

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

II. High-Temperature Expansion

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We perform a high-temperature expansion of the grand potential of the restrictive primitive model of electrolytes in the frame of the extended sine-Gordon theory exposed in the companion paper. We recover a result already obtained by Stell and Lebowitz (*J. Chem. Phys.* **49**, 3706 (1968)) by means of diagrammatic expansions.

KEY WORDS: Coulomb fluids; Sine-Gordon action; High-temperature expansion.

I. INTRODUCTION

In the first part of this work (hereafter referred as I⁽¹⁾) we have established an exact field theoretical representation of the statistical mechanics of the restricted primitive model of electrolytes (RPM), i.e. an equimolar mixture of positively and negatively charged hard spheres of the same diameter σ . Although the generalization to asymmetric models is certainly possible we have limited ourselves to the case where the cations and the anions bear opposite charges $\pm e$. By applying the Kac–Hubbard–Stratonovich–Siegert–Edwards^(2–7) transform to the Coulomb interaction we have obtained an exact new expression of the action $\mathcal{S}[\phi]$ very similar to the well-known Sine-Gordon action to which it reduces in the limit of vanishing hard-core diameters.^(8, 9)

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By contrast with recent works in that direction^(10, 11) our formalism incorporates correctly the hard-core effects and our Sine-Gordon action is well defined as a consequence of a smearing of the charge of the ions which regularizes the Coulomb interactions at short distances. In the companion paper we have applied our formalism to a derivation of the equation of state of the RPM in the low activity (z) regime. The old results obtained in the frame of the Mayer diagrammatic theory⁽¹²⁻¹⁴⁾ and recently rediscovered by Netz and Orland⁽¹¹⁾ are confirmed and our derivation precises the domain of validity of the (approximate) field theoretical formulation of Netz and Orland.

In the present paper we show that the formalism developed in I also enables a derivation of the equation of state of the RPM in the high-temperature regime and we recover the results obtained by Stell and Lebowitz⁽¹⁶⁾ in the frame of the γ -ordering theory of liquids.⁽¹⁷⁻¹⁹⁾ The latter is a sophisticated diagrammatic perturbation theory in which the "small" parameter is $\gamma \equiv \beta e^2$ (β inverse temperature), otherwise the density is arbitrary. Note that a derivation of the equation of state of the RPM at high density is clearly out of the scope of the theory of Netz and Orland in which hard-core effects are incorporated only at the level of the second virial coefficient.

Our paper is organized as follows. In Section II we reorganize the Sine-Gordon action $\mathcal{S}[\phi]$ of the RPM as an expansion in powers of γ . A γ -ordering of the grand-potential ω_{RPM} is then obtained by making use of the cumulant theorem.⁽²⁰⁾ Note that we thus make use of the same technics as in I to obtain the z -ordering of ω_{RPM} which confers an aesthetic unity to our approach. In Section III we derive an expression of ω_{RPM} valid at order $\gamma^{5/2}$. Moreover we show that our expression for ω_{RPM} is independent of the precise nature of the smearing (i.e. independent of the smearing diameter a , $0 < a \leq \sigma$) at this order. This result completes the independence of the z -expansion of ω_{RPM} upon a which was proved in the companion paper. Admitting this independence at higher orders in γ greatly facilitates the algebra of Section IV where ω_{RPM} is obtained at order $\gamma^{7/2}$ by performing the calculations with $a \rightarrow 0$. A Legendre transform then gives an expression of the free energy of the RPM at order $\gamma^{7/2}$ which coincides with the old result of Stell and Lebowitz.⁽¹⁶⁾ We conclude in Section V.

II. γ -ORDERING OF THE GRAND-POTENTIAL

Our starting point will be the expression of the grand potential per unit volume $\omega_{RPM}(\beta, \nu) \equiv -\ln[\mathcal{E}_{RPM}(\beta, \nu, L^3)]/L^3$ ($\mathcal{E}_{RPM}(\beta, \nu, L^3)$ grand-partition function) of the RPM, which was derived in I in the frame of a regularized Sine-Gordon^(2, 5-9) theory. Here $\nu = \beta\mu$ (β inverse temperature),

where $\mu = \mu_{\pm}$ denotes the chemical potentials of the anions and the cations which can be chosen equal for simplicity.⁽⁹⁾ Moreover, we implicitly assume that the ions are enclosed in a cubic box of side L , with periodic boundary conditions. Recall that (cf. Eq. (3.1) of ref. I).

$$\omega_{RPM}(\beta, v) = \omega_{HS}(v_0) + \omega_1 + \Delta\omega, \quad (2.1a)$$

$$\omega_1 = \frac{1}{2} \int \frac{d^3\vec{q}}{(2\pi)^3} \ln(1 + \gamma\rho_0\tilde{W}_{\tau}(q)) \quad (2.1b)$$

$$L^3\Delta\omega = -\ln\langle \exp(-\mathcal{H}[\phi]) \rangle_{X_{\tau}}. \quad (2.1c)$$

In eq. (2.1a) $\omega_{HS}(v_0)$ is the grand potential (per unit volume) of a fluid of neutral hard spheres at the chemical potential $v_0 = v + \ln(2)$. In Eq. (2.1b) we have denoted by $\rho_0 \equiv \rho_{HS}(v_0) = -\partial\omega_{HS}/\partial v_0$ the number density of this reference system. In Eq. (2.1b) $\tilde{W}_{\tau}(q)$ is the Fourier transform of the electrostatic interaction $W_{\tau}(r)$ between two balls of diameter a distant of r , each of unit charge and with an uniform surfacic charge density $1/\pi a^2$. The smearing of the charge over the surface of a sphere of diameter a smaller than the diameter σ of the ions was introduced in I in order to regularize the Sine-Gordon transform. Since

$$\tilde{W}_{\tau}(q) = \frac{4\pi}{q^2} \left(\frac{\sin(qa/2)}{qa/2} \right)^2, \quad (2.2)$$

the expression (2.1b) of the contribution ω_1 is convergent for $a \neq 0$ as a consequence of the smearing. It must be stressed that the expression (2.1) of ω_{RPM} is exact and does not depend on the value of the smearing diameter a (as long as $0 < a \leq \sigma$).

The last contribution (2.1c) to the grand potential involves the effective hamiltonian

$$\mathcal{H}[\phi] = U[\phi] - U_0[\phi], \quad (2.3a)$$

$$U_0[\phi] \equiv \frac{\rho_0\gamma}{2} \int d^3\vec{r}_1 \phi^2(1), \quad (2.3b)$$

$$U[\phi] \equiv - \sum_{n=1}^{\infty} \frac{\rho_0^n}{n!} \int d^3\vec{r}_1 \cdots d^3\vec{r}_n h_0^{(n)}(1, \dots, n) \prod_{i=1}^n [\exp(\gamma/a) \cos(\sqrt{\gamma} \phi(i)) - 1], \quad (2.3c)$$

where $\gamma = \beta e^2$ ($\pm e$ charges of the ions) and where the $h_0^{(n)}(1, \dots, n)$ are the connected n-body correlation functions of the reference hard sphere fluid at

the density ρ_0 . These functions, which are closely related to the Ursell distribution functions,⁽¹⁵⁾ are solution of a hierarchy of integral equations which is briefly rewied in Appendix A. In Eq. (2.1c) the brackets $\langle \dots \rangle_{X_\tau}$ denote a Gaussian average over the fluctuations of a real scalar field ϕ with covariance X_τ ; the latter is a screened potential related to the Coulombic potential W_τ by the relation

$$\tilde{X}_\tau(q) = \frac{\tilde{W}_\tau(q)}{1 + \gamma \rho_0 \tilde{W}_\tau(q)}. \quad (2.4)$$

In the companion paper I, we have given a low-fugacity expansion of ω_{RPM} , here we rather consider the behavior of the grand potential at high temperatures and arbitrary chemical potential ν . In that aim we first reorganize the Sine-Gordon Hamiltonian $\mathcal{H}[\phi]$ as an expansion in the (small) parameter γ of Stell and Lebowitz.⁽¹⁶⁾ It is easily established from Eqs. (2.3) that

$$\mathcal{H}[\phi] = -\gamma \rho_0 L^3 / a + \sum_{N=2}^{\infty} \gamma^N W_N, \quad (2.5)$$

where

$$W_N = \sum_{n=1}^N I_N^{(n)}, \quad (2.6a)$$

$$I_N^{(n)} = -\frac{\rho_0^n}{n!} \int d^3 \vec{r}_1 \dots d^3 \vec{r}_n h_0^{(n)}(1, \dots, n) \sum^* \mathcal{F}^{(p_1)}(\phi_1) \dots \mathcal{F}^{(p_n)}(\phi_n), \quad (2.6b)$$

$$\mathcal{F}^{(p)}(\phi) = \sum_{s=0}^p \frac{(-1)^s}{(2s)!} \frac{a^{s-p}}{(p-s)!} \phi^{2s}. \quad (2.6c)$$

The summations in the r.h.s of Eq. (2.6b) are restricted to all the integers $p_i \geq 1$ ($i = 1, \dots, n$) such that $\sum_{i=1}^n p_i = N$, which was denoted by the symbol \sum^* . Later, we shall need explicit expressions of W_2 and W_3 ; they are given in Appendix B.

In order to obtain a γ -expansion of $\Delta\omega$ we first apply the cumulant theorem⁽²⁰⁾ to Eq. (2.1c) which leads to

$$\ln \langle \exp(-\mathcal{H}[\phi]) \rangle_{X_\tau} = \frac{\gamma \rho_0 L^3}{a} - \langle \mathcal{H}[\phi] \rangle_{X_{\tau,c}} + \frac{1}{2} \langle \mathcal{H}^2[\phi] \rangle_{X_{\tau,c}} + \dots, \quad (2.7)$$

and then re-order the terms in the r.h.s with the help of Eq. (2.5) which yields

$$L^3 \Delta \omega \equiv -\ln \langle \exp(-\mathcal{H}[\phi]) \rangle_{X_\tau} = -\frac{\gamma \rho_0 L^3}{a} + \gamma^2 \langle W_2 \rangle_{X_{\tau,c}} + \gamma^3 \langle W_3 \rangle_{X_{\tau,c}} + \gamma^4 \left(\langle W_4 \rangle_{X_{\tau,c}} - \frac{1}{2} \langle W_2^2 \rangle_{X_{\tau,c}} \right) + \dots \quad (2.8)$$

Note that the subscript ‘‘c’’ in Eqs. (2.7), (2.8) denotes a cumulant average, for instance we have $\langle W_N \rangle_{X_{\tau,c}} \equiv \langle W_N \rangle_{X_\tau}$ and $\langle W_N^2 \rangle_{X_{\tau,c}} \equiv \langle W_N^2 \rangle_{X_\tau} - \langle W_N \rangle_{X_\tau}^2$. Gathering Eqs. (2.1), (2.8) we can write finally

$$\omega_{RPM}(\beta, v) = \omega_{HS}(v_0) + \delta \omega_1 + \Delta \bar{\omega}, \quad (2.9a)$$

$$\delta \omega_1 = \omega_1 - \frac{\rho_0 \gamma}{a}, \quad (2.9b)$$

$$L^3 \Delta \bar{\omega} = \gamma^2 \langle W_2 \rangle_{X_{\tau,c}} + \gamma^3 \langle W_3 \rangle_{X_{\tau,c}} - \frac{\gamma^4}{2} \langle W_2^2 \rangle_{X_{\tau,c}} + \mathcal{O}(\gamma^4) \dots \quad (2.9c)$$

Eq. (2.9c) needs some comments. The first order cumulants $\langle W_N \rangle_{X_{\tau,c}}$ which enter the equation originate from the γ -ordering of $\langle \mathcal{H}[\phi] \rangle_{X_{\tau,c}}$ which is a regular function of γ in the limit $\gamma \rightarrow 0$. Indeed $\langle \mathcal{H}[\phi] \rangle_{X_{\tau,c}}$ is obtained by applying Wick’s theorem^(20–22) to Eq. (2.3) and, since in the limit $\gamma \rightarrow 0$ we have $X_\tau \rightarrow W_\tau$ the resulting expression of $\langle \mathcal{H}[\phi] \rangle_{X_{\tau,c}}$ will involve integrals of products of long-range Coulombic terms by the n -body correlations $h_0^{(n)}$ of the hard sphere reference fluid which are assumed to be short-ranged and make the integrals convergent. Therefore the first order cumulants $\langle W_N \rangle_{X_{\tau,c}}$ are regular in the limit $\gamma \rightarrow 0$ but it could be that some higher order cumulants are singular. For instance, it will be shown in Section IV that $\langle W_2^2 \rangle_{X_{\tau,c}}$ diverges as $\gamma^{-1/2}$ in the limit $\gamma \rightarrow 0$. In writing Eq. (2.9c) we have assumed that, at this order, higher order cumulants do not contribute to $\Delta \bar{\omega}$, which is, admittedly, difficult to prove rigorously.

We stress again that, although the variable ‘‘a’’ appears explicitly in Eqs. (2.9a) as well as in the expressions (2.6) of the W_N , the grand-potential ω_{RPM} does not depend upon ‘‘a’’, $\forall a \in]0, \sigma]$. Moreover, in a perturbation scheme such as the γ -ordering this independence should certainly be satisfied for each term of the expansion. We have checked this point up to order $\gamma^{5/2}$. This result, which is discussed in details in the next section, completes the results of paper I where we have checked that each term of the low activity expansion of ω_{RPM} was actually independent of a .

III. γ -EXPANSION OF $\omega_{RPM}(\beta, \nu)$ UP TO ORDER $\gamma^{5/2}$

Since, in Eq. (2.9a), $\omega_{HS}(\nu_0)$ does not depend upon the temperature, we are left with the problem of finding a γ -expansion of the terms $\delta\omega_1$ and $\Delta\bar{\omega}$ of Eq. (2.9a) up to order $\mathcal{O}(\gamma^{5/2})$. We have shown in I that, for a given a , ω_1 was a function of the sole parameter $(\rho_0\gamma)^{1/2}$; therefore the expansions of ω_1 in powers of $(\rho_0\gamma)^{1/2}$ given in I are valid either at low activities (or equivalently at low ρ_0) or at high temperatures (i.e. at low γ), which is the case that we consider here. Recall that (cf. Eq. (3.6) of I)

$$\delta\omega_1 = -\frac{2}{3\pi}(\pi\rho_0\gamma)^{3/2} + \frac{7}{15\pi}(\pi\rho_0\gamma)^2 a - \frac{1}{3\pi}(\pi\rho_0\gamma)^{5/2} a^2 + \mathcal{O}((\gamma a)^3). \quad (3.1)$$

Note that $\delta\omega_1$ is regular in the limit $a \rightarrow 0$ and that $\lim_{a \rightarrow 0} \delta\omega_1 = -2(\pi\rho_0\gamma)^{3/2}/3\pi$ which is reminiscent of the well-known Debye-Hückel result.^(23, 24)

On the other hand, up to order $\mathcal{O}(\gamma^{5/2})$ we have, from Eq. (2.9c)

$$L^3 \Delta\bar{\omega} = \gamma^2 \langle W_2 \rangle_{X_{\tau,c}} + \mathcal{O}(\gamma^3). \quad (3.2)$$

The expression of W_2 is given in Appendix B. Taking the Gaussian average of Eq. (B1a) one finds

$$\begin{aligned} \langle W_2 \rangle_{X_{\tau}} = & -\rho'_0 \frac{L^3}{2a^3} + \frac{\rho'_0}{2a} \int d^3\vec{r}_1 \langle \phi^2(1) \rangle_{X_{\tau}} - \frac{\rho_0}{4!} \int d^3\vec{r}_1 \langle \phi^4(1) \rangle_{X_{\tau}} \\ & - \frac{\rho_0^2}{8} \int d^3\vec{r}_1 d^3\vec{r}_2 h_0^{(2)}(1, 2) \langle \phi^2(1) \phi^2(2) \rangle_{X_{\tau}}, \end{aligned} \quad (3.3)$$

where ρ'_0 is the derivative of the number density of the hard sphere reference fluid ρ_0 with respect to the chemical potential ν_0 . The Gaussian averages which enter Eq. (3.3) are computed with the help of Wick's theorem (details are given in Appendix C). Inserting Eqs. (C1), (C2), (C5) in Eq. (3.3) yields

$$\gamma^2 \langle W_2 \rangle_{X_{\tau}} L^{-3} = \rho'_0 \gamma^2 \left(-\frac{1}{2a^2} + \frac{X_{\tau}(0)}{2a} - \frac{X_{\tau}^2(0)}{8} \right) - \frac{\gamma^2 \rho_0^2}{4} \int d^3\vec{r} h_0^{(2)}(r) X_{\tau}^2(r), \quad (3.4)$$

where $h_0^{(2)}(r_{12}) \equiv h_0^{(2)}(12)$ is the usual pair correlation function in the limit of an infinite homogeneous and isotropic system. Note that, in the core, i.e. for $0 \leq r \leq \sigma$, $h_0^{(2)}(r) = -1$. In order to derive Eq. (3.4) we have also made

use of the compressibility sum rule for the reference hard sphere fluid,⁽²⁴⁾ i.e.

$$\rho_0^2 \tilde{h}_0^{(2)}(0) = \rho'_0 - \rho_0, \quad (3.5)$$

where $\tilde{h}_0^{(2)}(q)$ is the 3D Fourier transform of $h_0^{(2)}(r)$. We note that the screened potential $X_\tau(r)$ is a function which depends on the smearing diameter a and therefore, *a priori*, $\langle W_2 \rangle_{X_\tau}$ as given by Eq. (3.4) depends upon a in a complicated manner. It is this dependence that we want to study in detail now.

We have shown in the companion paper that, for a given smearing diameter a , the screened potential $X_\tau(r)$ was a function of the sole variable

$$\kappa_0 \equiv 2(\pi\rho_0\gamma)^{1/2}. \quad (3.6)$$

Note that κ_0 is not, strictly speaking, the inverse Debye length of the system since it involves the density ρ_0 of the reference system which is not equal, *a priori*, to the density ρ of the RPM. We have shown that, for $r=0$ (cf. Eq. (3.8) of I)

$$X_\tau(0) = \frac{2}{a} - 2(\pi\rho_0\gamma)^{1/2} + \frac{28}{15}(\pi\rho_0\gamma) a - \frac{5}{3}(\pi\rho_0\gamma)^{3/2} a^2 + \mathcal{O}(\gamma^2 a^3), \quad (3.7)$$

from which it follows that the first term of the r.h.s. of Eq. (3.4) is regular as $a \rightarrow 0$ and reads as

$$\rho'_0 \gamma^2 \left(-\frac{1}{2a^2} + \frac{X_\tau(0)}{2a} - \frac{X_\tau^2(0)}{8} \right) = -\frac{1}{2} \pi\rho_0 \rho'_0 \gamma^3 + \mathcal{O}(\gamma^{7/2} a). \quad (3.8)$$

For $r \neq 0$, $X_\tau(r)$ is a piecewise function defined as :

$$X_\tau^>(r) = q^2(\kappa_0 a/2) \frac{\exp(-\kappa_0 r)}{r} + \mathcal{O}(\gamma a) \quad \text{for } r \geq a, \quad (3.9a)$$

$$X_\tau^<(r) = \frac{2}{a} \left(1 - \frac{r}{2a} \right) - \kappa_0 + \mathcal{O}(\gamma a) \quad \text{for } r \leq a, \quad (3.9b)$$

where $q(x) \equiv \sinh(x/2)/(x/2)$. Note by passing that Eqs. (3.9) imply that

$$\lim_{a \rightarrow 0} X_\tau(r) \equiv y(r) = \exp(-\kappa_0 r)/r \quad \forall r. \quad (3.10)$$

Inserting the expressions (3.9) of $X_\tau(r)$ in the integral of the r.h.s. of Eq. (3.4) and noting that $h_0^{(2)}(r) = -1$ for $0 \leq r \leq a \leq \sigma$ yields

$$-\frac{\rho_0^2 \gamma^2}{4} \int d^3\vec{r} h_0^{(2)}(r) X_\tau^2(r) = -\frac{\rho_0^2 \gamma^2}{4} \int d^3\vec{r} h_0^{(2)}(r) X_\tau^{>2}(r) - \frac{7}{15\pi} (\pi\rho_0\gamma)^2 a + \frac{1}{3\pi} (\pi\rho_0\gamma)^{5/2} a^2 + \mathcal{O}((\gamma a)^3), \quad (3.11)$$

where the terms proportional to a and a^2 in the r.h.s. of Eq. (3.11) originate from the integration of $X_\tau^{<2}(r) - X_\tau^{>2}(r)$ in the core (where $h_0^{(2)}(r) = -1$). Moreover, note that, in Eq. (3.11) we can safely expand $X_\tau^{>2}(r)$ in powers of κ_0 since $h_0^{(2)}$ is a short range function of r . Performing this expansion and gathering Eqs. (3.1), (3.8) and (3.11) we obtain finally, at order $\gamma^{5/2}$

$$\omega_{RPM}(\beta, \nu) = \omega_{HS}(\nu_0) - \frac{2}{3\pi} (\pi\rho_0\gamma)^{3/2} - \frac{(\rho_0\gamma)^2}{4} \int d^3\vec{r} \frac{h_0^{(2)}(r)}{r^2} + \pi^{1/2} (\rho_0\gamma)^{5/2} \int d^3\vec{r} \frac{h_0^{(2)}(r)}{r} + \mathcal{O}(\gamma^3). \quad (3.12)$$

Due to a complex mechanism of compensations, the expression (3.12) of the grand potential at order $\gamma^{5/2}$ is, as anticipated, indeed independent of the value of the smearing diameter a .

IV. γ -EXPANSION OF THE GRAND POTENTIAL AND THE FREE ENERGY UP TO ORDER $\gamma^{7/2}$

In this section we obtain the expansion of $\omega_{RPM}(\beta, \nu)$ up to order $\gamma^{7/2}$. In order to make the derivations more tractable, we shall assume that the terms of order greater than $\gamma^{5/2}$ in the γ -expansion of $\omega_{RPM}(\beta, \nu)$ are still independent of a . Moreover we shall consider the limit $a \rightarrow 0$ of Eq. (2.9a) which allows us to replace $X_\tau(r)$ by its limiting expression $y(r) \equiv \exp(-\kappa_0 r)/r$ and greatly facilitates the derivations. Therefore one has

$$\omega_{RPM}(\beta, \nu) = \lim_{a \rightarrow 0} (\omega_{HS}(\nu_0) + \delta\omega_1 + \Delta\bar{\omega}), \quad (4.1a)$$

$$L^3 \Delta\bar{\omega} = \gamma^2 \langle W_2 \rangle_{X_{\tau,c}} + \gamma^3 \langle W_3 \rangle_{X_{\tau,c}} - \frac{\gamma^4}{2} \langle W_2^2 \rangle_{X_{\tau,c}} + \mathcal{O}(\gamma^4). \quad (4.1b)$$

The limit of $\delta\omega_1$ for $a \rightarrow 0$ is easily obtained from Eq. (3.1) and reads as

$$\lim_{a \rightarrow 0} \delta\omega_1 = -\frac{\kappa_0^3}{12\pi} = -\frac{2}{3\pi} (\pi\rho_0\gamma)^{3/2}. \quad (4.2)$$

The expression of the term $\langle W_2 \rangle_{X_{\tau,c}}$ in the r.h.s of Eq. (4.1b) has already been derived in Section III. We take the limit $a \rightarrow 0$ of Eq. (3.4) which gives

$$\begin{aligned} \lim_{a \rightarrow 0} \gamma^2 \langle W_2 \rangle_{X_{\tau,c}} L^{-3} &= -\frac{\pi \rho_0 \rho'_0 \gamma^3}{2} - \frac{\gamma^2 \rho_0^2}{4} \int d^3 \vec{r} h_0^{(2)}(r) \frac{\exp(-2\kappa_0 r)}{r^2}, \\ &= -\frac{\rho_0^2 \gamma^2}{4} \int d^3 \vec{r} h_0^{(2)}(r) \frac{1}{r^2} + \pi^{1/2} (\rho_0 \gamma)^{5/2} \int d^3 \vec{r} h_0^{(2)}(r) \frac{1}{r} \\ &\quad + \pi \rho_0 \gamma^3 \left(2\rho_0 - \frac{5}{2} \rho'_0 \right) \\ &\quad + \frac{8\pi^{3/2}}{3} (\rho_0 \gamma)^{7/2} \int d^3 \vec{r} h_0^{(2)}(r) r + \mathcal{O}(\gamma^4), \end{aligned} \quad (4.3)$$

where we have expanded the Yukawa potential in powers of κ_0 , taking advantage of the assumed short-range behaviour of $h_0^{(2)}(r)$ and also made use of the compressibility sum rule (3.5).

The expression of W_3 is given in Appendix B. Taking the Gaussian average of Eq. (B1b) and then making use of Wick's theorem and of the relation (A3b) of Appendix A yields

$$\begin{aligned} \langle W_3 \rangle_{X_{\tau,c}} L^{-3} &= w_3(a) + \int d^3 \vec{r} X_{\tau}^2(r) \frac{\partial}{\partial v_0} (\rho_0^2 h_0^{(2)}(r)) \left(-\frac{1}{4a} + \frac{X_{\tau}(0)}{8} \right), \\ &\quad + \frac{\rho_0^3}{6} \int d^3 \vec{r}_2 d^3 \vec{r}_3 h_0^{(3)}(1, 2, 3) X_{\tau}(1, 2) X_{\tau}(1, 3) X_{\tau}(2, 3) \\ \lim_{a \rightarrow 0} w_3(a) &= -\frac{\rho_0'' \kappa_0^3}{48}. \end{aligned} \quad (4.4)$$

We take now the limit $a \rightarrow 0$ of Eq. (4.4) and expand the resulting expansion in powers of κ_0 which gives

$$\begin{aligned} \lim_{a \rightarrow 0} \gamma^3 \langle W_3 \rangle_{X_{\tau,c}} L^{-3} &= \frac{(\rho_0 \gamma)^3}{6} \int d^3 \vec{r}_2 d^3 \vec{r}_3 \frac{h_0^{(3)}(1, 2, 3)}{r_{12} r_{13} r_{23}} \\ &\quad - \frac{\pi^{1/2} \rho_0^{1/2} \gamma^{7/2}}{4} \int d^3 \vec{r} \frac{\partial}{\partial v_0} (\rho_0^2 h_0^{(2)}(r)) \frac{1}{r^2} \\ &\quad - \pi^{1/2} (\rho_0 \gamma)^{7/2} \int d^3 \vec{r}_2 d^3 \vec{r}_3 \frac{h_0^{(3)}(1, 2, 3)}{r_{12} r_{23}} + \mathcal{O}(\gamma^4). \end{aligned} \quad (4.5)$$

Note that both cumulants $\langle W_2 \rangle_{X_{\tau}}$ and $\langle W_3 \rangle_{X_{\tau}}$ are regular in the limit $\gamma \rightarrow 0$ which confirms the analysis made at the end of Section II.

The analysis of the limit $a \rightarrow 0$ of the last contribution $-\gamma^4 \langle W_2^2 \rangle_{X_{\tau,c}} / (2L^3)$ of the r.h.s of Eq. (4.1b) is more delicate and postponed to Appendix D. One finds that this term can be written as

$$\lim_{a \rightarrow 0} \gamma^4 L^{-3} \langle W_2^2 \rangle_{X_{\tau,c}} = \frac{(\rho_0 \gamma)^{7/2}}{4\pi^{1/2}} \lim_{\kappa_0 \rightarrow 0} \int d^3 \vec{r}_2 d^3 \vec{r}_3 d^3 \vec{r}_4 h_0^{(2)}(1, 2) h_0^{(2)}(3, 4) \times \frac{\kappa_0 \exp(-\kappa_0(r_{12} + r_{23} + r_{34} + r_{41}))}{r_{12} r_{23} r_{34} r_{41}} + \mathcal{O}(\gamma^4). \quad (4.6)$$

By contrast with $\langle W_2 \rangle_{X_{\tau}}$ and $\langle W_3 \rangle_{X_{\tau}}$ the cumulant $\langle W_2^2 \rangle_{X_{\tau,c}}$ is singular as $\gamma^{-1/2}$ in the limit $\gamma \rightarrow 0$. It is of course very difficult to give a precise analysis of the singularities of higher order cumulants.

Gathering the intermediate results we get our final expression for the grand potential of the primitive model up to order $\mathcal{O}(\gamma^{7/2})$.

$$\omega_{RPM}(\beta, v) = \omega_{HS}(v_0) + \Delta\omega(\beta, v) + \mathcal{O}(\gamma^4), \quad (4.7a)$$

$$\Delta\omega(\beta, v) = \sum_{i=1}^9 \omega^{(i)}, \quad (4.7b)$$

$$\omega^{(1)} = -\frac{2}{3\pi} (\pi\rho_0\gamma)^{3/2}, \quad (4.7c)$$

$$\omega^{(2)} = -\frac{\rho_0^2 \gamma^2}{4} \int d^3 \vec{r} \frac{h_0^{(2)}(r)}{r^2}, \quad (4.7d)$$

$$\omega^{(3)} = \pi^{1/2} (\rho_0 \gamma)^{5/2} \int d^3 \vec{r} \frac{h_0^{(2)}(r)}{r}, \quad (4.7e)$$

$$\omega^{(4)} = \pi\rho_0 \left(2\rho_0 - \frac{5}{2} \rho'_0 \right) \gamma^3, \quad (4.7f)$$

$$\omega^{(5)} = \frac{(\rho_0 \gamma)^3}{6} \int d^3 \vec{r}_2 d^3 \vec{r}_3 \frac{h_0^{(3)}(1, 2, 3)}{r_{12} r_{13} r_{23}}, \quad (4.7g)$$

$$\omega^{(6)} = \frac{8}{3} \pi^{3/2} (\rho_0 \gamma)^{7/2} \int d^3 \vec{r} h_0^{(2)}(r) r, \quad (4.7h)$$

$$\omega^{(7)} = -\frac{(\pi\rho_0)^{1/2}}{4} \gamma^{7/2} \int d^3 \vec{r} \frac{\partial}{\partial v_0} (\rho_0^2 h_0^{(2)}(r)) \frac{1}{r^2}, \quad (4.7i)$$

$$\omega^{(8)} = -\pi^{1/2}(\rho_0\gamma)^{7/2} \int d^3\vec{r}_2 d^3\vec{r}_3 \frac{h_0^{(3)}(1, 2, 3)}{r_{12}r_{23}}, \quad (4.7j)$$

$$\begin{aligned} \omega^{(9)} = & -\frac{(\rho_0\gamma)^{7/2}}{8\pi^{1/2}} \lim_{\kappa_0 \rightarrow 0} \int d^3\vec{r}_2 d^3\vec{r}_3 d^3\vec{r}_4 h_0^{(2)}(1, 2) h_0^{(2)}(3, 4) \\ & \times \frac{\kappa_0 \exp(-\kappa_0(r_{12} + r_{23} + r_{34} + r_{41}))}{r_{12}r_{23}r_{34}r_{41}}, \end{aligned} \quad (4.7k)$$

where we have made a change of notation and redefined $\Delta\omega$. The free energy $f_{RPM}(\beta, \rho)$ is defined as the Legendre transform of $\omega_{RPM}(\beta, \nu)$ with respect to the chemical potential. ⁽²⁴⁾ i.e.

$$f_{RPM}(\beta, \rho) = \omega_{RPM}(\beta, \nu) + \rho(\beta, \nu) \nu, \quad (4.8)$$

where $\rho(\beta, \nu)$ is the density of the RPM which can be obtained by differentiating $-\omega_{RPM}$ as given by Eq. (4.7a) with respect to ν_0 . Therefore we have

$$\begin{aligned} \rho &= -\frac{\partial \omega_{RPM}}{\partial \nu_0} = \rho_0 + \Delta\rho, \\ \Delta\rho &= \pi^{1/2} \rho_0^{1/2} \rho_0' \gamma^{3/2} + \frac{\gamma^2}{4} \int d^3\vec{r} \frac{\partial}{\partial \nu_0} (\rho_0^2 h_0^{(2)}(r)) \frac{1}{r^2} + \mathcal{O}(\gamma^{5/2}). \end{aligned} \quad (4.9)$$

It should become clear in the sequel that an expansion of $\Delta\rho$ to order $\gamma^{5/2}$ is sufficient for our purpose. Let us denote by

$$\nu^* = \nu_0 + \Delta\nu, \quad (4.10)$$

the chemical potential of a fluid of hard spheres at the density ρ . Eq. (4.9) suggests that we search $\Delta\nu$ under the form

$$\Delta\nu = \nu_{3/2} \gamma^{3/2} + \nu_2 \gamma^2 + \mathcal{O}(\gamma^{5/2}), \quad (4.11)$$

In order to find the expressions of $\nu_{3/2}$ and ν_2 we note that, by definition of $\Delta\nu$ one has

$$\begin{aligned} \rho &= \rho_{HS}(\nu_0 + \Delta\nu) \\ &= \rho_0 + (\nu_{3/2} \gamma^{3/2} + \nu_2 \gamma^2) \rho_0' + \mathcal{O}(\gamma^{5/2}). \end{aligned} \quad (4.12)$$

Comparison of Eqs. (4.9) and (4.12) yields, by identification

$$v_{3/2} = \pi^{1/2} \rho_0^{1/2}, \quad (4.13a)$$

$$v_2 = \frac{1}{4\rho'_0} \int d^3\vec{r} \frac{\partial}{\partial v_0} (\rho_0^2 h_0^{(2)}(r)) \frac{1}{r^2}. \quad (4.13b)$$

We have now in hand all the ingredients to compute the free energy. Making use of Eqs. (4.9), (4.10) and (4.11) one finds, at order $\gamma^{7/2}$

$$\begin{aligned} f_{RPM}(\beta, \rho) &= \omega_{RPM}(\beta, v) + \rho v \\ &= \omega_{HS}(v^* - \Delta v) + \rho v + \Delta \omega \\ &= \omega_{HS}(v^*) + \rho \Delta v - \frac{1}{2} \rho'_0 (\Delta v)^2 + \rho v + \Delta \omega + \mathcal{O}(\gamma^4) \\ &= f_{HS}(\rho) + f^{(1)} + f^{(2)} + \Delta \omega + \mathcal{O}(\gamma^4), \end{aligned} \quad (4.14)$$

where $f_{HS}(\rho) \equiv \omega_{HS}(v^*) + \rho(v^* - \log 2)$ is the free energy of the reference hard sphere fluid at the same density ρ than that of the RPM (note that the free energy of the reference fluid and that of a fluid of identical hard spheres differ by a mixing entropy term) and

$$f^{(1)} = -\frac{1}{2} \rho'_0 v_{3/2}^2 \gamma^3 \quad (4.15a)$$

$$f^{(2)} = -\rho'_0 v_2 v_{3/2} \gamma^{7/2} \quad (4.15b)$$

In order to obtain a more transparent expression of f_{RPM} we first remark that

$$\omega^{(2)} + f^{(2)} = -\frac{\gamma^2}{4} \int d^3\vec{r} \frac{1}{r^2} \left[\rho_0^2 h_0^{(2)}(r) + \pi^{1/2} \rho_0^{1/2} \gamma^{3/2} \frac{\partial}{\partial v_0} (\rho_0^2 h_0^{(2)}(r)) \right], \quad (4.16)$$

and that the term in brackets in the integral can be interpreted as a Taylor expansion of the function $\rho_0^2 h_0^{(2)}(r)$. Since, from Eq. (4.11) $\Delta v = \pi^{1/2} \rho_0^{1/2} \gamma^{3/2} + \mathcal{O}(\gamma^2)$, we can rewrite (4.16) as

$$\omega^{(2)} + f^{(2)} = -\frac{\gamma^2 \rho^2}{4} \int d^3\vec{r} \frac{h^{*(2)}(r)}{r^2} + \mathcal{O}(\gamma^4), \quad (4.17)$$

where we have denoted by $h^{*(2)}(r)$ the pair correlation function of the hard spheres at the density ρ (i.e., that of the RPM).

Our second remark is that the combination of several terms occurring in Eq. (4.14) give the usual Debye–Hückel free energy $-\kappa^3/12\pi$. Here

$\kappa \equiv 2(\pi\rho\gamma)^{1/2}$ is the *true* Debye length of the RPM which differs from κ_0 by terms of order $\gamma^{3/2}$. Indeed one has

$$\begin{aligned} -\frac{\kappa^3}{12\pi} &\equiv -\frac{2}{3}\pi^{1/2}\rho^{3/2}\gamma^{3/2} \\ &= -\frac{2}{3}\pi^{1/2}\gamma^{3/2}\rho_0^{3/2}\left(1+\frac{\Delta\rho}{\rho_0}\right)^{3/2} \\ &= -\frac{2}{3}\pi^{1/2}\rho_0^{3/2}\gamma^{3/2}-\pi^{1/2}\rho_0^{1/2}\Delta\rho\gamma^{3/2}+\mathcal{O}(\gamma^4) \\ &= \omega^{(1)}-\pi\rho_0\rho_0'\gamma^3-\frac{(\pi\rho_0)^{1/2}\gamma^{7/2}}{4}\int d^3\vec{r}\frac{\partial}{\partial v_0}(\rho_0 h_0^{(2)}(r))\frac{1}{r^2}+\mathcal{O}(\gamma^4), \quad (4.18) \end{aligned}$$

By combining Eq. (4.18) and the expressions of ω_1 , ω_4 , ω_7 one finds

$$\begin{aligned} \omega^{(1)}+\omega^{(4)}+\omega^{(7)}+f^{(1)} &= -\frac{\kappa^3}{12\pi}+2\pi\rho_0(\rho_0-\rho_0')\gamma^3+\mathcal{O}(\gamma^4) \\ &= -\frac{\kappa^3}{12\pi}+2\pi\rho(\rho-\rho')\gamma^3+\mathcal{O}(\gamma^4) \\ &= -\frac{\kappa^3}{12\pi}-2\pi\rho^3\gamma^3\int d^3\vec{r}h^{*(2)}(r)+\mathcal{O}(\gamma^4), \quad (4.19) \end{aligned}$$

where the last line follows from the compressibility sum rule (3.5) and where we have noted that ρ' as well as ρ differ of respectively ρ_0' and ρ_0 by terms of order $\gamma^{5/2}$. The Legendre transform of ω_{RPM} is achieved by combining Eqs. (4.17), (4.19) and by noting that the correlation functions $h_0^{(n)}$ which enter terms of order $\gamma^{5/2}$ or higher can safely be replaced by the $h^{*(n)}$ since these functions differ by terms of order $\gamma^{3/2}$. Our final result for f_{RPM} is therefore

$$\begin{aligned} f_{RPM}(\beta, \rho) &= f_{HS}(\rho)-\frac{\kappa^3}{12\pi}-\frac{(\rho\gamma)^2}{4}\int d^3\vec{r}\frac{h^{*(2)}(r)}{r^2}+\pi^{1/2}(\rho\gamma)^{5/2}\int d^3\vec{r}\frac{h^{*(2)}(r)}{r} \\ &\quad -2\pi(\rho\gamma)^3\int d^3\vec{r}h^{*(2)}(r)+\frac{(\rho\gamma)^3}{6}\int d^3\vec{r}_2d^3\vec{r}_3\frac{h^{*(3)}(1, 2, 3)}{r_{12}r_{23}r_{31}} \\ &\quad +\frac{8}{3}\pi^{3/2}(\rho\gamma)^{7/2}\int d^3\vec{r}rh^{*(2)}(r)-\pi^{1/2}(\rho\gamma)^{7/2}\int d^3\vec{r}_2d^3\vec{r}_3\frac{h^{*(3)}(1, 2, 3)}{r_{12}r_{23}} \\ &\quad -\frac{\pi^{-1/2}}{8}(\rho\gamma)^{7/2}\lim_{\kappa\rightarrow 0}\int d^3\vec{r}_2d^3\vec{r}_3d^3\vec{r}_4h^{*(2)}(r_{12})h^{*(2)}(r_{34}) \\ &\quad \times\frac{\kappa\exp-\kappa(r_{12}+r_{23}+r_{34}+r_{41})}{r_{12}r_{23}r_{34}r_{41}}+\mathcal{O}(\gamma^4). \quad (4.20) \end{aligned}$$

Some comments are in order.

- (i) The expression (4.20) coincides with that derived by Stell and Lebowitz by means of diagrammatic expansions in the frame of the γ -ordering theory.⁽¹⁶⁻¹⁹⁾

- (ii) We have shown that (at least at order $\gamma^{5/2}$ and we are inclined to admit this result at any orders) the expansion (4.20) is independent of the smearing diameter a . Therefore the choice $a \rightarrow 0$ could have been made from the beginning, which extends the validity of (4.20) to other reference potentials than hard core repulsions (Lennard-Jones potentials for instance).

V. CONCLUSION

In this paper we have derived the γ -expansions of the grand-potential and free energies of the RPM in the frame work of the exact field theoretical formalism exposed in the companion paper.⁽¹⁾ In I we had obtained an activity expansion of the same quantities. In both cases of either high temperatures (and arbitrary densities) or low fugacities (and arbitrary temperatures) the perturbative expansions are obtained by a cumulant expansion of the exact Sine-Gordon representation of the grand partition function Ξ_{RPM} derived in the first paper. Of course one recovers in both cases expressions derived years ago by means of sophisticated diagrammatic expansions involving more or less complicated resummations of infinite series of graphs.^(12, 13, 16) The field theoretical representation of the grand partition function of a theoretically important model such as the RPM (of course other models can be considered too) can therefore be used to recover most of the results obtained in the past by more traditional methods of classical statistical mechanics. However we have now at our disposal approximation schemes such that the saddle point approximation, the loop expansions etc. which have no real counterparts in the conventional theory of liquids. Concerning the RPM, a mean field sine-Gordon approximation of Ξ_{RPM} is perhaps the correct starting point for a full understanding of ionic criticality wanted by M. E. Fisher.⁽²⁵⁾ Work in that direction is currently in progress and will be reported elsewhere.

APPENDIX A: THE HIERARCHY OF URSELL FUNCTIONS

Let us consider a classical fluid at inverse temperature β , chemical potential μ in an external potential $\varphi(\vec{r})$. We denote by $\Xi[\varphi]$ the grand partition function and by $z(\vec{r}) = \exp(-\beta\varphi(\vec{r}) + v)/\lambda^3$ the activity ($v \equiv \beta\mu$ and

$\lambda \equiv$ de Broglie thermal wavelength). In the absence of the external field φ , the n -body Ursell (or connected) correlation functions are defined as^(15, 24)

$$\rho_c^{(n)}(1, \dots, n) = \prod_{i=1}^n z(i) \frac{\delta^{(n)} \ln \Xi[\varphi]}{\prod_{i=1}^n \delta z(i)} \Big|_{\varphi=0}. \quad (\text{A1})$$

It can be shown⁽¹⁵⁾ that the $\rho_c^{(n)}(1, \dots, n)$ obey the following hierarchy:

$$\frac{\partial \rho_c^{(n)}(1, \dots, n)}{\partial v} = \int d^3 \vec{r}_{n+1} \rho_c^{(n+1)}(1, \dots, n+1) + n \rho_c^{(n)}(1, \dots, n). \quad (\text{A2})$$

Defining now the correlation functions $h^{(n)}(1, \dots, n) \equiv \rho_c^{(n)}(1, \dots, n) / \rho^n$ we deduce from Eq. (A2) important relations which are repeatedly used in the text, i.e.

$$\rho^2 \tilde{h}^{(2)}(0) = (\partial \rho / \partial v) - \rho, \quad (\text{A3a})$$

$$\rho^3 \int d^3 \vec{r}_3 h^{(3)}(1, 2, 3) = \frac{\partial}{\partial v} (\rho^2 h^{(2)}(1, 2)) - 2\rho^2 h^{(2)}(1, 2), \quad (\text{A3b})$$

$$\rho^3 \int d^3 \vec{r}_2 d^3 \vec{r}_3 h^{(3)}(1, 2, 3) = (\partial^2 \rho / \partial v^2) - 3(\partial \rho / \partial v) + 2\rho. \quad (\text{A3c})$$

APPENDIX B: EXPRESSION OF THE W_N S

The expressions of W_2 and W_3 which are needed in the text are obtained from Eqs. (2.6). The resulting expressions are further simplified by the use of the relations (A3) of Appendix A. After some elementary algebra one finds

$$\begin{aligned} W_2 = & -\rho'_0 \frac{L^3}{2a^2} + \frac{\rho'_0}{2a} \int d^3 \vec{r}_1 \phi^2(1) - \frac{\rho_0}{4!} \int d^3 \vec{r}_1 \phi^4(1) \\ & - \frac{\rho_0^2}{8} \int d^3 \vec{r}_1 d^3 \vec{r}_2 h_0^{(2)}(1, 2) \phi^2(1) \phi^2(2), \end{aligned} \quad (\text{B1a})$$

$$\begin{aligned} W_3 = & -\rho''_0 \frac{L^3}{6a^3} + \frac{\rho''_0}{4a^2} \int d^3 \vec{r}_1 \phi^2(1) - \frac{\rho'_0}{4!a} \int d^3 \vec{r}_1 \phi^4(1) + \frac{\rho_0}{6!} \int d^3 \vec{r}_1 \phi^6(1) \\ & - \frac{1}{8a} \int d^3 \vec{r}_1 d^3 \vec{r}_2 \frac{\partial}{\partial v_0} (\rho_0^2 h_0^{(2)}(1, 2)) \phi^2(1) \phi^2(2) \\ & + \frac{\rho_0^2}{48} \int d^3 \vec{r}_1 d^3 \vec{r}_2 h_0^{(2)}(1, 2) \phi^2(1) \phi^4(2) \\ & + \frac{\rho_0^3}{48} \int d^3 \vec{r}_1 d^3 \vec{r}_2 d^3 \vec{r}_3 h_0^{(3)}(1, 2, 3) \phi^2(1) \phi^2(2) \phi^2(3), \end{aligned} \quad (\text{B1b})$$

where ρ'_0 and ρ''_0 denote respectively the first and second derivatives of the density of the reference hard sphere fluid with respect to the chemical potential v_0 .

APPENDIX C: WICK'S THEOREM

We collect in this Appendix the averages $\langle \dots \rangle_{X_\tau}$ of the monomials of ϕ which are needed in the text. The following results have been obtained by making use of Wick's theorem.⁽²⁰⁻²¹⁾

$$\langle \phi(1)^2 \rangle_{X_\tau} = X_\tau(0) \quad (C1)$$

$$\langle \phi(1)^4 \rangle_{X_\tau} = 3X_\tau^2(0) \quad (C2)$$

$$\langle \phi(1)^6 \rangle_{X_\tau} = 15X_\tau^3(0) \quad (C3)$$

$$\langle \phi(1)^8 \rangle_{X_\tau} = 105X_\tau^4(0) \quad (C4)$$

$$\langle \phi(1)^2 \phi(2)^2 \rangle_{X_\tau} = 2X_\tau^2(12) + X_\tau^2(0) \quad (C5)$$

$$\langle \phi(1)^2 \phi(2)^4 \rangle_{X_\tau} = 12X_\tau^2(12) X_\tau(0) + 3X_\tau^3(0) \quad (C6)$$

$$\langle \phi(1)^4 \phi(2)^4 \rangle_{X_\tau} = 24X_\tau^4(12) + 72X_\tau^2(12) X_\tau^2(0) + 9X_\tau^4(0) \quad (C7)$$

$$\begin{aligned} \langle \phi(1)^2 \phi(2)^2 \phi(3)^2 \rangle_{X_\tau} &= X_\tau^3(0) + 8X_\tau(12) X_\tau(23) X_\tau(13) \\ &\quad + 2X_\tau(0)[X_\tau^2(12) + X_\tau^2(23) + X_\tau^2(13)] \end{aligned} \quad (C8)$$

$$\begin{aligned} \langle \phi(1)^4 \phi(2)^2 \phi(3)^2 \rangle_{X_\tau} &= 3X_\tau^4(0) + 48X_\tau(12) X_\tau(23) X_\tau(13) X_\tau(0) \\ &\quad + 24X_\tau^2(12) X_\tau^2(13) \\ &\quad + 12X_\tau^2(0)[X_\tau^2(12) + X_\tau^2(13)] + 6X_\tau^2(23) X_\tau^2(0) \end{aligned} \quad (C9)$$

$$\begin{aligned} \langle \phi(1)^2 \phi(2)^2 \phi(3)^2 \phi(4)^2 \rangle_{X_\tau} &= X_\tau^4(0) + 2X_\tau^2(0)[X_\tau^2(12) + X_\tau^2(13) + X_\tau^2(14) \\ &\quad + X_\tau^2(23) + X_\tau^2(24) + X_\tau^2(34)] \\ &\quad + 8X_\tau(0)[X_\tau(12) X_\tau(23) X_\tau(31) \\ &\quad + X_\tau(12) X_\tau(24) X_\tau(41) \\ &\quad + X_\tau(13) X_\tau(34) X_\tau(41) + X_\tau(23) X_\tau(34) X_\tau(42)] \\ &\quad + 4[X_\tau^2(12) X_\tau^2(34) + X_\tau^2(13) X_\tau^2(24) \\ &\quad + X_\tau^2(14) X_\tau^2(23)] \\ &\quad + 16[X_\tau(12) X_\tau(23) X_\tau(34) X_\tau(41) \\ &\quad + X_\tau(12) X_\tau(24) X_\tau(43) X_\tau(31) + \\ &\quad + X_\tau(13) X_\tau(32) X_\tau(24) X_\tau(41)] \end{aligned} \quad (C10)$$

APPENDIX D: COMPUTATION OF $\langle W_2^2 \rangle_{X_\tau, c}$

The cumulant $\langle W_2^2 \rangle_{X_\tau, c}$ is easily obtained from (B1a) and reads

$$\langle W_2^2 \rangle_{X_\tau, c} = \sum_{i=1}^6 X^i, \quad (\text{D1a})$$

$$X^1 = \frac{\rho_0^2}{4a^2} \int d^3\vec{r}_1 d^3\vec{r}_2 (\langle \phi^2(1) \phi^2(2) \rangle_{X_\tau} - \langle \phi^2(1) \rangle_{X_\tau} \langle \phi^2(2) \rangle_{X_\tau}), \quad (\text{D1b})$$

$$X^2 = \frac{\rho_0^2}{(4!)^2} \int d^3\vec{r}_1 d^3\vec{r}_2 (\langle \phi^4(1) \phi^4(2) \rangle_{X_\tau} - \langle \phi^4(1) \rangle_{X_\tau} \langle \phi^4(2) \rangle_{X_\tau}), \quad (\text{D1c})$$

$$X^3 = \frac{\rho_0^4}{64} \int d^3\vec{r}_1 d^3\vec{r}_2 d^3\vec{r}_3 d^3\vec{r}_4 h_0^{(2)}(1, 2) h_0^{(2)}(3, 4) (\langle \phi^2(1) \phi^2(2) \phi^2(3) \phi^2(4) \rangle_{X_\tau} - \langle \phi^2(1) \phi^2(2) \rangle_{X_\tau} \langle \phi^2(3) \phi^2(4) \rangle_{X_\tau}),$$

$$X^4 = -\frac{\rho_0 \rho_0'}{4!a} \int d^3\vec{r}_1 d^3\vec{r}_2 (\langle \phi^2(1) \phi^4(2) \rangle_{X_\tau} - \langle \phi^2(1) \rangle_{X_\tau} \langle \phi^4(2) \rangle_{X_\tau}), \quad (\text{D1d})$$

$$X^5 = -\frac{\rho_0' \rho_0^2}{8a} \int d^3\vec{r}_1 d^3\vec{r}_2 d^3\vec{r}_3 h_0^{(2)}(2, 3) (\langle \phi^2(1) \phi^2(2) \phi^2(3) \rangle_{X_\tau} - \langle \phi^2(1) \rangle_{X_\tau} \langle \phi^2(2) \phi^2(3) \rangle_{X_\tau}) \quad (\text{D1e})$$

$$X^6 = \frac{\rho_0^3}{4 \times 4!} \int d^3\vec{r}_1 d^3\vec{r}_2 d^3\vec{r}_3 h_0^{(2)}(2, 3) (\langle \phi^4(1) \phi^2(2) \phi^2(3) \rangle_{X_\tau} - \langle \phi^4(1) \rangle_{X_\tau} \langle \phi^2(2) \phi^2(3) \rangle_{X_\tau}). \quad (\text{D1f})$$

Each of the X^i are now computed by making use of Wick's theorem. It follows from (C1) and (C5) that

$$L^{-3} X^1 = \frac{\rho_0^2}{2a^2} I^{(2)}, \quad (\text{D2})$$

where

$$I^{(2)} = \int d^3\vec{r} X_\tau^2(r). \quad (\text{D3})$$

Similarly, making use of Eq. (C2) and (C7) one finds for X^2

$$L^{-3} X^2 = \frac{\rho_0^2 X_\tau^2(0)}{8} I^{(2)} + \frac{\rho_0^2}{24} I^{(4)}, \quad (\text{D4})$$

with

$$I^{(4)} = \int d^3\vec{r} X_{\tau}^4(r). \quad (\text{D5})$$

The term X^3 is considerably more complicated. It follows from Eqs. (C5) and (C10) that it can be splitted into four pieces

$$X^3 = X^{3(a)} + X^{3(b)} + X^{3(c)} + X^{3(d)} \quad (\text{D6})$$

We have defined $X^{3(a)}$ as

$$\begin{aligned} X^{3(a)} &= \frac{\rho_0^4 X_{\tau}^2(0)}{8} \int d^3\vec{r}_1 d^3\vec{r}_2 d^3\vec{r}_3 d^3\vec{r}_4 h_0^{(2)}(1, 2) h_0^{(2)}(3, 4) X_{\tau}^2(1, 3) \\ &= \frac{\rho_0^4}{8} L^3 \tilde{h}_0^2(0) I^{(2)} X_{\tau}^2(0) \\ &= \frac{1}{8} L^3 I^{(2)} (\rho'_0 - \rho_0)^2 X_{\tau}^2(0), \end{aligned} \quad (\text{D7})$$

where we made use of the compressibility relation (3.5) to obtain the last line of Eq. (D7). The second contribution $X^{3(b)}$ in Eq. (D6) reads as

$$\begin{aligned} X^{3(b)} &= \frac{1}{2} \rho_0^4 X_{\tau}(0) \int d^3\vec{r}_1 d^3\vec{r}_2 d^3\vec{r}_3 d^3\vec{r}_4 h_0^{(2)}(1, 2) h_0^{(2)}(3, 4) \\ &\quad \times X_{\tau}(1, 2) X_{\tau}(2, 3) X_{\tau}(3, 1) \\ &= \frac{\rho_0^2}{2} L^3 X_{\tau}(0) (\rho'_0 - \rho_0) \int d^3\vec{r} h_0^{(2)}(r) X_{\tau}(r) X_{\tau}^{*(2)}(r), \end{aligned} \quad (\text{D8})$$

where we have introduced the auto-convolution

$$X_{\tau}^{*(2)}(r) \equiv \int d^3\vec{r}' X_{\tau}(\vec{r}') X_{\tau}(\vec{r} - \vec{r}'). \quad (\text{D9})$$

The third contribution $X^{3(c)}$ is given by

$$X^{3(c)} = \frac{\rho_0^4}{8} \int d^3\vec{r}_1 d^3\vec{r}_2 d^3\vec{r}_3 d^3\vec{r}_4 h_0^{(2)}(1, 2) h_0^{(2)}(3, 4) X_{\tau}^2(1, 3) X_{\tau}^2(2, 4), \quad (\text{D10})$$

which can be recast under the simple form

$$X^{3(c)} = \frac{\rho_0^4}{8} L^3 \int d^3\vec{r} (h_0^{(2)} * X_{\tau}^2)^2, \quad (\text{D11})$$

where $h_0^2 * X_\tau^2$ denotes the convolution of the functions $h_0^{(2)}(r)$ and $X_\tau^2(r)$. Finally the last contribution $X^{3(d)}$ reads as

$$\begin{aligned} X^{3(d)} = & \frac{\rho_0^4}{4} \int d^3\vec{r}_1 d^3\vec{r}_2 d^3\vec{r}_3 d^3\vec{r}_4 h_0^{(2)}(1, 2) h_0^{(2)}(3, 4) \\ & [X_\tau(1, 2) X_\tau(2, 3) X_\tau(3, 4) X_\tau(4, 1) \\ & + X_\tau(1, 2) X_\tau(2, 4) X_\tau(4, 3) X_\tau(3, 1) \\ & + X_\tau(1, 3) X_\tau(3, 2) X_\tau(2, 4) X_\tau(4, 1)], \end{aligned} \quad (\text{D12})$$

which can be rewritten as

$$\begin{aligned} X^{3(d)} = & \frac{\rho_0^4}{2} L^3 \int d^3\vec{r} ((h_0^{(2)} X_\tau) * X_\tau)^2(r) \\ & + \frac{\rho_0^4}{4} \int d^3\vec{r}_1 d^3\vec{r}_2 d^3\vec{r}_3 d^3\vec{r}_4 h_0^{(2)}(1, 2) h_0^{(2)}(3, 4) \\ & \times X_\tau(1, 3) X_\tau(3, 2) X_\tau(2, 4) X_\tau(4, 1), \end{aligned} \quad (\text{D13})$$

where, once again, we have represented the convolution of the two functions $h_0^{(2)}(r) X_\tau(r)$ and $X_\tau(r)$ by the symbol “*”.

Let us quote now the expressions of the remaining X^i without further comments

$$L^{-3} X^4 = -\frac{1}{2a} \rho_0 \rho_0' X_\tau(0) I^{(2)}, \quad (\text{D14a})$$

$$L^{-3} X^5 = -\frac{1}{2a} \rho_0' (\rho_0' - \rho_0) X_\tau(0) I^{(2)} - \frac{\rho_0^2 \rho_0'}{a} \int d^3\vec{r} h_0^{(2)}(r) X_\tau(r) X_\tau^{*(2)}(r), \quad (\text{D14b})$$

$$\begin{aligned} L^{-3} X^6 = & \frac{\rho_0}{4} I^{(2)} X_\tau^2(0) (\rho_0' - \rho_0) + \frac{\rho_0^3}{4} \int d^3\vec{r} h_0^{(2)}(r) (X_\tau^2 * X_\tau^2)(r) \\ & + \frac{\rho_0^3}{2} X_\tau(0) \int d^3\vec{r} h_0^{(2)}(r) X_\tau(r) X_\tau^{*(2)}(r). \end{aligned} \quad (\text{D14c})$$

Collecting the expressions of the X^i one finds finally that

$$L^{-3} \langle W_2^2 \rangle_{X_{\tau,c}} = \sum_{i=1}^7 \omega_i, \quad (\text{D15a})$$

$$w_1 = A_1(a) I^{(2)} \quad (\text{D15b})$$

$$w_2 = A_2(a) \int d^3\vec{r} h_0^{(2)}(r) X_\tau(r) X_\tau^{*(2)}(r) \quad (\text{D15c})$$

$$w_3 = \frac{\rho_0^3}{4} \int d^3\vec{r} h_0^{(2)}(r) (X_\tau^2 * X_\tau^2)(r) \quad (\text{D15d})$$

$$w_4 = \frac{\rho_0^4}{8} \int d^3\vec{r} (h_0^{(2)} * X_\tau^2)^2(r) \quad (\text{D15e})$$

$$w_5 = \frac{\rho_0^4}{2} \int d^3\vec{r} ((h_0^{(2)} X_\tau) * X_\tau)^2(r) \quad (\text{D15f})$$

$$w_6 = \frac{\rho_0^4}{4L^3} \int d^3\vec{r}_1 d^3\vec{r}_2 d^3\vec{r}_3 d^3\vec{r}_4 h_0^{(2)}(1, 2) h_0^{(2)}(3, 4) \\ \times X_\tau(1, 3) X_\tau(3, 2) X_\tau(2, 4) X_\tau(4, 1) \quad (\text{D15g})$$

$$w_7 = \frac{\rho_0^2}{24} I^{(4)}, \quad (\text{D15h})$$

with complicated expressions for $A_1(a)$ and $A_2(a)$. However both functions are regular in the limit $a \rightarrow 0$; more precisely one has

$$A_1(a) = \frac{1}{8} \rho_0^2 \kappa_0^2 + \mathcal{O}(a), \quad (\text{D16a})$$

$$A_2(a) = -\frac{1}{2} \rho_0^2 \rho'_0 \kappa_0 + \mathcal{O}(a). \quad (\text{D16b})$$

We now proceed in two steps. We first examine the limit $a \rightarrow 0$ of each of the term in the r.h.s of Eq. (D15a) and then study the limit $\gamma \rightarrow 0$ of the resulting expression to decide whether or not it contributes to $\gamma^4 L^{-3} \langle W_2^2 \rangle_{X_\tau}$ at order $\mathcal{O}(\gamma^{7/2})$. In other words, we seek the terms of $\lim_{a \rightarrow 0} \langle W_2^2 \rangle_{X_\tau}$ which are singular in the limit $\gamma \rightarrow 0$ and discard the regular ones.

Since in the limit $a \rightarrow 0$ the potential $X_\tau(r)$ tends to the Yukawa potential $y(r) \equiv \exp(-\kappa_0 r)/r$ one has, taking into account Eq. (D16a)

$$\lim_{a \rightarrow 0} w_1 = \frac{\rho_0'}{8} \kappa_0^2 \int d^3\vec{r} \frac{\exp(-2\kappa_0 r)}{r^2} = \frac{\pi \rho_0'}{4} \kappa_0 = \mathcal{O}(\gamma^{1/2}), \quad (\text{D17})$$

and therefore the term w_1 can be discarded. Haga⁽¹³⁾ has shown that $y^{*(2)}(r) = 2\pi \exp(-\kappa_0 r)/\kappa_0$ from which it follows that

$$\lim_{a \rightarrow 0} w_2 = -\pi \rho_0^2 \rho'_0 \int d^3\vec{r} \frac{h_0^{(2)}(r)}{r} + \mathcal{O}(\gamma^{1/2}). \quad (\text{D18})$$

Since $h_0^{(2)}(r)$ is a short range function of r the integral in Eq. (D18) converges and the term w_2 can also be discarded.

In the limit $a \rightarrow 0$ the third term w_3 reads

$$\lim_{a \rightarrow 0} w_3 = \frac{\rho_0^3}{4} \int d^3 \vec{r} h_0^{(2)}(r) (y^{*(2)} * y^{*(2)})(r). \quad (\text{D19})$$

It turns out that the function $K(r) = y^{*(2)} * y^{*(2)}(r)$ has also been studied by Haga⁽¹³⁾ who proved that $K(r) = L(r)/r$ where $L(r)$ is an entire function of $\kappa_0 r$, from which we conclude that $\lim_{a \rightarrow 0} w_3$ is regular in the limit $\gamma \rightarrow 0$ and can thus be safely discarded.

In order to study $\lim_{a \rightarrow 0} w_4$ we rewrite the integral in Fourier space and obtain

$$\lim_{a \rightarrow 0} w_4 = \frac{\rho_0^4}{8} \int \frac{d^3 \vec{q}}{(2\pi)^3} [\tilde{h}_0^{(2)}(q)]^2 [TF(y^2)(q)]^2. \quad (\text{D20})$$

The Fourier transform of $y^2(r)$ has a simple analytical expression, also given by Haga,⁽¹³⁾ i.e.

$$TF(y^2)(q) = \frac{4\pi}{q} \arctan \frac{q}{2\kappa_0}, \quad (\text{D21})$$

and therefore

$$\lim_{\gamma \rightarrow 0} \lim_{a \rightarrow 0} w_4 = \frac{\pi^4 \rho_0^4}{2} \int \frac{d^3 \vec{q}}{(2\pi)^3} \frac{[\tilde{h}_0^{(2)}(q)]^2}{q^2}. \quad (\text{D22})$$

Since the integral (D22) is convergent the term w_4 can, as the previous ones, be discarded.

In order to study the limit $a \rightarrow 0$ of the term w_5 we have to consider the integral

$$\int d^3 \vec{r} [h_0^{(2)}(r) y(r) * y(r)]^2. \quad (\text{D23})$$

If we interpret $z(r) \equiv h_0^{(2)}(r) y(r)$ as a spherically symmetric distribution of Yukawa charges, then $v(r) = z * y(r)$ is the potential created by this distribution. Obviously $v(r) \sim \exp(-\kappa_0 r)/r$ for $r \rightarrow \infty$. Therefore the integrand of eq. (D23) behaves as $\exp(-2\kappa_0 r)/r^2$ for $r \rightarrow \infty$. The integral (D23) diverges thus as $1/\kappa_0$ in the limit $\gamma \rightarrow 0$. It follows from this remark that

$$\lim_{a \rightarrow 0} \gamma^4 w_5 = \frac{(\rho_0 \gamma)^{7/2}}{4\pi^{1/2}} \lim_{\kappa_0 \rightarrow 0} \int d^3 \vec{r}_1 d^3 \vec{r}_2 d^3 \vec{r}_3 h_0^{(2)}(1, 2) h_0^{(2)}(3, 4) \frac{\kappa_0 \exp(-\kappa_0(r_{12} + r_{23} + r_{34} + r_{41}))}{r_{12} r_{23} r_{34} r_{41}}. \quad (\text{D24})$$

We come now to the term w_6 . Taking advantage of the translational invariance we have

$$\lim_{\kappa_0 \rightarrow 0} \lim_{a \rightarrow 0} w_6 = \frac{\rho_0^4}{4} \int d^3\vec{r}_{12} d^3\vec{r}_{13} d^3\vec{r}_{14} h_0^{(2)}(r_{12}) h_0^{(2)}(r_{34}) \frac{1}{r_{13}} \frac{1}{r_{32}} \frac{1}{r_{24}} \frac{1}{r_{14}}, \quad (\text{D25})$$

which is a convergent integral due to the short range of the pair correlation $h_0^{(2)}(r)$. Therefore w_6 does not contribute to ω_{RPM} at order $\gamma^{7/2}$.

The last term to examine is w_7 which is a tricky one, since the integral $I^{(4)}$ diverges at short distances in the limit $a \rightarrow 0$. In order to study carefully this divergence we insert in I^4 the expression (3.9) of $X_\tau(r)$ which yields

$$\lim_{a \rightarrow 0} I^{(4)} = \frac{272}{35} \frac{\pi}{a} + 16\kappa_0^2(\gamma_E - 1 + \ln(a\kappa_0)) + \mathcal{O}(a), \quad (\text{D26})$$

where γ_E is Euler's constant. Note that the divergence of $\gamma^4 w_7$ occurs at order γ^4 and that we do not need to take it into account at the order of our calculation (i.e. $\gamma^{7/2}$). However we have checked that this divergence for $a \rightarrow 0$ originates from the fact that, till now, we have ignored contributions coming from the cumulant $\gamma^4 \langle W_4 \rangle_{X_\tau}$. Taking carefully account of one of the terms of this cumulant leads to consider the integral

$$I^{(4)} = \int d^3\vec{r} \frac{\exp(-4\kappa_0 r)}{r^4} g_0^{(2)}(r) + \mathcal{O}(\gamma a) \quad (\text{D27})$$

instead of I^4 . Recall that $g_0^{(2)}(r) \equiv h_0^{(2)}(r) + 1$ is zero in the core which makes $I^{(4)}$ convergent in the limit $a \rightarrow 0$ and $\lim_{\gamma \rightarrow 0} \lim_{a \rightarrow 0} I^{(4)}$ perfectly well defined. However the corresponding term $\gamma^4 \omega'_7$ contributes to ω_{RPM} at order γ^4 and can thus be discarded.

The conclusion of this lengthy discussion is that

$$\begin{aligned} \gamma^4 \langle W_2^2 \rangle_{X_{\tau,c}} L^{-3} &= \frac{(\rho_0 \gamma)^{7/2}}{4\pi^{1/2}} \lim_{\kappa_0 \rightarrow 0} \int d^3\vec{r}_1 d^3\vec{r}_2 d^3\vec{r}_3 h_0^{(2)}(1, 2) h_0^{(2)}(3, 4) \\ &\times \frac{\kappa_0 \exp(-\kappa_0(r_{12} + r_{23} + r_{34} + r_{41}))}{r_{12} r_{23} r_{34} r_{41}} + \mathcal{O}(\gamma^4). \end{aligned} \quad (\text{D28})$$

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