabla \cdot f_{DP} (|r_a - r_b|)$ and $\lambda_a \xi_a \cdot \nabla \cdot f_{DP} (|r_a - r_b|)$ (see Fig. 7).

Only the leading contribution of this graph has to be retained since it is of order $\rho^{3/2}$. It is obtained by replacing $\rho g(\mathcal{E}_1)$ by $\rho_a$ and reads

$$
\frac{1}{2} \sum_{a,b} \beta_{ab} \beta \rho_a \rho_b \rho_{a} \rho_{a} \lambda_a \lambda_b \frac{1}{K} \int_0^1 \frac{d g}{g} \int_0^1 \frac{d x}{x} \int_0^1 \frac{d s}{s} \int_0^1 \frac{d t}{t} \xi_a(s) \cdot \nabla_s \frac{e^{-x}}{x} \xi_b(t) \cdot \nabla_s \frac{e^{-x}}{x} \frac{4 \pi u}{u^2 + 1} + \frac{4 \pi u}{u^2 + 1} = \frac{1}{150} \sum_a \beta e_a \lambda_a^2 \rho_a,
$$

(4.4)

where we have used the covariance (2.2) of the Gaussian measure $\mathcal{D}(\xi)$, Fourier-Plancherel identity, and $\int_0^1 du u^2 / (u^2 + 1) = \pi / 4$. In the following cases, there proves to be no other diagram with $\lambda_a \xi_a \cdot \nabla \cdot f_{DP}$ bonds and/or $f_{DP}$ bonds that contributes to the order $\rho^{3/2}$.

C. Chain graphs with one $f_R$ bond

(i) First we consider the simple graph $\Pi_R (N = 0, M_R = 1)$ with only one bond $f_R (\mathcal{E}_a, \mathcal{E}_b)$ (see Fig. 8). The leading contribution of this graph is of order $\rho^2$ and is obtained by replacing $f_R$ by either $f_T$ or $f_D^*$ in the scaling decomposition (3.7), and $\rho g(\mathcal{E}_a)$ by $\rho_a$ (or $\rho_b$). In each, of the two graphs $\Pi_{\text{Hed}}(\Pi_\text{Hed})$ built with $f_T$ or $f_D^*$ gives a divergent contribution to the free energy of a spurious singularity at the origin. In accordance with the general arguments exposed in Sec. III B, this nonphysical divergency is removed by merely adding both contributions. The finite total contribution of these two graphs can then be calculated as

$$
\frac{1}{2} \sum_{a,b} \beta \rho_a \rho_b \rho_{a} \rho_{b} \int_0^1 \frac{d g}{g} \lim_{R \to \infty} \int_{R \ll r} \frac{d r}{r} \left[ (2 \pi \lambda_a \lambda_b \right]^{3/2} \frac{\exp(-\beta h_{ab}(r))}{r} - 1 + \frac{\beta}{r} \frac{\beta^2}{2} \left[ 1 - \exp(-2 \beta^2 r) \right] \right]

= -\frac{1}{2} \sum_{a,b} \beta \rho_a \rho_b \lim_{R \to \infty} \left[ \beta_{ab} \frac{1}{2} \int_0^1 \frac{d g}{g} \frac{2 \pi^2}{4} \int_0^{2 \pi^2 \lambda a} \frac{e^{-x}}{x} \right] \left[ \beta_{ab} \frac{1}{2} \int_0^1 \frac{d g}{g} \frac{2 \pi^2}{4} \int_0^{2 \pi^2 \lambda b} \frac{e^{-x}}{x} \right] = \frac{\beta^2}{6} \sum_{a,b} \beta e_a \lambda_a^2 \rho_a \rho_a

= -\frac{1}{2} \sum_{a,b} \beta \rho_a \rho_b \lim_{R \to \infty} \left[ \int_{R \ll r} \left[ 2 \pi \lambda_a \lambda_b \right]^{3/2} \left[ \exp(-\beta h_{ab}(r)) - 1 + \frac{\beta}{r} \frac{\beta^2}{2} \left[ 1 - \exp(-2 \beta^2 r) \right] \right] \right] = \frac{\pi}{3} (C + \ln 2 - \frac{1}{2}) \sum_{a,b} \beta e_a \lambda_a^2 \rho_a \rho_a

= \frac{\pi}{3} (C + \ln 2 - \frac{1}{2}) \sum_{a,b} \beta e_a \lambda_a^2 \rho_a \rho_a

\right)

(4.5)

where $h_{ab}$ is the one-body Coulomb Hamiltonian of the relative particle with reduced mass $m_a m_b / (m_a + m_b)$ in the potential $ge_a e_b / r$ ($h_{ab}^{-1} = h_{ba}$) and $\lambda_{ab}$ is the corresponding thermal de Broglie wavelength ($C$ is Euler-Mascheroni's constant). The matrix elements of $\exp(-\beta h_{ab})$ are introduced by applying backwards the Feynman-Kac formula [3] and by factoring out the trivial kinetic contribution of the center of mass, i.e.,

$$
\int \mathcal{D}(\xi_a) \mathcal{D}(\xi_b) \exp \left[ -\beta g e_a e_b \int_0^1 ds v_c (|r + \lambda_a \xi_a(s) - \lambda_a \xi_a(s)|) \right]

= (2 \pi \lambda_a \lambda_b)^{3/2} \left( 0 \right) \exp \left[ -\beta \left( \frac{\hat{\nabla}}{2 m_a} - \Delta_a + \frac{g e_a e_b}{r_{ab}} \right) \right] \left( 0 \right)

= (2 \pi \lambda_a \lambda_b)^{3/2} \left( 0 \right) \exp \left[ -\beta h_{ab}^2 \right] \left( 0 \right),
$$
In the first line of (4.5), the introduction of \( \lim_{R \to \infty} \) is just a mathematical trick (the integral does converge). The second line is obtained through the identity (A13) derived in the Appendix. This identity is a suitable extension to the Coulomb case of the usual differentiation trace identity

\[
(\partial / \partial g) \text{Tr}[\exp(-\beta(h_0 + gV_{int})) - \exp(-\beta h_0)] = -\beta \text{Tr}[V_{int} \exp(-\beta(h_0 + gV_{int}))],
\]

valid for any integrable potential \( V_{int} \) (\( h_0 \) is the kinetic Hamiltonian). The long-range part of the Coulomb potential gives rise to the last additional term in the second line of (4.5). It turns out that this term vanishes because of the neutrality condition. In the third line of (4.5) the logarithmic divergence when \( R \to \infty \) of the truncated trace of \( \exp(-\beta h_{ab}) \) and the logarithmic term \( (2\pi/3) \beta^2 e_a^2 e_b^2 \ln(\kappa R) \) cancel out, as it should be. The resulting quantity \( \lim_{R \to \infty} \) takes the form \( \text{Const} \times \ln(\text{Const} \times \kappa) \) where the involved “constants” depend on the temperature and are built with the Landau and de Broglie lengths, i.e., \( \beta e_a^2 e_b^2 \) and \( \lambda_{ab} \).

The next contribution of order \( \rho^{5/2} \) of \( \Pi_\chi (N = 0, M = 1) \) is given by the mixed function \( \kappa H_1(x)f \tau \) and by the \( \kappa \)-scaled function \( \kappa^2 \beta_{ab}^3 [1 - \exp(-3x)] / 6x^3 \) in (3.7). It can be expressed as

\[
\left. \frac{1}{2} \sum_{a_1 a_2} \beta_{ab} \beta_{a_2 a_3} \rho_{ab} \right|_{0}^{1} dg \int dr \left| \frac{r}{r} \right| \left\{ \frac{g \beta_{ab}}{r} \left[ 1 - \exp(-g^{1/2} \kappa r) \right] \left[ (2\pi \lambda_{a_2 a_3}^2)^{1/2} \langle r | \exp(-\beta h_{a_2 a_3}) | r \rangle - 1 + \frac{g \beta_{ab}}{r} \right] - \frac{g \beta_{ab}^3}{2 \rho^{3}} \left[ 1 - \exp(-g^{1/2} \kappa r) \right] + \frac{g \beta_{ab}^3}{6 \rho^{3}} \left[ 1 - \exp(-3g^{1/2} \kappa r) \right] \right. \\
= \frac{1}{2} \sum_{a_1 a_2} \beta_{ab} \beta_{a_2 a_3} \rho_{ab} \left|_{0}^{1} dg \int dr \frac{g \beta_{ab}}{r} \left[ 1 - \exp(-g^{1/2} \kappa r) \right] \frac{1}{r} \left[ (2\pi \lambda_{a_2 a_3}^2)^{1/2} \langle r | \exp(-\beta h_{a_2 a_3}) | r \rangle - 1 + \frac{g \beta_{ab}}{r} \right] \\
- \kappa \beta_{ab}^3 \int_{0}^{1} dg \frac{g^{7/4} \pi}{\pi} \int_{0}^{\infty} dx \frac{(1 - e^{-x})(2 - e^{-x} - e^{-2x})}{x^2} \right. \right). \tag{4.6}
\]

The integral \( \int dr \) in the right-hand side of (4.6) can be rewritten as the sum of \( \int_{r < R} dr \) and \( \int_{r > R} dr \) for any given \( R \). By choosing \( R \) large enough compared to \( \beta e_a^2 e_b^2 \), \( \lambda_{a_2 a_3} \), and \( \lambda_{a_3} \), we can replace \( \int_{r > R} dr \) by

\[
\int_{r < R} dr \frac{g \beta_{ab}}{r} \left[ 1 - \exp(-g^{1/2} \kappa r) \right] \frac{g \beta_{ab}^3}{2 \rho^{3}} = 2\pi g^{7/2} \kappa \beta_{ab}^3 \int_{g^{1/2} \kappa R}^{\infty} dx \frac{(1 - e^{-x})}{x^2}, \tag{4.7}
\]

disregarding terms that go to zero when \( R \to \infty \) uniformly with respect to \( \kappa \). In the integral \( \int_{r < R} dr \), we can first replace \( g \beta_{ab} \left[ 1 - \exp(-g^{1/2} \kappa r) \right] / r \) by \( g^{3/2} \beta_{ab}^3 \) and then proceed to an integration by parts over \( g \) by using the differentiation trace identity (A13). The resulting expression for the term of order \( \rho^{5/2} \) in the contribution (4.6) then reads

\[
-\frac{1}{2} \sum_{a \beta} \beta e_a^2 e_b^2 \rho_{ab} \beta_{ab} \left|_{R \to \infty}^{R} \frac{2\pi g^{3/2} \beta_{ab}^3 \lambda_{a_2 a_3}^2 \ln(\kappa R)}{3} + \int_{r < R} dr \left[ (2\pi \lambda_{a_2 a_3}^2)^{1/2} \langle r | \exp(-\beta h_{a_2 a_3}) | r \rangle - 1 + \frac{\beta e_a^2 e_b^2}{r} - \frac{\beta e_a^2 e_b^2}{2 r^2} \right] \right. \\
+ \frac{1}{2} \sum_{a \beta} \beta e_a^2 e_b^2 \rho_{ab} \beta_{ab} \int_{0}^{1} dg \left|_{0}^{1} \frac{g^{3/2} \beta_{ab}^3 \lambda_{a_2 a_3}^2 \ln(\kappa R)}{3} + \int_{r < R} dr \left[ (2\pi \lambda_{a_2 a_3}^2)^{1/2} \langle r | \exp(-\beta h_{a_2 a_3}) | r \rangle - 1 + \frac{\beta e_a^2 e_b^2}{r} - \frac{g \beta_{ab}^3}{2 r^2} \right] \right. \right) \right. \right) \right). \tag{4.8}
\]

(ii) We turn now to the contributions of the chain graphs \( \Pi_{\chi} \) with one bond \( f_R \) and one or two bonds \( f_{\beta} \), i.e., the three graphs shown in Fig. 9. The leading contributions of these graphs are associated to the graphs \( G_{\Pi, \min}^{\text{scaled}} \) arising from the replacement of \( f_R \) by \( f_{\beta}^2 / 2 \). The total contribution of the latter graphs is of order \( \rho^2 \) and can be calculated as
\[
\frac{1}{2} \sum_{a, a_b} \rho_b \rho_a \rho_{a_b} \int_0^1 d g \int d x \frac{x}{x_1} \left[ -\frac{2}{\kappa^2} \sum_{a_1} \rho_{a_1} \rho_{a_b} \rho_{a_1} \int d x_i \frac{e^{-x_1} e^{-2|x_1-x|}}{2|x_1-x_i|^2} \right. \\
+ \frac{1}{\kappa^4} \sum_{a_1, a_2} \rho_{a_1} \rho_{a_2} \rho_{a_1} \rho_{a_2} \int d x_i d x_j \frac{e^{-x_1} e^{-2|x_1-x_j|} e^{-|x_1-x_j|}}{2|x_1-x_j|^2} \\
\left. \right] \\
= \frac{1}{24\pi} \sum_{a, b} \beta_i e_a e_b \rho_a \rho_b \left[ -\frac{1}{(2\pi)^3} \int d u \frac{4\pi}{u^2} \frac{4\pi}{(1+u^2)} \frac{4\pi}{u} \arctan \left( \frac{u}{2} \right) \\
+ \frac{1}{8\pi} (2\pi)^3 \int d u \frac{4\pi}{u} \left( \frac{4\pi}{(1+u^2)} \frac{4\pi}{u} \arctan \left( \frac{u}{2} \right) \right)^2 \right] \\
= \frac{\pi}{3} (\ln 2 - \ln 3 - \frac{1}{3}) \sum_{a, b} \beta_i e_a e_b \rho_a \rho_b , \\
(4.9)
\]
where we have used the Fourier-Plancherel identity together with the convolution theorem \((4\pi/u) \arctan (u/2)\) is the Fourier transform of \(\exp(-2x)/x^2\).

The next contributions of the above chain graphs are of order \(\rho^5/4\) and arise either from the \(\kappa\)-scaled term \(\kappa^3 \beta_i^3 / 1 - \exp(-3x) / 6x^3\) or from \(f_T\) in the scaling decomposition \((3.7)\) of \(f_R\) (here the term of order \(\kappa^3\) linear in the \(\xi\)'s does not give any contribution for parity reasons). The contributions associated to the \(\kappa\)-scaled term can be again calculated along similar lines to \((4.9)\) by using the Fourier transform of \([1 - \exp(-3x)]/x^3\), which is \(4\pi \left( \frac{1}{3} \ln (9 + u^2)/u^2 + (3/\pi) \arctan (u/3) \right)\). Their sum is equal to

\[
\frac{\pi}{9} (2\ln 3 - 3\ln 4) \sum_{a, b} \beta_i e_a e_b \rho_a \rho_b . \\
(4.10)
\]

For calculating the contributions of order \(\rho^5/4\) associated to the decomposed graphs with \(f_T\) in place of \(f_R\), we can replace \(\rho(E_i)\) by \(\rho_{a_i}\). Since these decomposed graphs have a chain structure, their total contribution can be easily expressed in Fourier space as

\[
-\frac{1}{\pi} \sum_{a, b} \beta_i e_a e_b \rho_a \rho_b \int_0^1 d g g^{1/2} \int_0^\infty d u \tilde{f}_{T, a b}(g^{1/2} \kappa u) \left[ \frac{2}{1 + u^2} - \frac{1}{(1 + u^2)^2} \right] , \\
\]

with

\[
\tilde{f}_{T, a b}(k) = \int d r \exp(ik \cdot r) \left[ \frac{2\pi \rho_{a_b}^2}{r} \langle r | \exp(-\beta h_{a_b}) | r \rangle - 1 \right] + \frac{g \beta e_a e_b}{r} - g^2 e^2 e^2 b^2 \frac{2\pi}{2 r^2} . \\
(4.11)
\]

When \(k \to 0\), \(\tilde{f}_{T, a b}(k)\) diverges logarithmically as

\[
\hat{f}_{T, a b}(k) = \lim_{R \to \infty} \left[ \int_{r < R} d r \left[ \frac{2\pi \rho_{a_b}^2}{r} \langle r | \exp(-\beta h_{a_b}) | r \rangle - 1 \right] + \frac{g \beta e_a e_b}{r} - g^2 e^2 e^2 b^2 \frac{2\pi}{2 r^2} \right] + \frac{\pi}{3} g^3 \rho_{a_b}^3 (\ln R) - 2g^3 \rho_{a_b}^3 (1 - C) + o(1) . \\
(4.13)
\]

The resulting low-density behavior of \((4.11)\) follows by inserting \((4.13)\) with \(k = g^{1/2} \kappa u\), and reads at the order \(\rho^5/4\)

\[
\frac{\pi}{9} (\frac{1}{\sqrt{C}} - C) \sum_{a, b} \beta_i e_a e_b \rho_a \rho_b - \frac{1}{4} \sum_{a, b} \beta_i e_a e_b \rho_a \rho_b \int_0^1 d g g^{1/2} \lim_{R \to \infty} \left[ \int_{r < R} d r \left[ \frac{2\pi \rho_{a_b}^2}{r} \langle r | \exp(-\beta h_{a_b}) | r \rangle - 1 \right] + \frac{g \beta e_a e_b}{r} - g^2 e^2 e^2 b^2 \frac{2\pi}{2 r^2} \right] + \frac{\pi}{3} g^3 \rho_{a_b}^3 (\ln R) , \\
\]

where we have used \(\int_0^\infty d u (\ln u) [2/(1 + u^2) - 1/(1 + u^2)] = \pi/4\) and \(\int_0^\infty d u [2/(1 + u^2) - 1/(1 + u^2)]^2 = 3\pi/4\).
D. Loop graphs with one $f_R$ bond

The two simplest loop graphs with one $f_R$ bond and two $f_D$ bonds are shown in Figs. 10(a) and 10(b). Their leading contributions are of order $p^{5/2}$ and are obtained by replacing $f_R$ by $f_D^2/2$. Using the Fourier-Plancherel identity and the convolution theorem, we find that the sum of these contributions reads

$$\frac{32\pi}{9} \int_0^\infty du \arctan\left(\frac{u}{2}\right) \arctan(u) \sum_{\alpha\beta} \beta^\alpha e_\alpha^3 e_\beta^3 \kappa^{-1} \rho_\alpha \rho_\beta \rho_\gamma \ . \quad (4.15)$$

The loop graphs shown in Fig. 11 are obtained by convoluting the graphs in Figs. 10(a) and 10(b) with one or two bonds $f_D$. Their total leading contribution is also of order $p^{5/2}$ and reads

$$\frac{32\pi}{9} \int_0^\infty du \arctan\left(\frac{u}{2}\right) \arctan\left(\frac{u}{2}\right) - \arctan\left(\frac{u}{2}\right) - \arctan\left(\frac{u}{2}\right) - \arctan\left(\frac{u}{2}\right) \sum_{\alpha\beta\gamma} \beta^\alpha e_\alpha^3 e_\beta^3 e_\gamma^3 \kappa^{-1} \rho_\alpha \rho_\beta \rho_\gamma \ . \quad (4.16)$$

The loop graph with three bonds $f_D$ shown in Fig. 12 also gives a leading contribution of order $p^{5/2}$, i.e.,

$$- \frac{64\pi^2}{9} \int_0^\infty du \arctan\left(\frac{u}{2}\right) \arctan(u) \sum_{\alpha\beta\gamma} \beta^\alpha e_\alpha^3 e_\beta^3 e_\gamma^3 \kappa^{-1} \rho_\alpha \rho_\beta \rho_\gamma \ . \quad (4.17)$$

as well as the three other graphs obtained by convolutions with one or two bonds $f_D$ (see Fig. 13), the total contribution of which reads

$$\frac{64\pi^2}{9} \int_0^\infty du \frac{1}{(u^2 + 1)^2} \arctan\left(\frac{u}{2}\right) \arctan(u) - \arctan\left(\frac{u}{2}\right) + \frac{u}{2(u^2 + 4)} \sum_{\alpha\beta\gamma} \beta^\alpha e_\alpha^3 e_\beta^3 e_\gamma^3 \kappa^{-1} \rho_\alpha \rho_\beta \rho_\gamma \ . \quad (4.18)$$

E. Chain graphs with two $f_R$ bonds

The corresponding graphs are built with two bonds $f_R$ and at most three bonds $f_D$. These graphs are shown in Figs. 14–17. Their leading contributions are of order $p^{5/2}$ and arise from the replacement of the two bonds $f_R$ by $f_D^2/2$. After use of the convolution theorem in Fourier space, they can be rewritten as

$$\frac{32\pi^2}{9} \int_0^\infty du \arctan\left(\frac{u}{2}\right) \arctan\left(\frac{u}{2}\right) - \frac{1}{2(1 + u^2)} + \frac{1}{2(1 + u^2)^2} \sum_{\alpha\beta\gamma} \beta^\alpha e_\alpha^3 e_\beta^3 e_\gamma^3 \kappa^{-3} \rho_\alpha \rho_\beta \rho_\gamma \ . \quad (4.19)$$

for the four graphs shown in Figs. 14 and 15, and

$$\frac{8\pi}{9} \int_0^\infty du \arctan\left(\frac{u}{2}\right) \arctan\left(\frac{u}{2}\right) - \frac{1}{2(1 + u^2)} + \frac{1}{2(1 + u^2)^2} \sum_{\alpha\beta\gamma} \beta^\alpha e_\alpha^3 e_\beta^3 e_\gamma^3 \kappa^{-1} \rho_\alpha \rho_\beta \rho_\gamma \ . \quad (4.20)$$

for the four remaining graphs shown in Figs. 16 and 17.

F. Final results and comments

The final expression of the excess free-energy density at the order $p^{5/2}$ is obtained by summing the contributions [(4.1)–(4.5), (4.8)–(4.10), and (4.14)–(4.20)] with the result

$$\frac{\beta F}{\Lambda} = \frac{\beta F_{id}}{\Lambda} - \frac{3}{12\pi} (C + \ln 3) \sum_{\alpha, \beta} \beta^\alpha e_\alpha^3 e_\beta^3 \rho_\alpha \rho_\beta \beta e_{\alpha e_\beta}^3 \rho_\alpha \rho_\beta + \frac{1}{3} \int_{r < R} \frac{dr}{r} \left( (2\pi \lambda_{ab}^2)^{3/2} \langle r \exp(-\beta h_{ab}) | r \rangle - 1 + \frac{\beta e_{\alpha e_\beta}^3}{r} \frac{\beta^2 e_{\alpha e_\beta}^3}{2r^2} + \frac{2\pi}{3} \beta^3 e_{\alpha e_\beta}^3 \ln(\kappa R) \right)$$

$$+ \frac{\pi}{3} (1 - C - 2 \ln 2) \sum_{\alpha, \beta} \beta^\alpha e_\alpha^3 e_\beta^3 \rho_\alpha \rho_\beta + \frac{1}{3} C_1 \sum_{\alpha, \beta, \gamma} \beta^\alpha e_\alpha^3 e_\beta^3 e_\gamma^3 \kappa^{-1} \rho_\alpha \rho_\beta \rho_\gamma$$

$$+ \frac{2\pi}{3} \sum_{\alpha, \beta, \gamma} \beta^\alpha e_\alpha^3 e_\beta^3 e_\gamma^3 \kappa^{-1} \rho_\alpha \rho_\beta \rho_\gamma + \frac{1}{3} \sum_{\alpha, \beta, \gamma} \beta^\alpha e_\alpha^3 e_\beta^3 e_\gamma^3 \kappa^{-1} \rho_\alpha \rho_\beta \rho_\gamma$$

$$- \frac{1}{3} \sum_{\alpha, \beta} \beta e_{\alpha e_\beta}^3 \kappa^{-1} \rho_\alpha \rho_\beta \lim_{R \to \infty} \int_{r < R} \frac{dr}{r} \left( (2\pi \lambda_{ab}^2)^{3/2} \langle r \exp(-\beta h_{ab}) | r \rangle - 1 + \frac{\beta e_{\alpha e_\beta}^3}{r} \frac{\beta^2 e_{\alpha e_\beta}^3}{2r^2} + \frac{2\pi}{3} \beta^3 e_{\alpha e_\beta}^3 \ln(\kappa R) \right)$$

$$+ \frac{2\pi}{3} \beta^3 e_{\alpha e_\beta}^3 \ln(\kappa R) + O(\rho^7 \ln \rho), \quad (4.21)$$
where the pure constants \( C_1 \) and \( C_2 \) have been estimated by numerical evaluations of the dimensionless integrals involved in [(4.2), (4.3), and (4.15)-(4.20)] as \( C_1 \approx 15.201 \pm 0.001 \) and \( C_2 \approx -14.734 \pm 0.001 \) [28]. All the graphs \( G_{\Pi}^{\text{scaled}} \) that contribute to (4.21) are represented in Fig. 18.

The truncated expansion (4.21) does exhibit the structure (3.12) obtained from the general qualitative analysis of Sec. III B. The various terms can be associated to specific physical effects. The purely classical terms "à la Debye" arise from graphs \( G_{\Pi}^{\text{scaled}} \) built with only \( \kappa \)-scaled bonds independent of the shapes of the filaments. Consequently, they can be viewed as long-range contributions of the classical part of the interactions screened with the Debye length \( \kappa^{-1} \). The term of order \( \rho^{5/2} \) exactly proportional to \( \kappa^{3/2} \) is of the diffraction type in the sense that it describes quantum corrections to a classical treatment of the long-range part of the interactions. These quantum effects are associated to multipolelike interactions between the filaments, which enter in shape-dependent bonds like \( f_T \) or \( \lambda_{a, \xi_j} \nabla f_D \), for instance. Note, in particular, that both graphs \( \Pi_N \) \((N=0, M_R=1)\) [with \( \kappa H(x)f_T \) in place of \( f_R \)] and the purely diffraction graph \( \Pi_{\text{diff}} \) \((N=1, M_D=0, M_D'=2, M_D''=0)\) contribute to the above diffraction term of order \( \rho^{5/2} \), as shown by Eq. (4.8) and (4.4), respectively. We stress that the presence of these diffraction terms shows that the interactions cannot be entirely treated at a classical level at large distances. Eventually, there are terms that involve truncated traces of the quantum Gibbs factor for a finite number of charges. They describe short-range quantum effects and take into account the contributions of both bound and scattering states. They arise from graphs \( G_{\Pi}^{\text{scaled}} \) made with at least one function \( f_T \). Here, at the present order \( \rho^{5/2} \), it turns out that the short-range quantum contributions can be entirely expressed in terms of the one-body density matrix \( \langle r| \exp (-\beta \hbar a_0)| r \rangle \) [the last terms of (4.8) and (4.14), which are related to nontrivial integrals over \( g \) of \( \langle r| \exp (-\beta \hbar a_0)| r \rangle \), cancel out]. Such simplifications in favor of few-body density matrices calculated at \( g = 1 \) only, might no longer occur at higher orders [in particular because of the functional dependence of \( \rho_g(\xi) \), which has then to be taken into account].

At the order \( \rho^3 \), the above physical effects are completely disentangled. At higher orders, they may be coupled together in graphs \( G_{\Pi}^{\text{scaled}} \) involving simultaneously classical \( \kappa \)-scaled bonds, purely diffraction bonds (with a polynomial dependence in the \( \xi \)'s) and the truncated bonds \( f_T \). These graphs describe the many-body screening effects on the quantum states with a finite number of charges. It turns out that the quantum aspect of these collective phenomena can be treated perturbatively, as shown by the occurrence of the classical and diffraction bonds. Physically, this is due to the fact that the charges belonging to the screening clouds behave almost classically, i.e., their de Broglie wavelength becomes small compared to their relative distances in the low-density limit. The previous coupling mechanism appears already at the order \( \rho^{5/2} \), and is illustrated by the term involving the truncated trace of \( \exp (-\beta \hbar a_0) \).

**G. Comparisons and checkings**

At the order \( \rho^3 \), we recover exactly the MB part of the expressions computed by Ebeling et al. [16, 17]. For instance, the truncated trace of \( \exp (-\beta \hbar a_0) \), i.e., \( \lim_{\rho \to \infty} \int d\rho \) is nothing but the second virial quantum coefficient first introduced by Ebeling. All our terms of order \( \rho^{5/2} \) do coincide with those determined from the effective-potential method, except the purely diffraction term.
\[ \frac{1}{24} \sum_{\alpha} \frac{\beta^2 \hbar^2 \kappa^2}{m_{\alpha}} \rho_{\alpha}. \]  

(4.22)

In this method, the term (4.22) arises in part [29] from the three-body effective interactions, which decay slowly for large triangular configurations [18]. The collective screening of these long-range interactions leads to contributions that are of order $\rho^{5/2}$ instead of $\rho^3$ (a similar mechanism makes the Debye correction be of order $\rho^{3/2}$ instead of $\rho^3$).

By specifying (4.21) to the case of the classical one-component plasma, we do recover the result of Cohen and Murphy [20]. Moreover, the first quantum correction to this classical expression can be obtained by expanding the truncated trace of $\exp(-\beta \hbar_{aa})$ in powers of $\hbar$. It reduces to

\[ \frac{\pi \beta^2 e^2 \rho^2 \hbar^2}{6m}, \]  

(4.23)

which is nothing but the well-known $\hbar^2$ correction calculated by the Wigner-Kirkwood method [19]. Since this $\hbar^2$ correction is exactly proportional to $\rho^2$, the $\hbar^2$ contributions of all the virial coefficients of order larger than $\rho^2$ must vanish. This remarkable property is indeed satisfied by our $\rho^{5/2}$ coefficient, because of the presence of the diffraction term (4.22), which cancels the $\hbar^2$ contribution of

\[ -\frac{1}{2} \beta e^2 \kappa^2 \lim_{R \to \infty} \int_{r < R} dx \cdots. \]

Eventually, by using the $\beta$ expansions of the truncated traces of $\exp(-\beta \hbar_{ab})$ [17], we have checked that the high-temperature form of (4.21) up to order $\beta^{5/2}$ do reduce to the MB part of the expressions derived by De Witt [24].
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FIG. 12. The loop graph $\Pi_{\text{loop}} (N = 2, M_R = 1, M_B = 3)$.

V. EVALUATION OF THE PRESSURE AND OF THE OTHER THERMODYNAMIC FUNCTIONS

The virial expansion of any thermodynamic function can be inferred from (4.21) by using thermodynamic identities. The quantities that are related to the free energy via partial differentiations with respect to the density are the most easy to calculate because of the simple polynomial and logarithmic structure in the densities of (4.21). In particular, the pressure is calculated by inserting (4.21) in the thermodynamic relation

$$
\beta P = \sum_{\alpha} \rho_{\alpha} \frac{\partial}{\partial \rho_{\alpha}} \left[ \frac{\beta F}{\Lambda} \right] \bigg|_{\beta} - \frac{\beta F}{\Lambda}.
$$

(5.1)

Since $\kappa$ is a homogeneous function of the $\rho_{\alpha}$'s of order $\frac{1}{2}$,

$$
\sum_{\alpha} \frac{\partial}{\partial \rho_{\alpha}} \kappa = \frac{1}{2} \kappa,
$$

(5.2)

$$
\sum_{\alpha} \frac{\partial}{\partial \rho_{\alpha}} \ln(\text{const} \times \kappa) \big|_{\beta} = \frac{1}{2},
$$

(5.3)

and we find

$$
\beta P = \sum_{\alpha} \rho_{\alpha} - \frac{\kappa^3}{24\pi} - \frac{\pi}{3} \left( \frac{1}{2} + C + \ln 3 \right) \sum_{\alpha, \beta} \rho_{\alpha} \rho_{\beta} \rho_{\beta} - \frac{1}{2} \sum_{\alpha, \beta} \rho_{\alpha} \rho_{\beta} \left. \lim_{R \to \infty} \right\} + \frac{1}{2} - \frac{C}{2} - \ln 2 \sum_{\alpha, \beta} \beta^2 e_{\alpha} e_{\beta} \rho_{\alpha} \rho_{\beta}
$$

$$
+ C_1 \sum_{\alpha, \beta, \gamma} \beta^2 e_{\alpha} e_{\beta} e_{\gamma} \rho_{\alpha} \rho_{\beta} \rho_{\gamma} + C_2 \sum_{\alpha, \beta, \gamma, \delta} \beta^2 e_{\alpha} e_{\beta} e_{\gamma} e_{\delta} \rho_{\alpha} \rho_{\beta} \rho_{\gamma} \rho_{\delta}
$$

$$
+ \frac{1}{4 \pi} \sum_{\alpha} \frac{\beta^2 \kappa^2 e_{\alpha}^2}{m_{\alpha}} \rho_{\alpha} - \frac{1}{4 \pi} \sum_{\alpha, \beta} \beta e_{\alpha} e_{\beta} \rho_{\alpha} \rho_{\beta} \left. \lim_{R \to \infty} \right\} + O(\rho^3 \ln \rho),
$$

(5.4)

FIG. 13. The three graphs obtained by convoluting the graph shown in Fig. 12 with one or two bonds $f_\beta$. 
where \( \lim_{R \to \infty} \) is the truncated trace of \( \exp(-\beta h_{ab}) \) appearing in (4.21).

The calculations of the quantities that are related to the free energy via partial differentiations with respect to the temperature, like the internal energy or the specific heat at constant volume, for instance, require the knowledge of the temperature dependence of the virial coefficients of the density expansion (4.21). For the classical and diffraction terms, these coefficients merely reduce to polynomials in \( \beta \). The temperature dependence of the short-range quantum contributions enters in the truncated trace of \( \exp(-\beta h_{ab}) \), for which, to our knowledge, no simple analytic expressions are available in the literature. However, there exist high-temperature expansions, the coefficients of which are all known in terms of Riemann’s functions [17]. Eventually, all the other thermodynamic functions (like the adiabatic coefficients, for instance) are calculated in terms of the above virial coefficients by combining thermodynamic identities and relations between Jacobians.

We recall that all the present density expansions have been calculated in the framework of Maxwell-Boltzmann statistics. The exchange contributions will be included in a future paper.

APPENDIX

In this Appendix, we derive a differentiation trace identity for the Coulomb Hamiltonian \( h_{ab} = -\vec{R}^2/(2m_{ab})\Delta + g v_{ab}(r) \) with \( v_{ab}(r) = e_a e_b \psi_c(r) \), which is the extension of the familiar identity

\[
\beta \text{Tr}[V_{\text{int}} \exp(-\beta(h_{ab}^{0} + g V_{\text{int}}))] = -\frac{\partial}{\partial g} \text{Tr}[\exp(-\beta(h_{ab}^{0} + g V_{\text{int}})) - \exp(-\beta h_{ab}^{0})],
\]

valid for any integrable potential \( V_{\text{int}}(r) \). Of course, in the present case, the traces have to be defined via suitable truncations, which eliminate the long-range Coulomb divergencies and we set

\[
I_g = \int dr \left[ (2\pi \lambda_{ab}^2)^{3/2} (r|\exp(-\beta h_{ab}^{0})|r) - 1 + g \beta v_{ab}^{3}(r) \right. \\
\left. - \frac{g^2}{2} \beta^2 v_{ab}^{2}(r) + \frac{g^3}{6} \beta^3 v_{ab}^{3}(r) g(r) \right],
\]

where \( g(r) \) is a given function of \( r \) such that \( g(r) \sim \text{const} \times r \) when \( r \to 0 \), and \( g(r) \to 1 \) when \( r \to \infty \). Using

\[
\frac{\partial}{\partial g} \langle r | \exp(-\beta h_{ab}^{0}) | r \rangle = -\int_0^\beta d\tau \int dr' dr \langle r' | \exp[-(\beta - \tau) h_{ab}^{0}] | r' \rangle v_{ab}(r') \langle r | \exp(-\tau h_{ab}^{0}) | r \rangle,
\]

which follows from the Dyson equation, we find

\[
\frac{\partial}{\partial g} I_g = -\int dr \int dr' \psi_g(r,r'),
\]
with
\[
\psi_g(r, r') = u_{ab}(r') \left\{ (2\pi \lambda_{ab}^2)^{3/2} \int_0^\beta d\tau \langle r|\exp[-(\beta - \tau)h_{ab}^g]|r'\rangle \langle r'|\exp(-\tau h_{ab}^g)|r\rangle 
- \beta \delta(r - r') \left[ 1 - g\beta u_{ab}(r) + \frac{g^2 \beta^2}{2} v_{ab}^2(r)g(r) \right] \right\}. 
\]
(A5)

The integral in the right-hand side of (A4) is not absolutely convergent because, when \( r \) and \( r' \) are sent simultaneously to infinity, \( \psi_g(r, r') \) decays as the Coulomb potential itself, which is not integrable. In fact, we can rewrite \( \psi_g(r, r') \) as
\[
\psi_g(r, r') = \psi_g(r, r') + D_g^{(as)}(r, r') + R_g(r, r'), 
\]
(A6)

where \( D_g^{(as)}(r, r') \) is the nonabsolutely integrable asymptotic part of the difference \([\psi_g(r, r') - \psi_g(r', r)]\),

\[
D_g^{(as)}(r, r') = \left[ u_{ab}(r') - u_{ab}(r) \right] \left[ 1 - g\beta \int_0^1 ds v_{ab}((1-s)r' + sr) \right] 
\times (2\pi \lambda_{ab}^2)^{3/2} \int_0^\beta d\tau \langle r|\exp[-(\beta - \tau)h_{ab}^0]|r'\rangle \langle r'|\exp(-\tau h_{ab}^0)|r\rangle, 
\]
(A7)

and \( R_g(r, r') \) is the corresponding rest,

\[
R_g(r, r') = \left[ u_{ab}(r') - u_{ab}(r) \right] \left[ (2\pi \lambda_{ab}^2)^{3/2} \int_0^\beta d\tau \left\{ \langle r|\exp[-(\beta - \tau)h_{ab}^g]|r'\rangle \langle r'|\exp(-\tau h_{ab}^g)|r\rangle 
- \langle r|\exp[-(\beta - \tau)h_{ab}^0]|r'\rangle \langle r'|\exp(-\tau h_{ab}^0)|r\rangle \right\} 
\times \left[ 1 - g\beta \int_0^1 ds v_{ab}((1-s)r' + sr) \right] \right\}. 
\]
(A8)

In (A7) and (A8), \( h_{ab}^0 \) is the purely kinetic Hamiltonian, \( h_{ab}^0 = -\hbar^2/(2m_{ab})\Delta \). Inserting (A6) in (A4), we obtain

FIG. 17. The three graphs obtained by convoluting the graph shown in Fig. 16 with one or two bonds \( f_B \).
FIG. 18. The 12 primary graphs $G_i^{\text{pd}}$, which contribute to the expansion (4.21) of the free energy (all the other graphs obtained by convoluting these primary graphs with one or two bonds $f_j$ are not drawn). The dashed-dotted lines represent bonds $kH_j(x)$. The bubble with the symbol $G_5$ inside represents the function $k^2G_5$, which appears in the scaling decomposition (3.7). At the present order $p^{5/2}$, this function can be replaced by $(k^2)^2H_1/2 + k^2H_1/2 + k^2H_1/6$, as illustrated at the bottom of the figure.

\[
\frac{\partial}{\partial g} I_g = -\beta \int dr v_{ab}(r) \left( (2\pi \lambda_{ab}^2)^{1/2} \langle r | \exp(-\beta h_{ab}^+)|r \rangle - 1 + g \beta v_{ab}(r) - \frac{g^2}{2} \beta^2 v_{ab}^2(r) g(r) \right) - \int dr \int dr' D_g^{(as)}(r, r') - \int dr \int dr' R_g(r, r') ,
\]

(A9)

where we have used the closure relation $\int dr' |r'| (r')^2 = 1$. The nonabsolutely convergent integral with $D_g^{(as)}$ can be evaluated by expanding $[v_{ab}(r') - v_{ab}(r)]$ and $v_{ab}[(1-s)r' + sr]$ in Taylor series with respect to $(r' - r)$ and $(1-s)(r' - r)$, respectively. Taking into account the harmonicity of the Coulomb potential $[\Delta v_\nu(r) = -4\pi \delta(r)]$ and the symmetries of the matrix elements of $\exp(-\tau h_{ab}^+)$, we find that only one term in these series contributes, i.e.,

\[
\int dr \int dr' D_g^{(as)}(r, r') = \int dr \int dr' \frac{1}{2!} \sum_{\mu \nu} (r'_\mu - r_\mu)(r'_\nu - r_\nu) \frac{\partial^2 v_{ab}}{\partial r_\mu \partial r_\nu} \frac{1}{(2\pi \lambda_{ab}^2)^{3/2}} \times \int_0^\beta d\tau \frac{\beta}{\tau^{3/2}(\beta - \tau)^{3/2}} \exp \left[ - \frac{\beta}{\tau^2} + \frac{\beta}{\tau (\beta - \tau)} \right] \frac{(r - r')^2}{2\lambda_{ab}^2} \exp \left[ - \frac{\beta^2 t^2}{2\lambda_{ab}^2} \right] = \frac{1}{6} \int dr \Delta v_{ab}(r) \frac{1}{(2\pi \lambda_{ab}^2)^{3/2}} \int_0^\beta d\tau \frac{\beta^2}{\tau^{3/2}(\beta - \tau)^{3/2}} \int dt t^2 \exp \left[ - \frac{\beta^2 t^2}{2\lambda_{ab}^2} \right] \right] = -\frac{\pi}{3} \beta e_x^2 \beta^2 \lambda_{ab}^2 .
\]

(A10)

As it can be seen from the Feynman-Kac representation of the matrix elements of $\exp(-\tau h_{ab}^+)$,

\[
\langle r'|\exp(-\tau h_{ab}^+)|r \rangle = \frac{\exp \left[ - \frac{\beta}{2\lambda_{ab}^2} (r - r')^2 \right]}{(2\pi \lambda_{ab}^2)^{3/2}} \int D(\xi) \exp \left[ -\tau g \int_0^1 ds v_{ab}[(1-s)r + sr + \lambda_{ab} \xi(s)] \right] ,
\]

$R_g(r, r')$ remains integrable for any spatial configuration. Consequently, the integral with $R_g(r, r')$ is absolutely convergent, and it vanishes because of the antisymmetry of $R_g$, i.e., $R_g(r, r') = -R_g(r', r)$. Combining this result to (A10) and (A9), we infer the required identity

\[
\beta \int dr v_{ab}(r) \left( (2\pi \lambda_{ab}^2)^{3/2} \langle r | \exp(-\beta h_{ab}^+)|r \rangle - 1 + g \beta v_{ab}(r) - \frac{g^2}{2} \beta^2 v_{ab}^2(r) g(r) \right) 
\]

\[
= -\frac{\partial}{\partial g} \int dr \left( (2\pi \lambda_{ab}^2)^{3/2} \langle r | \exp(-\beta h_{ab}^+)|r \rangle - 1 + g \beta v_{ab}(r) - \frac{g^2}{2} \beta^2 v_{ab}^2(r) + \frac{g^3}{6} \beta^3 v_{ab}^3(r) g(r) \right) + \frac{\pi}{3} \beta e_x^2 \beta^2 \lambda_{ab}^2 .
\]

(A11)
A first difference between the identities (A1) and (A11) is the presence of the substituted terms built with \( v_{ab} \) and \( g \), which ensure the convergence of the integrals over \( r \) in (A11). The additional term \( \frac{\pi}{3} \beta e_a e_b \lambda_{ab}^2 \) is more subtle and, to our knowledge, has always been omitted in the literature. It arises from the long-range nature of the Coulomb potential, which prevents the inversion of the integrals over \( r \) and \( r' \) in (A4). It can then be interpreted as resulting from a diffraction effect (as suggested by its structure). We have checked the identity (A11) when the charge \( e_a \) and \( e_b \) have the same sign, i.e. \( e_a e_b = +1 \). In this repulsive case, both integrals in (A11) remain finite in the classical limit and can be expanded in powers of \( \beta^2 \). The presence of the above diffraction term ensures that the Wigner-Kirkwood expansions of both sides of (A11) are identical, as it should be.

Both convergent integrals in (A11) can be rewritten as finite integrals \( \int_{r<R} dr \) over a sphere of radius \( R \) plus terms that go to zero when \( R \rightarrow \infty \) uniformly with respect to \( g \). The identity (A11) then becomes

\[
\beta \int_{r<R} dr \frac{v_{ab}(r)}{(2\pi \lambda_{ab}^2)^{3/2}} \left( \exp(-\beta h_{ab}^g) \right) r \left( 1 + g \beta v_{ab}(r) \right) - \frac{\beta^2 v_{ab}^2(r)}{2} (g(r)) \right)
\]

\[
= -\frac{\partial}{\partial g} \int_{r<R} dr \frac{\left( (2\pi \lambda_{ab}^2)^{3/2} \left( \exp(-\beta h_{ab}^g) \right) r \left( 1 + g \beta v_{ab}(r) \right) - \frac{\beta^2 v_{ab}^2(r)}{2} \right) (g(r)) + \frac{\pi}{3} \beta e_a e_b \lambda_{ab}^2 }{ \beta^3 v_{ab}^3(r) } \]

(A12)

disregarding uniformly decaying terms in the limit \( R \rightarrow \infty \). Each integral \( \int_{r<R} dr \) reduces to a sum of similar integrals associated to the terms appearing in the truncated quantities \( (2\pi \lambda_{ab}^2)^{3/2} \left( \exp(-\beta h_{ab}^g) \right) r \left( 1 + g \beta v_{ab}(r) \right) \) (all these integrals do converge because the integration domain is finite). The corresponding integrals of the substituted terms obviously cancel out side to side, and (A12) becomes

\[
\beta \int_{r<R} dr v_{ab}(r) \left( (2\pi \lambda_{ab}^2)^{3/2} \left( \exp(-\beta h_{ab}^g) \right) r \right) = -\frac{\partial}{\partial g} \int_{r<R} dr \frac{(2\pi \lambda_{ab}^2)^{3/2} \left( \exp(-\beta h_{ab}^g) \right) r}{(2\pi \lambda_{ab}^2)^{3/2} \left( \exp(-\beta h_{ab}^g) \right) r} + \frac{\pi}{3} \beta e_a e_b \lambda_{ab}^2 ,
\]

(A13)

disregarding terms which go to zero when \( R \rightarrow \infty \) uniformly with respect to \( g \). The identity (A13) is, of course, equivalent to (A11). This finite-domain version of the differentiation trace identity is the most convenient for the calculations of the graphs carried out in the main text.

[26] For a review, see, e.g., F. J. Rogers, in *The Equation of State in Astrophysics* (Ref. [18]).


[28] These values of $C_1$ and $C_2$ are slightly different from those given in Ref. [13]. This difference comes from a better numerical estimation of the dimensionless integrals involved in (4.21).

[29] In fact, part of (4.22) also arises from the diffraction term in the trace identity (A13), which was not properly used in previous calculations.