

# Sine-Gordon Theory for the Equation of State of Classical Hard-Core Coulomb Systems.

## I. Low Fugacity Expansion

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We present an exact field theoretical representation of the statistical mechanics of classical hard-core Coulomb systems. This approach generalizes the usual sine-Gordon theory valid for point-like charges or lattice systems to continuous Coulomb fluids with additional short-range interactions. This formalism is applied to derive the equation of state of the restricted primitive model of electrolytes in the low fugacity regime up to order  $\rho^{5/2}$  ( $\rho$  number density). We recover the results obtained by Haga by means of Mayer graphs expansions.

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**KEY WORDS:** Coulomb fluids; sine-Gordon action; low-fugacity expansion.

## I. INTRODUCTION

The aim of this paper and of the following one is to present a formally exact field theory which allows for the calculation of thermodynamic functions of classical hard-core Coulomb systems. It is well known that the grand-canonical partition function of the Coulomb gas can be represented by a sine-Gordon action.<sup>(1-3)</sup> However this mapping is applicable only for pointlike charges, or for lattice systems.<sup>(4)</sup> If necessary, the short-range repulsion is frequently included post-facto by introducing a suitable cutoff in momentum space integrals. In this work, we derive a formally exact sine-

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Gordon field theory without the use of any arbitrary cutoff. This off-lattice formalism is used in two complementary directions. In the present paper we recover the low fugacity expansion of the thermodynamic functions obtained years ago by Mayer<sup>(6)</sup> and Haga<sup>(7)</sup> by means of graph resummation techniques. In the companion paper, we consider rather the high temperature regime and the results obtained by Stell and Lebowitz<sup>(12)</sup> in the frame of the so-called  $\gamma$ -ordering theory are also recovered.

The simplest sound theory of electrolytes is due to Debye and Hückel<sup>(5)</sup> who showed, nearly eighty years ago, that, at least in the low density limit, the potential of mean force  $\psi_{12}(r)$  between two ions of respective charges  $e_1$  and  $e_2$  behaves like  $e_1 e_2 \exp(-\kappa r)/r$  as  $r \rightarrow \infty$  rather than like the Coulomb potential itself  $e_1 e_2/r$ , where  $\kappa = (4\pi\beta \sum_i \rho_i e_i^2)^{1/2}$  is the inverse Debye shielding length. Here  $\beta = 1/kT$  ( $k$  Boltzmann constant,  $T$  temperature),  $\rho_i$  is the density of ionic species  $i$  and the dielectric constant  $D$  of the solvent has been absorbed in the definition of the charges. An important consequence of the shielding effect is the non-analyticity of the specific excess osmotic free energy  $f(\rho)$  as a function of the mean ionic density  $\rho$ . Actually, in Debye-Hückel theory one obtains  $f(\rho) \sim \kappa^3 \sim \rho^{3/2}$  for  $\rho \rightarrow 0$ .

The results of Debye and Hückel are valid only at very low densities and discrepancies between their theory and experimental data on real electrolytes have motivated an enormous amount of theoretical works to improve the theoretical scheme. A first systematic perturbative expansion of  $f(\rho)$  in which the density  $\rho$  is taken to be the ordering (small) parameter was proposed by Mayer.<sup>(6)</sup> Improvements on this seminal work were made later by Haga,<sup>(7)</sup> Meeron,<sup>(8)</sup> Abe,<sup>(9)</sup> and Friedman.<sup>(10)</sup> All these works are based on diagrammatic techniques and the more elaborate of them provide a reasonably accurate description of the thermodynamic properties of ionic solutions in the low fugacity regime. A monography by Friedman<sup>(11)</sup> summarizes the above-mentioned works.

In a more recent work,<sup>(12)</sup> Stell and Lebowitz have proposed a perturbation scheme in which the ordering parameter is  $\gamma = \beta e^2$  where  $e$  is the electron charge. Their theory is also based on a sophisticated diagrammatic analysis which gives an explicit high temperature expansion of  $f(\rho)$  for symmetric and asymmetric electrolytes.

Edwards<sup>(1)</sup> seems to have been the first to use the so-called sine-Gordon (SG) transformation in the field of the statistical mechanics of classical Coulomb systems as an alternative to the above-mentioned diagrammatic techniques although Kac,<sup>(2)</sup> Siegert,<sup>(3)</sup> Hubbard,<sup>(13)</sup> and Stratonovich<sup>(14)</sup> also pioneered the method in other domains of statistical physics or in field theory. In his work, Edwards considers a model of charged hard spheres which allows a clear splitting of the pair potential

into a long range electrostatic part for which the sine-Gordon transformation applies and a repulsive part for which low density virial expansion techniques can be employed. This leads to an intricate double expansion in  $\gamma$  and in  $\rho$ . The sine-Gordon formalism for both classical and quantum Coulomb systems has been reviewed recently by Brydges and Martin.<sup>(15)</sup>

A decade later, Hubbard and Schofield<sup>(16)</sup> have shown that a general fluid Hamiltonian with long-range and short-range interactions can be mapped onto a reference system with short-range interactions only. Then the cumulant expansion is used to map the original fluid Hamiltonian onto a magneticlike Hamiltonian. Brilliantov and al.<sup>(17)</sup> have explored this route for ionic fluids in order to study the Coulombic criticality. The equation of state of a multicomponent system of *pointlike* ions embedded in a neutralizing background has also been studied by Ortner<sup>(18)</sup> along these lines. Recently Netz and Orland<sup>(21)</sup> tried to improve on Edwards theory by performing a double SG transform, both on the Coulomb and the hard core parts of the pair potential. As stressed by Brydges and Martin<sup>(15)</sup> a SG transform of the singular hard core potential and more generally that of a repulsive short range potential such that  $\sim 1/r^{12}$ , is strictly speaking impossible, since these singular potentials do not have a Fourier transform.

The present work is along the lines of the papers of Brilliantov, Ortner, Netz and Orland. We limit ourselves to the case of a symmetric fluid of charged hard spheres with only two species of ions of equal diameters  $\sigma$  and carrying opposite charges (the so-called restrictive primitive model (RPM) of electrolytes<sup>(6)</sup>). In a first step, we regularize the Coulomb potential by a smearing of the charges over the surface of a sphere of diameter  $a \leq \sigma$ , and therefore give a precise meaning to the SG transformation.<sup>(15, 19)</sup> Obviously other kinds of smearing are possible and would lead to the same results; in another context an uniform volumic smearing of the charge has been proposed.<sup>(20)</sup> This allows us to derive rigorously a result which seems to belong to Siegert<sup>(3)</sup> in the general case and which states that the grand-partition function of charged hard spheres is equal to the average over a Gaussian measure of the grand-partition function  $\mathcal{E}_{HS}$  of bare hard spheres in the sine-Gordon field. This is our Eq. (2.10). In a second step, making a connection with liquid theory,<sup>(22)</sup> we perform a functional expansion of  $\ln \mathcal{E}_{HS}$  with respect to the sine-Gordon field  $\phi$  which yields the exact expression (2.14) of the sine-Gordon action  $\mathcal{S}[\phi]$  of the model. This action involves the connected correlation functions of the hard sphere fluids which are supposed to be known. It can be checked that this action reduces to the usual sine-Gordon action in the limit of vanishing hard-core diameters. This formalism is very handy since it allows to obtain either low fugacity or high temperature expansions of  $f(\rho)$  via cumulant expansions for off-lattice Coulombic systems.

The paper is organized as follows. In Section II, we derive the generalized sine-Gordon representation of the grand-partition function of the RPM model. The low-density expansion of the grand potential (or pressure) of the model is obtained in Section III up to the order  $\rho^{5/2}$ . We check that each term of this expansion is actually independent of the smearing diameter  $a$ . Comparisons with the results of Haga and of Netz–Orland are carried out in Section IV. All approaches yield identical results at order  $\rho^{5/2}$ . In addition we explain why the approximate derivation of Netz–Orland leads to the correct result at this order but could fail at higher orders in  $\rho$ . Conclusions are drawn in Section V.

## II. MODEL AND FORMALISM

### A. The Boltzmann Factor

Throughout this paper we consider the three dimensional (3D) and symmetric version of the RPM, i.e. a system made of  $N_+$  hard spheres of diameter  $\sigma$  and charge  $e$  and  $N_-$  spheres of the same diameter but with an opposite charge  $-e$ .<sup>(11)</sup>

With obvious notations, the configurational energy of the model reads as

$$\beta V(\vec{r}^{N_+}, \vec{r}^{N_-}) = \frac{\beta}{2} \sum_{i \neq j} \left( \frac{e_i e_j}{r_{ij}} + v_{hs}(r_{ij}) \right), \quad (2.1)$$

where  $e_i = \pm e$  and  $v_{hs}(r)$  denotes the hard core potential. For the moment the ions are supposed to be confined in some arbitrary volume  $V \subset \mathbb{R}^3$ .

We first note that only configurations  $(\vec{r}^{N_+}, \vec{r}^{N_-})$  of ions without overlaps of the spheres do contribute to the canonical (or grand-canonical) partition functions. For these configurations, the charge  $\pm e$  of any ion of center  $\vec{r}_i$  can be smeared out uniformly on any spherical surface of diameter  $0 < a \leq \sigma$ . The interaction energy of two balls of charge density  $\tau(r) = \delta(r - a/2)/(\pi a^2)$ , located respectively at point  $\vec{r}$  and  $\vec{r}'$  will be noted  $W_\tau(\vec{r} - \vec{r}')$  and we have obviously

$$W_\tau(\vec{r} - \vec{r}') = \int_V \int_V d^3\vec{x} d^3\vec{y} \tau(|\vec{r} - \vec{x}|) \frac{1}{|\vec{x} - \vec{y}|} \tau(|\vec{y} - \vec{r}'|). \quad (2.2)$$

We note that the self-energy  $\mathcal{E}_S \equiv W_\tau(0)/2 = 1/a$  of each spherical distribution is a finite quantity for  $a > 0$ .

It follows from the preceding remarks that the electrostatic part of the Boltzmann factor can be written, for any configuration  $(\vec{r}^{N_+}, \vec{r}^{N_-})$ , as

$$\exp\left(-\frac{\beta}{2} \sum_{i \neq j} \frac{e_i e_j}{r_{ij}}\right) = \exp(N\gamma \mathcal{E}_S) \exp\left(-\frac{\gamma}{2} \langle n | W_\tau | n \rangle\right). \quad (2.3)$$

where  $\gamma \equiv \beta e^2$  and  $N = N_+ + N_-$  is the total number of ions. In Eq. (2.3)

$$n(\vec{r}) \equiv \sum_{i=1}^{N_+} \delta(\vec{r} - \vec{r}_{i+}) - \sum_{i=1}^{N_-} \delta(\vec{r} - \vec{r}_{i-}) \quad (2.4)$$

is the microscopic charge distribution (divided by  $e$ ) and

$$\langle n | W_\tau | n \rangle \equiv \int_V \int_V d^3\vec{r} d^3\vec{r}' n(\vec{r}) W_\tau(|\vec{r} - \vec{r}'|) n(\vec{r}'). \quad (2.5)$$

Note that it follows from the positivity of the Fourier transform  $\tilde{W}_\tau(\vec{k}) = 4\pi\tilde{\tau}(k)^2/k^2$  that the quadratic form  $\langle n | W_\tau | n \rangle$  is definite positive. We can take advantage of this positivity to perform a SG transform<sup>(15)</sup> and re-express the Boltzmann factor (2.3) as an average over a Gaussian scalar field  $\phi$ , i.e.

$$\begin{aligned} \exp\left(-\frac{\gamma}{2} \langle n | W_\tau | n \rangle\right) &= \left\langle \exp\left(i \int_V d^3\vec{x} n(\vec{x}) \bar{\phi}(\vec{x})\right) \right\rangle_{W_\tau} \\ &= \left\langle \exp\left(i \sum_{i=1}^{N_+} \bar{\phi}(\vec{r}_{i+}) - i \sum_{i=1}^{N_-} \bar{\phi}(\vec{r}_{i-})\right) \right\rangle_{W_\tau}, \end{aligned} \quad (2.6)$$

where  $\bar{\phi}(\vec{x}) \equiv \sqrt{\gamma} \phi(\vec{x})$  is a real random field. The precise meaning of the average in Eq. (2.6) is given in Appendix A.

## B. Grand Partition Function

For reasons which should become clear below, the grand-canonical ensemble is considerably more handy than the canonical one. For simplicity we choose the same chemical potential  $\mu \equiv \mu_+ = \mu_-$  for the anions and the cations<sup>(15)</sup>. The grand-canonical partition function is given by<sup>(22)</sup>

$$\Xi^{RPM}(v_+, v_-) \equiv \sum_{N_+=0}^{\infty} \sum_{N_-=0}^{\infty} \frac{z^{N_+}}{(N_+)!} \frac{z^{N_-}}{(N_-)!} \int_V d^3\vec{r}^{N_+} d^3\vec{r}^{N_-} \exp(-\beta V(\vec{r}^{N_+}, \vec{r}^{N_-})). \quad (2.7)$$

where we have introduced the usual notation  $v \equiv v_{\pm} = \beta\mu$  and the activity  $z \equiv z_{\pm} = \Lambda^{-3} \exp(\beta\mu)$  of both species (the thermal length  $\Lambda$  is assumed to be the same for the anions and the cations).

Gathering the intermediate results (2.3), (2.6) we get :

$$\mathcal{E}^{RPM}(v_+, v_-) = \sum_{N_+=0}^{\infty} \sum_{N_-=0}^{\infty} \frac{\bar{z}^{N_+}}{(N_+)!} \frac{\bar{z}^{N_-}}{(N_-)!} \int_V d^3\vec{r}^{N_+} d^3\vec{r}^{N_-} \exp\left(-\sum_{i < j} v_{hs}(r_{ij})\right) \quad (2.8)$$

$$\times \left\langle \exp\left(+i \sum_{i=1}^{N_+} \bar{\phi}(\vec{r}_{i+}) - i \sum_{i=1}^{N_-} \bar{\phi}(\vec{r}_{i-})\right) \right\rangle_{W_{\tau}}. \quad (2.9)$$

where we have defined renormalized chemical potentials  $\bar{v}_{\pm} \equiv v_{\pm} + \beta e^2 \mathcal{E}_S = v + \gamma/a$  and renormalized activities  $\bar{z} \equiv \bar{z}_{\pm} = \exp(\bar{v}_{\pm})/\Lambda^3$ .

This last equation can be elegantly rewritten as

$$\mathcal{E}^{RPM}(v_+, v_-) = \langle \mathcal{E}_{+,-}^{HS}(\bar{v}_+, \bar{v}_-; i\bar{\phi}, -i\bar{\phi}) \rangle_{W_{\tau}}, \quad (2.10)$$

where  $\mathcal{E}_{+,-}^{HS}(\bar{v}_+, \bar{v}_-; i\bar{\phi}, -i\bar{\phi})$  denotes the grand-canonical partition function of a mixture of two species of equal size hard spheres labelled + and - with chemical potentials  $\bar{v}_+$  and  $\bar{v}_-$  respectively. The spheres with the label + are in the external field  $i\bar{\phi}$  whereas those labelled - are in the field  $-i\bar{\phi}$ . Eq. (2.10) is a special case of a more general result due to Siegert.<sup>(3)</sup>

In order to get a more explicit expression of the action we perform now a Taylor functional expansion of  $\ln \mathcal{E}_{+,-}^{HS}$  with respect to the activity  $\bar{z}_{\pm}(\vec{r}) \equiv z \exp(\gamma/a) \exp(\pm i\bar{\phi}(\vec{r}))$ .

We have, from standard liquid theory<sup>(22)</sup>

$$\begin{aligned} & \ln\left(\frac{\mathcal{E}_{+,-}^{HS}(\bar{v}_+, \bar{v}_-, V, \beta; i\bar{\phi}, -i\bar{\phi})}{\mathcal{E}_{+,-}^{HS}(v, v, V, \beta)}\right) \\ &= \sum_{n=1}^{\infty} \frac{1}{n!} \sum_{\alpha_1 \dots \alpha_n = \pm} \int_V d^3\mathbf{1} \dots d^3\mathbf{n} \frac{\delta^n \ln \mathcal{E}_{+,-}^{HS}}{\delta \bar{z}_{\alpha_1}(1) \dots \delta \bar{z}_{\alpha_n}(n)} \Big|_{\bar{z}_{\alpha_i}(i)=z} \prod_{i=1}^n (\bar{z}_{\alpha_i}(i) - z), \end{aligned} \quad (2.11)$$

In the absence of an external field, we have, for sufficiently large systems  $\mathcal{E}_{+,-}^{HS}(v, v) = \mathcal{E}^{HS}(v_0)$ , where  $v_0 \equiv v + \ln 2$  (i.e.  $z_0 = 2z$ ) and  $\mathcal{E}^{HS}(v_0)$  is the grand partition function of a fluid of identical hard spheres. The integral kernels in Eq. (2.11) are related to the correlation functions  $h_0^{(n)}(1, \dots, n)$  of the hard sphere mixture<sup>(22)</sup>

$$z^n \frac{\delta^n \ln \mathcal{E}_{+,-}^{HS}}{\delta \bar{z}_{\alpha_1}(1) \dots \delta \bar{z}_{\alpha_n}(n)} \Big|_{\bar{z}_{\alpha_i}(i)=z} = \frac{\rho_0^n}{2^n} h_0^{(n)}(1, \dots, n). \quad (2.12)$$

In Eq. (2.12),  $\rho_0 = V^{-1} \partial \ln \Xi^{HS} / \partial v_0$  is the number density of this fluid. Making use of the identity

$$\sum_{\alpha_i = \pm} \frac{\bar{z}_{\alpha_i}(i) - z}{2z} = \exp(\gamma/a) \cos \bar{\phi}(i) - 1 \quad (2.13)$$

we can rewrite Eq. (2.11) as a functional integral

$$\frac{\Xi^{RPM}(v_+, v_-)}{\Xi^{HS}(v_0)} = \langle \exp(-U[\phi]) \rangle_{W_\tau} = \mathcal{N}_W^{-1} \int \mathcal{D}\phi \exp(-\mathcal{S}[\phi]), \quad (2.14)$$

where  $\mathcal{N}_W \equiv \int \mathcal{D}\phi \exp(-\frac{1}{2} \langle \phi | W_\tau^{-1} | \phi \rangle)$  is a normalization constant and

$$\mathcal{S}[\phi] = \frac{1}{2} \langle \phi | W_\tau^{-1} | \phi \rangle + U[\phi], \quad (2.15)$$

$$U[\phi] = \sum_{n=1}^{\infty} U_n[\phi],$$

$$U_n[\phi] = -\frac{\rho_0^n}{n!} \int_V d^3 1 \cdots d^3 n h_0(1, \dots, n) \prod_{i=1, n} [\exp(\gamma/a) \cos \bar{\phi}(i) - 1]. \quad (2.16)$$

The above expression of the sine-Gordon like action  $\mathcal{S}[\phi]$  of the RPM is an exact result; note that  $\mathcal{S}[\phi]$  is an even function of the field. In the limit  $\sigma \rightarrow 0$  only the term  $n=1$  of Eq. (2.16) survives and one checks that one recovers the usual sine-Gordon action of the Coulomb gas.<sup>(15)</sup>

A similar result along the Hubbard-Schofield scheme has been used by Brilliantov and al.<sup>(17)</sup> in their study of the criticality of the RPM model. However their approach is developed in Fourier space and without the explicit regularization obtained with the smearing of the charges. As a final remark, we note that we might have been tempted to perform the Taylor functional expansion, not around  $z$  but around  $\bar{z}_\pm = z \exp(\gamma/a)$ . In that case a low-fugacity expansion is valid only at high temperatures since  $\bar{z} \sim z$  requires  $\gamma \rightarrow 0$ .

### C. The Generalised Screened Potential $X_\tau(r)$

The program is now to perform a systematic cumulant expansion of the expression (2.14) and to compute the cumulants by an extensive use of Wick's theorem.<sup>(29, 30)</sup> However, as it stands, this expansion will involve cumulants which diverge in the thermodynamic limit due to the long range of  $W_\tau(r)$ . The same problem arises in low fugacity or high temperature diagrammatic expansions of the RPM where one is led to resum classes of diagrams in order to get finite results.<sup>(6, 12, 22)</sup> Formally it amounts to intro-

duce a screened (Yukawa) potential. In the field theoretical formalism discussed here, a screened (or Hartree <sup>(31)</sup>) field can also be introduced as follows. We denote  $U_0[\phi]$  the high temperature approximation of  $U[\phi]$ , i.e.

$$U_0[\phi] = \frac{\rho_0}{2} \int d^3\vec{r} \bar{\phi}(\vec{r})^2. \quad (2.17)$$

Writing now the triviality  $U[\phi] = (U[\phi] - U_0[\phi]) + U_0[\phi]$ , we get

$$\langle \exp(-U[\phi]) \rangle_{W_\tau} = \frac{\mathcal{N}_X}{\mathcal{N}_W} \langle \exp(-(U[\phi] - U_0[\phi])) \rangle, \quad (2.18)$$

where  $\mathcal{N}_A \equiv \int \mathcal{D}\phi \exp(-\frac{1}{2} \langle \phi | A^{-1} | \phi \rangle)$  with  $A = X_\tau, W_\tau$  and where  $X_\tau(r)$  is a real operator defined by the relation  $X_\tau(r)^{-1} \equiv W_\tau(r)^{-1} + \rho_0 \gamma \mathbf{I}$  ( $\mathbf{I}$  denotes the identity).

Using the precise definition of the functional integration given in Appendix A, we obtain

$$\frac{\mathcal{N}_X}{\mathcal{N}_W} = \exp\left(-\frac{V}{2} \int \frac{d^3\vec{q}}{(2\pi)^3} \ln(1 + \gamma \rho_0 \tilde{W}_\tau(\vec{q}))\right), \quad (2.19)$$

Note that, in Eq. (2.19), we have replaced a series by an integral, which is valid for large systems. Moreover the integral converges for  $a \neq 0$ , which is a happy consequence of the regularization of the Coulomb potential via the smearing of the charge.

The Fourier transform  $\tilde{X}_\tau(q)$  reads :

$$\tilde{X}_\tau(q) = \frac{\tilde{W}_\tau(q)}{1 + \gamma \rho_0 \tilde{W}_\tau(q)} = \frac{\sin^2(qa/2)}{(qa/2)^2} \frac{4\pi}{q^2 + \kappa_0^2} \frac{\sin^2(qa/2)}{(qa/2)^2}. \quad (2.20)$$

with  $\kappa_0^2 = 4\pi\gamma\rho_0$ .

It is easily checked that for a fixed  $\kappa_0$  and in the limit  $a \rightarrow 0$ ,  $X_\tau(r)$  reduces to the familiar screened Yukawa potential, i.e.  $X_\tau(r) \sim \exp(-\kappa_0 r)/r$  ( $\forall r$ ). Conversely, for a fixed  $a$  and in the limit  $\kappa_0 \rightarrow 0$  we have obviously  $X_\tau(r) = W_\tau(r)$ . For arbitrary  $(a, \kappa_0)$ , the large  $r$  behavior of  $X_\tau(r)$  is determined by the small  $q$  behavior of  $\tilde{X}_\tau(q) \sim 4\pi/(q^2 + \kappa_0^2)$  which implies  $X_\tau(r) \sim \exp(-\kappa_0 r)/r$  at large  $r$ . The function  $X_\tau(r)$  is thus a short range function of  $r$  which, however, for large  $\kappa_0$ , can have a non monotoneous behavior. Expansions of  $X_\tau(r)$  at low  $\kappa_0$  will be given in Section III.



We shall see in the next Section that the use of the screened potential  $X_\tau(r)$  instead of the long range (Coulombic) potential  $W_\tau(r)$  ensures the convergence of the cumulants.

### III. LOW-FUGACITY EXPANSION

In this section, we use the general result of Eq. (2.14) to perform a systematic low-fugacity expansion of the pressure of the RPM model, at the order 5/2 in the density  $\rho$ .

Although this theory must not depend explicitly of the smearing parameter  $a$ , we shall explicitly verify below that it is effectively the case for each order of the expansion.

#### A. The Grand Potential

Using the results of Eqs. (2.14), (2.18), (2.19), and the cumulant theorem<sup>(30)</sup> we obtain the specific grand potential  $\omega_{RPM} \equiv -\ln \mathcal{E}_{RPM}/V$

$$\omega_{RPM}(v) = \omega_{HS}(v_0) + \frac{1}{2} \int \frac{d^3\vec{q}}{(2\pi)^3} \ln(1 + \gamma\rho_0 \tilde{W}_\tau(q)) - \frac{1}{V} \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \langle \mathcal{H}^n[\phi] \rangle_{X_\tau, c}. \quad (3.1)$$

where  $\mathcal{H}[\phi] \equiv U[\phi] - U_0[\phi]$  and  $\langle \dots \rangle_{X_\tau, c}$  denotes a cumulant average.

Since we are interested in a low-density expansion, we keep only the first two terms  $U_1$  and  $U_2$  of the series (2.16), which is equivalent to take into account all contributions with one and two point correlations functions. Then,  $\mathcal{H}[\phi] = U_1[\phi] + U_2[\phi] - U_0[\phi]$ , and the grand potential can be recast in the following form :

$$\omega_{RPM}(v) = \omega_{HS}(v_0) + \omega_1 + \omega_2 + \mathcal{O}(\rho_0^3), \quad (3.2)$$

with the following definitions:

$$\omega_1 \equiv \frac{1}{2} \int \frac{d^3\vec{q}}{(2\pi)^3} \ln(1 + \gamma\rho_0 \tilde{W}_\tau(q)), \quad (3.3)$$

$$\omega_2 \equiv \frac{\langle \mathcal{H} \rangle_{X_\tau} \langle \mathcal{H}^2 \rangle_{X_\tau} - \langle \mathcal{H} \rangle_{X_\tau}^2}{2V}. \quad (3.4)$$

The well-known *HS* contribution is given by :

$$\omega_{HS}(v_0) = -\rho_0 - \frac{2\pi}{3} \rho_0^2 \sigma^3 + \mathcal{O}(\rho_0^3). \quad (3.5)$$

$\omega_1$  is a generalization, when smearing is taken into account, of the familiar DH expression of the free energy. Notice that, unlike the point-like DH approach, the integral (3.3) which defines  $\omega_1$  is convergent at large  $k$  (within the conventional theory, an infinite self-energy must be subtracted to recover finite results). Since it includes  $\tilde{W}(q)$ ,  $\omega_1$  is a function of  $a$  (and  $\kappa_0$ ); its expansion in powers of  $\kappa_0$  is given in Appendix B and reads :

$$\frac{1}{2} \int \frac{d^3\vec{q}}{(2\pi)^3} \ln(1 + \gamma\rho_0\tilde{W}_\tau(q)) - \frac{\rho_0\gamma}{a} = -\frac{2\sqrt{\pi}}{3} \rho_0^{3/2}\gamma^{3/2} + \frac{7\pi a}{15} \rho_0^2\gamma^2 - \frac{\pi\sqrt{\pi}a^2}{3} \rho_0^{5/2}\gamma^{5/2} + \mathcal{O}(\rho_0^3). \quad (3.6)$$

The first term recast in the form  $-\kappa_0^3/12\pi$  is reminiscent of the familiar DH contribution to the free energy.

$\omega_2$  contains averages over the gaussian field  $\bar{\phi}$  which can be obtained from application of Wick's theorem; the detailed calculation is reported in Appendix C and one finds

$$\begin{aligned} \omega_2 = & -\frac{\gamma\rho_0}{a} - \frac{\rho_0\Delta_0}{2} + \rho_0[1 - \exp(-\Delta_0/2)] \\ & - \frac{\rho_0^2}{4} [1 - \exp(-\Delta_0/2)]^2 \int d\vec{r} \psi_\tau^2(r) \\ & - \frac{\rho_0^2}{2} [1 - \exp(-\Delta_0/2)]^2 \tilde{h}_0(0) + \frac{\rho_0^2}{4} \exp(-\Delta_0) \int_{r < \sigma} d\vec{r} \psi_\tau^2(r) \\ & - \frac{\rho_0^2}{2} \exp(-\Delta_0) \sum_{n=2}^{\infty} \int_{r > \sigma} d\vec{r} \frac{\psi_\tau^{2n}(r)}{(2n)!}. \end{aligned} \quad (3.7)$$

where  $\tilde{h}_0(0)$  denotes the 3D Fourier transform of  $h_0^{(2)}(r)$ . We have introduced in this last expression the dimensionless potential  $\psi_\tau(r) \equiv \gamma X_\tau(r)$  and the quantity  $\Delta_0 \equiv \psi_\tau(0) - \frac{2\gamma}{a}$ . Expansions of  $\psi_\tau(r)$  and  $\Delta_0$  at low  $\kappa_0$  are given in Appendix B

$$\Delta_0 \equiv \psi_\tau(0) - \frac{2\gamma}{a} = \gamma \left[ -\kappa_0 + \frac{7}{15} \kappa_0^2 a - \frac{5}{24} \kappa_0^3 a^2 + \mathcal{O}(\kappa_0^4) \right], \quad (3.8)$$

while

$$\psi_\tau(r) = \frac{2\gamma}{a} - \frac{\gamma}{a^2} r - \gamma\kappa_0 + \mathcal{O}(\kappa_0^2) \quad \text{for } r < a, \quad (3.9)$$

$$\psi_\tau(r) = \gamma q_0^2 \frac{\exp(-\kappa_0 r)}{r} + \mathcal{O}(\kappa_0^2) \quad \text{for } r > a. \quad (3.10)$$

with  $q_0 = 2 \sinh(\kappa_0 a/2)/(\kappa_0 a)$ .

Using (3.8), (3.9) and (3.10) each contribution to (3.7) can be easily expanded in powers of  $\rho_0$ . The first two terms give

$$-\frac{\rho_0 \Delta_0}{2} + \rho_0 [1 - \exp(-\Delta_0/2)] = -\frac{\pi}{2} \rho_0^2 \gamma^3 - \frac{\pi \sqrt{\pi} \gamma^{9/2} \rho_0^{5/2}}{6} + \frac{14\pi \sqrt{\pi} \gamma^{7/2} \rho_0^{5/2} a}{15} + \mathcal{O}(\rho_0^3). \quad (3.11)$$

The prefactor of the third term is  $\rho_0^2 [1 - \exp(-\Delta_0/2)]^2 = \pi \gamma^3 \rho_0^3 + \mathcal{O}(\rho_0^{7/2})$  and the integral must be splitted into two components :

$$\int_{r < \sigma} d\vec{r} \psi_\tau^2(r) = \left( \frac{32\pi\gamma^2 a}{15} - \frac{20\pi \sqrt{\pi} \gamma^{5/2} \rho_0^{1/2} a^2}{3} \right) + 4\pi\gamma^2(\sigma - a) + 8\pi \sqrt{\pi} \gamma^{5/2} \rho_0^{1/2} (a^2 - \sigma^2) + \mathcal{O}(\rho_0), \quad (3.12)$$

$$\int_{r > \sigma} d\vec{r} \psi_\tau^2(r) = \frac{\sqrt{\pi} \gamma^{3/2}}{\rho_0^{1/2}} + \mathcal{O}(1). \quad (3.13)$$

Notice that the last integral is singular in  $\rho_0$  when  $\rho_0 \rightarrow 0$ . Consequently the term under investigation will contribute at the order  $\rho_0^{5/2}$ .

The expansion of the prefactor  $\rho_0^2 \exp(-\Delta_0)$  is straightforward  $\rho_0^2 \exp(-\Delta_0) = \rho_0^2 + 2 \sqrt{\pi} \gamma^{3/2} \rho_0^{5/2} + \mathcal{O}(\rho_0^3)$ , while  $\int_{r > \sigma} d\vec{r} \psi_\tau^{2n}(r)$  for  $n \geq 2$  is related to the exponential integral function  $E_n(z) = \int_1^\infty dt \exp(-zt) t^{-n}$ . Indeed one finds

$$\begin{aligned} \sum_{n=2}^{\infty} \int_{r > \sigma} d\vec{r} \frac{\psi_\tau^{2n}(r)}{(2n)!} &= 4\pi\sigma^3 \sum_{n=2}^{\infty} \frac{(\gamma/\sigma)^{2n} q_0^{4n}}{(2n)!} E_{2n-2}(2n\kappa_0\sigma) \\ &= 4\pi\sigma^3 \sum_{n=2}^{\infty} \frac{(\gamma/\sigma)^{2n}}{(2n)!(2n-3)} + \gamma^4 \frac{2\pi\kappa_0}{3} (\gamma_E + \ln(4\kappa_0\sigma) - 1) \\ &\quad - 4\pi\sigma^3 \kappa_0 \gamma \sum_{n=2}^{\infty} \frac{(\gamma/\sigma)^{2n+1}}{(2n+1)!(2n-2)} + \mathcal{O}(\rho_0) \end{aligned} \quad (3.14)$$

where the last equality is obtained with the help of the series representation of the exponential integral function<sup>(32)</sup>.

Gathering all these results, it can be checked that all contributions involving the smearing diameter  $a$  exactly cancel each other and that we indeed obtain a result independent on  $a$ ; more precisely we get

$$\begin{aligned} \omega_{RPM}(v) = & -\rho_0 - \frac{2\sqrt{\pi}}{3} \rho_0^{3/2} \gamma^{3/2} - \rho_0^2 \left( \frac{2\pi\sigma^3}{3} - \pi\gamma^2\sigma + \frac{\pi}{2} \gamma^3 + 2\pi\sigma^3 S(\gamma/\sigma) \right). \\ & - \frac{\pi\sqrt{\pi} \gamma^{9/2} \rho_0^{5/2}}{12} [8\gamma_E - 3 + 8 \ln(8\sqrt{\pi} \gamma^{1/2}\sigma)] \\ & + 2\pi \sqrt{\pi} \gamma^{7/2} \rho_0^{5/2} \sigma - 2\pi \sqrt{\pi} \gamma^{5/2} \rho_0^{5/2} \sigma^2 \\ & - 4\pi \sqrt{\pi} \gamma^{3/2} \rho_0^{5/2} \sigma^3 [S(\gamma/\sigma) - T(\gamma/\sigma)] \\ & - \frac{\pi\sqrt{\pi} \gamma^{9/2}}{3} \rho_0^{5/2} \ln(\rho_0) + \mathcal{O}(\rho^3). \end{aligned} \quad (3.15)$$

where we have introduced the two following series

$$\begin{aligned} S(\gamma/\sigma) & \equiv \sum_{n=2}^{\infty} \frac{(\gamma/\sigma)^{2n}}{(2n)! (2n-3)}, \\ T(\gamma/\sigma) & \equiv \sum_{n=2}^{\infty} \frac{(\gamma/\sigma)^{2n+1}}{(2n+1)! (2n-2)}. \end{aligned} \quad (3.16)$$

## B. Pressure of the RPM Model

In this section we derive the pressure for low density systems at arbitrary temperatures. In order to obtain these quantities, we must first performed a transformation from the density  $\rho_0$  (corresponding to the chemical potential  $v_0$ ) to the activity  $z$  of the model. For that purpose we use the relation:

$$\rho_0 = -z_0 \frac{\partial \omega_{HS}(v_0)}{\partial z_0} = z_0 - \frac{4\pi\sigma^3}{3} z_0^2 + \mathcal{O}(z_0^3) = 2z - \frac{16\pi\sigma^3}{3} z^2 + \mathcal{O}(z^3). \quad (3.17)$$

Inserting (3.17) in (3.15) we get the expression of  $\omega_{RPM}$  as a function of  $z$  and  $\gamma$

$$\begin{aligned} \omega_{RPM}(z, \gamma) = & -2z - \frac{4\sqrt{2\pi}\gamma^{3/2}}{3} z^{3/2} + 4\pi\sigma^3 \left( \frac{2}{3} + \left(\frac{\gamma}{\sigma}\right)^2 - \frac{1}{2} \left(\frac{\gamma}{\sigma}\right)^3 - 2\mathbf{S}(\gamma/\sigma) \right) z^2 \\ & + z^{5/2} 4\sqrt{2}\pi^{3/2} \left( -\frac{\gamma^{9/2}}{12} (8\gamma_E + 8\ln(8\sqrt{\pi}\gamma^{1/2}\sigma) - 3) \right. \\ & \left. + 2\gamma^{7/2}\sigma - 2\gamma^{5/2}\sigma^2 \right) \\ & + z^{5/2} \frac{16\sqrt{2}\pi^{3/2}\gamma^{3/2}\sigma^3}{3} (1 - 3[\mathbf{S}(\gamma/\sigma) - \mathbf{T}(\gamma/\sigma)]) \\ & - z^{5/2} \ln(2z) \frac{4\sqrt{2}\pi^{3/2}\gamma^{9/2}}{3} + \mathcal{O}(z^3). \end{aligned} \quad (3.18)$$

The density of the system is obtained by the relation  $\rho = -z\partial\omega_{RPM}(z)/\partial z$  which is easily inverted and reads

$$\begin{aligned} z = & \frac{\rho_0}{2} - \frac{\sqrt{\pi}\gamma^{3/2}}{2} \rho_0^{3/2} + \pi\sigma^3 \left( \frac{2}{3} + \left(\frac{\gamma}{\sigma}\right)^2 + \frac{1}{4} \left(\frac{\gamma}{\sigma}\right)^3 - 2\mathbf{S}(\gamma/\sigma) \right) \rho_0^2 \\ & + \rho_0^{5/2} \pi^{3/2} \left( -\frac{\gamma^{9/2}}{12} (10\gamma_E + 10\ln(8\sqrt{\pi}\gamma^{1/2}\sigma) - 7) - \gamma^{7/2}\sigma - \frac{5\gamma^{5/2}\sigma^2}{2} \right) \\ & + \rho_0^{5/2} \pi^{3/2} \gamma^{3/2} \sigma^3 \left( -\frac{2}{3} + 2\mathbf{S}(\gamma/\sigma) + 5\mathbf{T}(\gamma/\sigma) \right) - \rho_0^{5/2} \ln(\rho_0) \frac{5\pi^{3/2}\gamma^{9/2}}{12} + \mathcal{O}(\rho_0^3). \end{aligned} \quad (3.19)$$

Using this last equation in (3.18) we obtain the pressure  $\beta P_{RPM} \equiv -\omega_{RPM}(\rho, \gamma)$  of the RPM model

$$\begin{aligned} \beta P_{RPM} = & \rho - \frac{\sqrt{\pi}\gamma^{3/2}}{3} \rho^{3/2} + \sigma^3 \left( \frac{2\pi}{3} + \pi \left(\frac{\gamma}{\sigma}\right)^2 - 2\pi\mathbf{S}(\gamma/\sigma) \right) \rho^2 \\ & - \left( \pi\sqrt{\pi}\gamma^{9/2} \left( -\frac{2}{3} + \gamma_E + \ln(8\sqrt{\pi}\gamma^{1/2}\rho^{1/2}\sigma) \right) \right. \\ & \left. + 3\pi\sqrt{\pi}\gamma^{5/2}\sigma^2 - 6\pi\sqrt{\pi}\gamma^{3/2}\sigma^3\mathbf{T}(\gamma/\sigma) \right) \rho^{5/2} \\ & + \mathcal{O}(\rho^3) \end{aligned} \quad (3.20)$$

which can be recasted in the following form :

$$\begin{aligned} \beta P_{RPM} = & \rho - \frac{\kappa^3}{24\pi} + \frac{2\pi\sigma^3}{3} \rho^2 + \frac{\kappa^4\sigma}{16\pi} - 2\pi\rho^2\sigma^3 S(\gamma/\sigma) \\ & - \frac{\kappa\kappa_2^4}{512\pi^3} \left( -\frac{2}{3} + \gamma_E + \ln(4\kappa\sigma) \right) - \frac{3\kappa^5\sigma^2}{32\pi} \\ & + \frac{3}{4} (4\pi\gamma)^{3/2} \sigma^3 \rho^{5/2} T(\gamma/\sigma) + \mathcal{O}(\rho^3) \end{aligned} \quad (3.21)$$

with  $\kappa_2^2 \equiv 4\pi\gamma\kappa^2$  and  $\kappa^2 = 4\pi\gamma\rho$ , the square of the usual inverse DH length.  $S(\gamma/\sigma)$  and  $T(\gamma/\sigma)$  are defined by Eq. (3.16).

#### IV. DISCUSSION

In this section we briefly compare the results obtained above with the classical diagrammatic results of Haga<sup>(7)</sup> and with the field theoretical approach of Netz–Orland.<sup>(21)</sup> It will be shown below, as expected, that these three different routes yield the same result.

Haga's expression for the equation of state (Eq. (29) of ref. 7) is easily compared with Eq. (3.21); both results coincide except for the terms proportionnal to  $\kappa^5$  which differ by a factor of 1/2. In a recent paper by Bekiranov and Fisher,<sup>(33)</sup> a slip in Haga's Eq. (25.4) was noted by these authors who pointed out that the last term of Haga's equation should read  $\kappa^5 a^2 / 16\pi$  instead of  $\kappa^5 a^2 / 32\pi$ . When this correction is taken into account Haga's results and ours are identical.

In their paper,<sup>(21)</sup> Netz and Orland do not compare explicitly their results with those of Haga. This can be done by confronting our expression of the grand potential in terms of the fugacity (cf. Eq. (3.18)) with Eq. (22) of ref. 21. Their results are given in terms of the hyperbolic sine-integral function  $\text{Shi}(\gamma/\sigma)$  and of the incomplete Gamma function  $\Gamma(0, \gamma/\sigma)$ . As shown in Appendix D these functions can be reexpressed in terms of the series  $S(\gamma/\sigma)$  and  $T(\gamma/\sigma)$  defined by Eq. (3.16) and it appears that the two results coincide. Let us now explain, why the approximate theory of Netz and Orland gives the correct result at this order. Recall that these authors also perform a Hubbard-Stratonovich transformation on the singular hardcore potential. The associate random field is denoted  $\psi(r)$  and the following average is needed (Eq. (12) of ref. 21)

$$\langle h(1) h(2) \rangle = \exp(-w(12)) \quad (4.1)$$

where  $h(r) \equiv \exp(-i\psi(r) + w(0)/2)$  and  $w(r)$  denotes the hard-core potential. Two consequences result from Eq. (4.1). On the one hand, as noted by the authors,  $\exp(-w(12))$  (contrary to  $w$ ) is finite, which regularizes the theory. On the other hand, since  $\exp(-w(r)) = 1 - \theta(r-a)$  ( $\theta$  is the Heaviside function), this procedure amounts to incorporate hard-core effects only at the level of the second virial coefficient. It appears (see Eqs. (C12, C13) of Appendix C), that this approximation is sufficient for an expansion up to  $\rho^{5/2}$  but will miss some contributions at the next order.

## V. CONCLUSION

In conclusion we have proposed in this work a formally exact field theory for hard-core Coulomb systems. This approach generalizes the usual sine-Gordon theory valid for pointlike charges to realistic Coulomb fluids with additional short range interactions. Within this formalism we derive the equation of state of the RPM model up to  $\rho^{5/2}$ . Our results confirm the classical diagrammatic expansions of the Mayer–Haga diagrammatic theory. Going to next order is perhaps not out of reach although there is a delicate analysis of the relevant contributions to the cumulants to perform. Note that an equation of state for pointlike ions as been recently obtained by Ortner<sup>(18)</sup> using the Hubbard–Schofield approach, up to the  $\rho^3$  contribution. In this latter case, however, the reference system is the ideal gas system which, in turn, greatly simplify the calculations. In the companion paper, we derive an equation of state of the RPM in the high temperature regime, at any density, by using the formalism developed in the present paper. This two complementary limits show the ability of our formulation to tackle in a coherent way the equation of state of Coulomb systems.

Another problem, which remains a challenge to theory, is the understanding of ionic criticality<sup>(34)</sup>. We believe that our formalism might be used to give some insights upon these interesting questions. Work in that direction is currently in progress.

## APPENDIX A: FUNCTIONAL INTEGRATION

For any operator of the real field  $\phi(\vec{r})$  we define the average  $\langle A[\phi] \rangle_{w_\tau}$  by the following relation

$$\langle A[\phi] \rangle_{w_\tau} = \int \mathcal{D}\phi P_{w_\tau}[\phi] A[\phi], \quad (\text{A1})$$

where  $\int \mathcal{D}\phi$  denotes a functional integration and the Gaussian weight  $P_{W_\tau}[\phi]$  is defined as

$$P_{W_\tau}[\phi] = \frac{\exp(-\frac{1}{2} \langle \phi | W_\tau^{-1} | \phi \rangle)}{\int \mathcal{D}\phi \exp(-\frac{1}{2} \langle \phi | W_\tau^{-1} | \phi \rangle)}. \quad (\text{A2})$$

In order to give an unambiguous definition of the measure  $\mathcal{D}\phi$  and thus a precise meaning to the SG transform we henceforth consider a cubic volume  $V = L^3$  with periodic boundary conditions (PBC). The  $1/r$  Coulomb potential which enters the configurational energy (2.1) of the RPM must therefore be replaced by the Ewald potential<sup>(24-27)</sup>

$$E(\vec{r}) = \frac{4\pi}{L^3} \sum_{\vec{q} \neq 0} \frac{\exp(i\vec{q} \cdot \vec{r})}{\vec{q}^2}, \quad (\text{A3})$$

where  $\vec{q} = 2\pi\vec{n}/L$  ( $\vec{n} \equiv (n_x, n_y, n_z) \in \mathbb{Z}^3$ ) is a vector of the reciprocal lattice. Recall that  $E(\vec{r})$  is the periodic electrostatic potential of a point charge embedded in a uniform neutralizing background which kills the term  $\vec{q} = 0$  in the series (A3).<sup>(27, 28)</sup> This causes a (hopefully) slight difficulty since configurations with  $N_+ \neq N_-$  are associated with the presence of a background which ensures the electric neutrality of the system. The periodical system considered here is therefore slightly different from the usual RPM; however, this should make no difference in the thermodynamic limit.

Assuming PBC we thus have<sup>(29)</sup>

$$\int \mathcal{D}\phi \equiv \prod'_{\vec{q}} \int_{-\infty}^{+\infty} d\tilde{\phi}_{\vec{q}}^R \int_{-\infty}^{+\infty} d\tilde{\phi}_{\vec{q}}^I, \quad (\text{A4})$$

where  $\tilde{\phi}_{\vec{q}}^R$  and  $\tilde{\phi}_{\vec{q}}^I$  denote respectively the real and imaginary parts of the Fourier component

$$\tilde{\phi}_{\vec{q}} = \int_V d^3\vec{r} \phi(\vec{r}) \exp(-i\vec{q} \cdot \vec{r}) \quad (\text{A5})$$

of the real field  $\phi$ . The infinite product in Eq. (A4) runs over the vectors  $\vec{q} \neq \vec{0}$  of the reciprocal lattice. In fact, since, due to the reality of the field  $\phi$ ,  $\phi_{\vec{q}} = \tilde{\phi}_{-\vec{q}}^*$ , only half of the vectors has to be considered, for instance those with  $n_x \geq 0$ .<sup>(29)</sup> That is what is meant by the subscript ' in Eq. (A4).

## APPENDIX B: LOW $\kappa_0$ EXPANSIONS

In this Appendix, we give the calculation of the expansions of  $\Delta_0$ ,  $\psi_\tau(r)$  and  $\omega_1$  with respect to  $\kappa_0$ .



1. Let us begin with  $\Delta_0$ ; we recall that  $\Delta_0 \equiv \psi_\tau(0) - 2\gamma/a$  where  $\psi_\tau(0) = \gamma X_\tau(0)$ . Using Eq. (2.20) we get

$$\begin{aligned} X_\tau(0) &= \int \frac{d^3\vec{q}}{(2\pi)^3} \tilde{X}_\tau(q) = \frac{2}{\pi a} \int_{-\infty}^{+\infty} \frac{\sin^2 x}{x^2 + \xi_0^2} \frac{\sin^2 x}{x^2} dx \\ &= \frac{2}{\pi a} \int_{-\infty}^{+\infty} \frac{\sin^2 x}{x^2 + \xi_0^2} \frac{1}{1 + \nu(x)} dx, \end{aligned} \quad (\text{B1})$$

where the dimensionless parameter  $\xi_0 = \kappa_0 a/2$  and the function

$$\nu(x) = \frac{\xi_0^2}{x^2 + \xi_0^2} \left[ \frac{\sin^2 x}{x^2} - 1 \right] \quad (\text{B2})$$

satisfies  $|\nu(x)| < 1 \forall x$ . Therefore the fraction  $1/(1 + \nu(x))$  in Eq. (B1) can be replaced by its series representation which yields

$$\begin{aligned} X_\tau(0) &= \frac{2}{\pi a} \sum_{n=0}^{\infty} (-)^n \mathcal{J}_n(\xi_0), \\ \mathcal{J}_n(\xi_0) &= \int_{-\infty}^{+\infty} \frac{\sin^2 x}{x^2 + \xi_0^2} \nu^n(x) dx, \end{aligned} \quad (\text{B3})$$

where it should be noted that the integrals  $\mathcal{J}_n(\xi_0)$  in Eq. (B3) are entire functions of  $\xi_0$ . Consequently we get at order  $\xi_0^3$

$$X_\tau(0) = \frac{2}{\pi a} [\mathcal{J}_0(\xi_0) - \mathcal{J}_1(\xi_0)] + \mathcal{O}(\xi_0^4),$$

where  $\mathcal{J}_0(\xi_0)$  and  $\mathcal{J}_1(\xi_0)$  can be computed by means of the residue theorem

$$\begin{aligned} \mathcal{J}_0(\xi_0) &= \frac{\pi}{2\xi_0} (1 - \exp(-2\xi_0)), \\ \mathcal{J}_1(\xi_0) &= \frac{\pi}{16\xi_0^3} (-9 + 8\xi_0 + (12 + 8\xi_0) \exp(-2\xi_0) - (3 + 4\xi_0) \exp(-4\xi_0)) \\ &\quad - \frac{\pi}{4\xi_0} + \frac{\pi}{2} \exp(-2\xi_0) \left( 1 + \frac{1}{2\xi_0} \right). \end{aligned} \quad (\text{B4})$$

With the help of Mapple<sup>®</sup> one finds

$$X_\tau(0) - \frac{2}{a} = -\xi_0 + \frac{14}{15}\xi_0^2 - \frac{5}{6}\xi_0^3 + \mathcal{O}(\xi_0^4) = -\kappa_0 + \frac{7}{15}\kappa_0^2 a - \frac{5}{24}\kappa_0^3 a^2 + \mathcal{O}(\kappa_0^4). \quad (\text{B5})$$

from which we deduce Eq. (3.8).

2. The same method can be used for the expansion of  $X_\tau(r)$ .

$$X_\tau(r) = \int \frac{d^3\vec{q}}{(2\pi)^3} \tilde{X}_\tau(q) \exp(i\vec{q} \cdot \vec{r}) = \frac{1}{\pi r} \int_{-\infty}^{+\infty} \frac{\sin^2 x \sin(2xr/a)}{x(x^2 + \xi_0^2)} \frac{1}{1 + \nu(x)} dx. \quad (\text{B6})$$

thus,

$$X_\tau(r) = \frac{1}{\pi r} \int_{-\infty}^{+\infty} \frac{\sin^2 x \sin(2xr/a)}{x(x^2 + \xi_0^2)} dx + \mathcal{O}(\xi_0^2), \quad (\text{B7})$$

is a piecewise function defined for  $r > a$  by the expression

$$\begin{aligned} X_\tau^<(r) &= \frac{1}{2r\xi_0^2} \left( 1 - \exp\left(-\frac{2r}{a}\xi_0\right) - \exp(-2\xi_0) \sinh\left(\xi_0 \frac{2r}{a}\right) \right) + \mathcal{O}(\xi_0^2) \\ &= \frac{2}{a} - \frac{r}{a^2} - \kappa_0 + \mathcal{O}(\kappa_0^2), \end{aligned} \quad (\text{B8})$$

and for  $r > a$  by

$$X_\tau^>(r) = \frac{\sinh^2(\xi_0)}{\xi_0^2} \frac{\exp\left(-\frac{2r}{a}\xi_0\right)}{r} = \frac{\sinh^2(\kappa_0 a/2)}{(\kappa_0 a/2)^2} \frac{\exp(-\kappa_0 r)}{r} + \mathcal{O}(\kappa_0^2). \quad (\text{B9})$$

(B8) and (B9) are equivalent to (3.9) and (3.10).

3. We give now the expansion of  $\omega_1$ . We have first

$$\omega_1 \equiv \frac{1}{2} \int \frac{d^d\vec{q}}{(2\pi)^d} \ln(1 + \gamma\rho_0 \tilde{W}_\tau(q)) = \frac{2}{\pi^2 a^3} \int_0^\infty x^2 \ln\left(1 + \xi_0^2 \frac{\sin^2 x}{x^4}\right) dx \quad (\text{B10})$$

which can be written as the sum of three terms

$$\begin{aligned} \omega_1 = & \frac{2}{\pi^2 a^3} \int_0^\infty x^2 \left[ \ln \left( 1 + \frac{\xi_0^2}{x^2} \right) - \frac{\xi_0^2}{x^2 + \xi_0^2} \right] dx + \frac{\xi_0^2}{\pi^2 a^3} \int_{-\infty}^\infty \frac{\sin^2 x}{x^2 + \xi_0^2} dx \\ & + \frac{1}{\pi^2 a^3} \sum_{n=2}^\infty \frac{(-)^{n-1}}{n} \int_{-\infty}^\infty x^2 v^n(x) dx \end{aligned} \quad (\text{B11})$$

The first integral of the last expression can be easily integrated by parts with the result

$$\int_0^\infty x^2 \left[ \ln \left( 1 + \frac{\xi_0^2}{x^2} \right) - \frac{\xi_0^2}{x^2 + \xi_0^2} \right] dx = \frac{\pi \xi_0^3}{6}. \quad (\text{B12})$$

Thus,

$$\omega_1 = \frac{\xi_0^3}{3\pi a^3} + \frac{1}{\pi^2 a^3} \mathcal{J}_0(\xi_0) - \frac{1}{\pi^2 a^3} \int_{-\infty}^\infty x^2 v^2(x) dx + \mathcal{O}(\xi_0^6). \quad (\text{B13})$$

Using

$$\begin{aligned} \int_{-\infty}^\infty x^2 v^2(x) dx = & \frac{\pi}{16\xi_0} [-9 + 8\xi_0 + (12 + 8\xi_0) \exp(-2\xi_0) \\ & - (3 + 4\xi_0) \exp(-4\xi_0)] + \frac{\pi \xi_0^3}{2} \\ & - \frac{\pi \xi_0}{2} + \pi \xi_0 \exp(-2\xi_0) \left( 1 + \frac{1}{2\xi_0} \right). \end{aligned} \quad (\text{B14})$$

we obtain

$$\omega_1 = \frac{1}{\pi a^3} \left( \xi_0^2 - \frac{2\xi_0^3}{3} + \frac{7\xi_0^4}{15} - \frac{\xi_0^5}{3} + \mathcal{O}(\xi_0^6) \right) = \frac{\kappa_0^2}{4\pi a} - \frac{\kappa_0^3}{12\pi} + \frac{7\kappa_0^4 a}{240\pi} - \frac{\kappa_0^5 a^2}{96\pi} + \mathcal{O}(\kappa_0^6), \quad (\text{B15})$$

which is the result used in Eq. (3.6).

### APPENDIX C: COMPUTATION OF $\omega_2$

In this section we give the expansion of  $\omega_2$  for low  $\kappa_0$ . We have

$$\omega_2 \equiv \frac{\langle \mathcal{H} \rangle_{X_\tau} - \langle \mathcal{H}^2 \rangle_{X_\tau} + \langle \mathcal{H} \rangle_{X_\tau}^2}{2V}, \quad (C1)$$

with  $\mathcal{H}[\phi] = U_1[\phi] + U_2[\phi] - U_0[\phi]$ .

Each cumulant implies several averages over the field  $\phi(\vec{r})$  which can all be deduced from the general average  $X \equiv \langle \cos(\lambda_1 \phi_1) \cos(\lambda_2 \phi_2) \cos(\lambda_3 \phi_3) \rangle_{X_\tau}$ , where  $\lambda_1, \lambda_2, \lambda_3$  are real constants. Starting from

$$X = \frac{1}{8} \sum_{\epsilon_1, \epsilon_2, \epsilon_3} \langle \exp(i(\lambda_1 \epsilon_1 \phi_1 + \lambda_2 \epsilon_2 \phi_2 + \lambda_3 \epsilon_3 \phi_3)) \rangle_{X_\tau} \quad (C2)$$

$$= \frac{1}{8} \sum_{\epsilon_1, \epsilon_2, \epsilon_3} \left\langle \exp \left( i \int d^3 \vec{r} \phi(\vec{r}) (\epsilon_1 \lambda_1 \delta(\vec{r} - \vec{r}_1) + \epsilon_2 \lambda_2 \delta(\vec{r} - \vec{r}_2) + \epsilon_3 \lambda_3 \delta(\vec{r} - \vec{r}_3)) \right) \right\rangle_{X_\tau}, \quad (C3)$$

where  $\epsilon_i = \pm 1$  and using the fundamental relation for Gaussian integrals

$$\left\langle \exp \left( i \int d^3 \vec{r} \phi(\vec{r}) \zeta(\vec{r}) \right) \right\rangle_{X_\tau} = \exp \left( -\frac{1}{2} \int d^3 \vec{r}_1 d^3 \vec{r}_2 X_\tau(\vec{r}_1 - \vec{r}_2) \zeta(\vec{r}_1) \zeta(\vec{r}_2) \right), \quad (C4)$$

one gets

$$\begin{aligned} X &= \frac{1}{8} \exp \left( -\frac{X_\tau(0)}{2} \sum_{i=1}^3 \lambda_i^2 \right) \sum_{\epsilon_i} \exp(-\lambda_1 \lambda_2 \epsilon_1 \epsilon_2 X_\tau(12)) \\ &\quad - \lambda_2 \lambda_3 \epsilon_2 \epsilon_3 X_\tau(23) - \lambda_1 \lambda_3 \epsilon_1 \epsilon_3 X_\tau(13)) \\ &= \exp \left( -\frac{X_\tau(0)}{2} \sum_{i=1}^3 \lambda_i^2 \right) (\cosh(\lambda_1 \lambda_2 X_\tau(12)) \cosh(\lambda_2 \lambda_3 X_\tau(23)) \cosh(\lambda_1 \lambda_3 X_\tau(13)) \\ &\quad - \sinh(\lambda_1 \lambda_2 X_\tau(12)) \sinh(\lambda_2 \lambda_3 X_\tau(23)) \sinh(\lambda_1 \lambda_3 X_\tau(13))) \end{aligned} \quad (C5)$$

from which all useful formula can be obtained.

It is convenient to recast the various contribution of  $\omega_2$  in the following way

$$\frac{-\langle U_0[\phi] \rangle_{x_\tau} + \langle U_1[\phi] \rangle_{x_\tau}}{L^3} = -\frac{\rho_0 \Delta_0}{2} - \rho_0 [\exp(-\Delta_0/2) - 1] - \frac{\gamma \rho_0}{a}, \quad (C6)$$

$$-\frac{\langle U_0^2 \rangle_{x_\tau} - \langle U_0 \rangle_{x_\tau}^2}{2L^3} = -\frac{\rho_0^2}{4} \int d\vec{r} \psi_\tau^2(r), \quad (C7)$$

$$\frac{\langle U_0 U_1 \rangle_{x_\tau} - \langle U_0 \rangle_{x_\tau} \langle U_1 \rangle_{x_\tau}}{L^3} = \frac{\rho_0^2}{2} \exp(-\Delta_0/2) \int d\vec{r} \psi_\tau^2(r), \quad (C8)$$

$$\frac{\langle U_2[\phi] \rangle_{x_\tau} - \langle U_1^2 \rangle_{x_\tau} - \langle U_1 \rangle_{x_\tau}^2}{L^3} = -\frac{\rho_0^2}{2} [1 - 2 \exp(-\Delta_0/2)] \tilde{h}_0(0) \quad (C9)$$

$$-\frac{\rho_0^2}{2} \exp(-\Delta_0) \int d\vec{r} [g_0(r) \cosh(\psi_\tau(r)) - 1] \quad (C10)$$

$$= -\frac{\rho_0^2}{2} [1 - \exp(-\Delta_0/2)]^2 \tilde{h}_0(0) \quad (C11)$$

$$-\frac{\rho_0^2}{2} \exp(-\Delta_0) \int d\vec{r} g_0(r) [\cosh(\psi_\tau(r)) - 1]. \quad (C12)$$

where  $\Delta_0$  and  $\psi_\tau(r)$  are given by Eq. (3.8), (3.9) and (3.10), and we have introduced  $g_0(r) \equiv 1 + h_0(r)$ .

At the lowest order in density the correlation function  $g_0^{(0)}(r) = 0$  for  $r < \sigma$  and 1 otherwise; thus

$$\begin{aligned} \int d\vec{r} g_0^{(0)}(r) [\cosh(\psi_\tau(r)) - 1] &= \frac{1}{2} \int d\vec{r} g_0^{(0)}(r) \psi_\tau^2(r) + \sum_{n=2}^{\infty} \int d\vec{r} g_0^{(0)}(r) \frac{\psi_\tau^{2n}(r)}{(2n)!} \\ &= \frac{1}{2} \int d\vec{r} \psi_\tau^2(r) - \frac{1}{2} \int_{r < \sigma} d\vec{r} \psi_\tau^2(r) \\ &\quad + \sum_{n=2}^{\infty} \int_{r > \sigma} d\vec{r} \frac{\psi_\tau^{2n}(r)}{(2n)!}. \end{aligned} \quad (C13)$$

Gathering together the two precedent results, we obtain Eq. (3.7).

## APPENDIX D: COMPARISON WITH NETZ-ORLAND'S PAPER

In this Appendix we give some technical details allowing the comparison of Eq. (3.18) with the expression of the grand potential in terms of the fugacity calculated by Netz and Orland.

Eq. (22) of Netz-Orland's paper can be written in our notations ( $\lambda \rightarrow z, a \rightarrow \sigma$ )

$$-\omega_{RPM} = 2z - b_{3/2} z^{3/2} \sigma^{3/2} - b_2 z^2 \sigma^3 - b_{5/2} z^{5/2} \sigma^{9/2} - b_{\ln 5/2} z^{5/2} \sigma^{9/2} \ln(z\sigma^3) - \dots \quad (D1)$$

where

$$b_{3/2} = -\frac{4}{3} \sqrt{2\pi} \epsilon^{3/2}, \quad (D2)$$

$$b_2 = -2\pi\epsilon^3 - \frac{2\pi}{3} (2\epsilon^3 \text{Shi}(\epsilon) - \cosh(\epsilon)[4 + 2\epsilon^2] - 2\epsilon \sinh(\epsilon)) \quad (D3)$$

$$b_{5/2} = -\frac{(2\pi)^{3/2}}{3} \epsilon^{9/2} - 2 \frac{(2\pi\epsilon)^{3/2}}{3} \left( 2\epsilon^3 \left[ \Gamma(0, \epsilon) + 2\gamma_E + \frac{1}{2} \ln(128\pi\epsilon^3) \right] - 2 \exp(-\epsilon)[2 - \epsilon + \epsilon^2] - \frac{59}{12} \epsilon^3 \right) \quad (D4)$$

$$b_{\ln 5/2} = -2 \frac{(2\pi\epsilon)^{3/2}}{3} \epsilon^3 \quad (D5)$$

with  $\epsilon \equiv \gamma/\sigma$ .

It can be easily checked that  $b_{3/2}$  coincides with our coefficient in Eq. (3.18).  $b_2$  is recovered using the following identity

$$\epsilon^3 \text{Shi}(\epsilon) - \epsilon^2 \cosh(\epsilon) - 2 \cosh(\epsilon) - 2\epsilon \sinh(\epsilon) = 6S(\epsilon) - 3\epsilon^2 - 2 \quad (D6)$$

where  $S(\epsilon)$  is the series given by Eq. (3.16).

$b_{5/2}$  involves the incomplete Gamma function  $\Gamma(0, \epsilon)$  which is related to exponential integral functions by the following relations<sup>(32)</sup>

$$\Gamma(0, \epsilon) = E_1(\epsilon), \quad (D7)$$

$$E_{n+1}(\epsilon) = \frac{1}{n} (\exp(-\epsilon) - \epsilon E_n(\epsilon)) \quad \text{for } n > 1. \quad (D8)$$

Thus, from  $\epsilon^3 \Gamma(0, \epsilon) - \exp(-\epsilon)(\epsilon^2 - \epsilon + 2) = -6E_4(\epsilon)$  we get

$$\begin{aligned} \epsilon^3 \Gamma(0, \epsilon) - \exp(-\epsilon)(\epsilon^2 - \epsilon + 2) &= \epsilon^3 \left( -\ln \epsilon - \gamma_E + \frac{11}{6} \right) - 2 + 3\epsilon - 3\epsilon^2 \\ &+ 6 \sum_{m=4}^{\infty} \frac{(-\epsilon)^m}{(m-3)m!}, \end{aligned} \quad (\text{D9})$$

where it can be noted that

$$\sum_{m=4}^{\infty} \frac{(-\epsilon)^m}{(m-3)m!} = S(\epsilon) - T(\epsilon). \quad (\text{D10})$$

Inserting Eqs (D9) and (D10) in Eq. (D4) gives our expression of the  $z^{5/2}$  coefficient in Eq. (3.18).

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