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

Jean-Michel Caillol[1]

We present an exact field theoretical representation of an ionic solution made of charged hard spheres. The action of the field theory is obtained by performing a Hubbard–Stratonovich transform of the configurational Boltzmann factor. It is shown that the Stillinger–Lovett sum rules are satisfied if and only if all the field correlation functions are short range functions. The mean field, Gaussian and two-loops approximations of the theory are derived and discussed. The mean field approximation for the free energy constitutes an exact lower bound for the exact free energy, while the mean field pressure is an exact upper bound. The one-loop order approximation is shown to be identical with the random phase approximation of the theory of liquids. Finally, at the two-loop order and in the pecular case of the restricted primitive model, one recovers results obtained in the framework of the mode expansion theory.

1. INTRODUCTION

Various ionic systems including electrolyte solutions, molten salts, and colloids can be studied with a good approximation in the framework of the so-called primitive model (PM) which consists in a mixture of M species of charged hard spheres (HS) which differ by their respective charges and (or) diameters.[1] Of special interest is the restricted primitive model (RPM) where $M = 2$, the hard spheres have all the same diameter, and the cations and anions bear opposite charges $\pm q$. In many instances, we shall also consider the special primitive model (SPM), where the number M of

---

[1] LPT - CNRS (UMR 8627), Bât. 210, Université de Paris Sud, F-91405 Orsay Cedex, France; e-mail: Jean-Michel.Caillol@th.u-psud.fr

species as well as the charges are arbitrary but all the ions have the same diameter σ.

In the two first parts of this work, published some years ago and hereafter referred to as I and II, we have established an exact field theoretical representation of the RPM.[2, 3] The action of this field theory, which is obtained by applying the Kac–Siegert–Stratonovich–Hubbard–Edwards (KSSHE)[4–9] transform to the Coulomb potential, looks like the sine-Gordon action to which it reduces in the limit of point-like ions,[10–12] hence the slightly abusive title of this series of papers. Nowadays we prefer the acronym KSSHE to christen the action. The extended sine-Gordon action derived in paper I for the RPM is obtained here for a general PM. The regularization of the Coulomb potential which is required to define properly the KSSHE transform is obtained by a smearing of the charge over the HS volume. A more general treatment where a part of the Coulomb interaction is incorporated in the reference system is discussed in the review of Brydges and Martin.[11]

The developments of refs. I and II are based on a cumulant expansion of the grand partition function reorganized in ascending powers of either the fugacity or the inverse temperature. In this way one can obtain the exact low fugacity and high temperature expansions of the pressure and the free energy of the RPM. Of course the expressions obtained in that manner are already known from the theory of liquids and were derived years ago in the framework of Mayer graph expansions.[13, 14] In the present paper we proceed differently. After having obtained the KSSHE action for the general PM (see Section 2), we reorganize the cumulant expansion by grouping some classes of Feynman diagrams. The resulting loopwise expansion is explicitly computed up to order two in the number of loops. In the case of the RPM, the two-loop order free energy turns out to coincide with an expression derived more than thirty years ago by Chandler and Andersen[15] in the framework of the so-called mode expansion theory.[16, 17] Reorganizing the loop-expansion in ascending powers of the inverse temperature gives back the high-temperature expansions of paper II and ref. 14.

Our paper is organized in the following way. In Section 2 we show how to construct a well-defined KSSHE transform by regularizing the Coulomb potential at short distances by means of a smearing of the charges inside the volumes of the HS. In Section 3 we establish the general relations between the charge correlation functions and the correlations of the KSSHE field. From the known asymptotic behavior of the former one can deduce that of the latter. The conclusion, which is detailed at length in Section 4, is that the n-body correlations of the KSSHE field are short-ranged functions; stated otherwise, the KSSHE field is a noncritical field.

The so-called Stillinger–Lovett sum rules, both for the homogeneous[18] and the inhomogeneous fluid[19] emerge as a consequence of this behavior. In Section 5 the mean field (MF) level of the theory is studied in detail. The MF free energy $\beta \mathscr{A}_{MF}$ is shown to be a strictly convex functional of the M partial densities and to constitute a rigorous lower bound of the exact free energy. The former property excludes a fluid–fluid transition at the MF level while the latter serves to define an optimized MF free energy by maximizing $\beta \mathscr{A}_{MF}$ with respect to the variations of the smearing functions. An explicit expression of the optimized $\beta \mathscr{A}_{MF}$ is obtained in the case of an homogeneous fluid. From the MF solution for the inhomogeneous system we also deduce the expressions of the n-body correlation and vertex functions of the homogeneous system in the Gaussian approximation.[20] This Gaussian approximation is discussed in Section 6 and shown to be equivalent to the random phase approximation (RPA) of the theory of liquids.[1, 21] Finally, a two-loop order calculation is performed in Section 7. The resulting expression for the free energy of the RPM is shown to be identical with that obtained by Chandler and Andersen[15] in the framework of the first version of the mode expansion theory. Conclusions are drawn in Section 8.

Note that some technical details and disgressions have been skipped in the final version of the paper; they can be found in an extended version of this work which can be consulted at the arXiv:cond-mat data basis.[22]

2. THE KSSHE TRANSFORM

2.1. The Model

We shall consider only the three dimensional (3D) version of the (PM), i.e., a mixture of M species of charged hard spheres.[1] The ions of the species α ($\alpha = 1,..., M$) are characterized by their diameter σ_α and their electric charge q_α. The molecular structure of the solvent is ignored and it is treated as a continuum, the dielectric constant of which has been absorbed in the definition of the charges q_α. The solution is made of *both* positive *and* negative ions so that the electroneutrality in the bulk can be satisfied without adding any unphysical neutralizing background to the system. The particles occupy a domain $\Omega \subset \mathbb{R}^3$ of volume Ω of the ordinary space with free boundary conditions. Only configurations $\omega \equiv (N_1; \vec{r}_1^1,..., \vec{r}_{N_1}^1 | \cdots | N_\alpha; \vec{r}_1^\alpha,..., \vec{r}_{N_\alpha}^\alpha | N_M; \vec{r}_1^M,..., \vec{r}_{N_M}^M)$ $(\vec{r}_{i_\alpha}^\alpha \in \Omega)$ without overlaps of the spheres, i.e., such that $\|\vec{r}_{i_\alpha}^\alpha - \vec{r}_{i_\beta}^\beta\| \geqslant (\sigma_\alpha + \sigma_\beta)/2$ do contribute to the partition or grand partition functions. In such a configuration, the charge q_α of each ion can be smeared out inside its volume according to a spherically symmetric distribution $q_\alpha \tau_\alpha(r)$ without altering the configurational energy as a

consequence of Gauss theorem. The distribution $\tau_\alpha(r)$ is *a priori* arbitrary, provided it satisfies the following properties:

$$\tau_\alpha(r) = 0 \qquad \text{if} \quad r \geqslant \bar{\sigma}_\alpha \equiv \sigma_\alpha/2, \tag{2.1a}$$

$$\int d^3\vec{r}\, \tau_\alpha(r) = 1. \tag{2.1b}$$

The electrostatic interaction energy of two charge distributions τ_α and τ_β the centers of which are located at the points $\vec{r}_1$ and $\vec{r}_2$ of Ω respectively will be noted $w_{\alpha,\beta}(1, 2)$. It reads as

$$w_{\alpha,\beta}(1, 2) = \int d^3r_{1'} \int d^3r_{2'}\, \tau_\alpha(\|\vec{r}_1 - \vec{r}_{1'}\|)\, v_c(\|\vec{r}_{1'} - \vec{r}_{2'}\|)\, \tau_\beta(\|\vec{r}_{2'} - \vec{r}_2\|),$$

$$\equiv \tau_\alpha(1, 1')\, v_c(1', 2')\, \tau_\beta(2', 2), \tag{2.2}$$

where $v_c(r) = 1/r$ is the Coulomb potential. Note that in this paper, summation over repeated, either discrete or continuous indices will always be meant (except if explicitly stated otherwise). As a consequence of Eqs. (2.1) and of Gauss theorem $w_{\alpha,\beta}(1, 2) = 1/r_{12}$ for $r_{12} \geqslant \bar{\sigma}_\alpha + \bar{\sigma}_\beta$. Note that the Fourier transform $\tilde{w}_{\alpha,\beta}(k)$ of the interaction takes the simple form

$$\tilde{w}_{\alpha,\beta}(k) = \frac{4\pi}{k^2}\, \tilde{\tau}_\alpha(k)\, \tilde{\tau}_\beta(k), \tag{2.3}$$

which diverges for $k \to 0$ as $4\pi/k^2$ since $\tilde{\tau}_\alpha(0) = 1$, as follows from Eq. (2.1b). Finally we shall denote by

$$v_{\alpha,\beta}(1, 2) = q_\alpha q_\beta\, w_{\alpha,\beta}(1, 2) \tag{2.4}$$

the pair interaction of two ions.

The electrostatic potential energy of the configuration ω times the inverse temperature $\beta = 1/kT$ can be written as

$$\beta U_{el}(\omega) = \frac{\beta}{2}\, \hat{\rho}_C(1)\, v_c(1, 2)\, \hat{\rho}_C(2) - N_\alpha v_\alpha^S, \tag{2.5}$$

where $\hat{\rho}_C(1)$ is the microscopic charge density in the configuration ω at the point $\vec{r}_1$ and v_α^S is the self-energy of the charge distribution $q_\alpha\tau_\alpha(r)$. In general, for a sufficiently regular distribution $\tau_\alpha(r)$, the self-energy

$$v_\alpha^S = \frac{\beta q_\alpha^2}{2}\, w_{\alpha,\alpha}(0) = \frac{\beta q_\alpha^2}{2} \int d^\vee k\, \frac{4\pi}{k^2}\, \tilde{\tau}_\alpha(k)^2, \tag{2.6}$$

where $d^\vee k \equiv d^3\vec{k}/(2\pi)^3$, is a well-defined positive and finite quantity. Of course v_α^S diverges for point-like charges which makes the KSSHE transform, to be introduced in the next section, an ill-defined object in that case. The microscopic smeared charge density $\hat{\rho}_C(\vec{r})$ which enters Eq. (2.5) reads

$$\hat{\rho}_C(1) = q_\alpha \tau_\alpha(1, 1')\, \hat{\rho}_\alpha(1'), \tag{2.7}$$

where

$$\hat{\rho}_\alpha(1) = \sum_{i_\alpha = 1}^{N_\alpha} \delta^3(\vec{r}_1 - \vec{r}_{i_\alpha}^\alpha) \tag{2.8}$$

is the microscopic number density of the species α at the point $\vec{r}_1$.

It will prove convenient to make use of Dirac's notations for matrix elements and scalar products and to rewrite the energy (2.5) as

$$\begin{aligned}
\tfrac{1}{2}\, \hat{\rho}_C(1)\, v_c(1, 2)\, \hat{\rho}_C(2) &= \tfrac{1}{2} \langle \hat{\rho}_C|\, v_c\, |\hat{\rho}_C \rangle, \\
&= \langle \hat{\rho}_C\, |\hat{V} \rangle,
\end{aligned} \tag{2.9}$$

where $\hat{V}(1) \equiv \hat{\rho}_C(1')\, v_c(1', 1)$ denotes the microscopic electric potential at the point $\vec{r}_1$ in the configuration ω. Of course $\hat{V}$ is solution of the $3D$ Poisson equation, i.e.,

$$\Delta_1 \hat{V}(1) = -4\pi \hat{\rho}_C(1). \tag{2.10}$$

2.2. The KSSHE Transform of the Boltzmann Factor

The Boltzmann factor in the configuration ω is equal to

$$\exp(-\beta U(\omega)) = \exp(-\beta U_{\mathrm{HS}}(\omega))\, \exp(-\beta U_{el}(\omega)), \tag{2.11}$$

where $U_{\mathrm{HS}}(\omega)$ denotes the contribution of the hard cores to the configurational energy. We perform now a KSSHE transform in order to rewrite Eq. (2.11) as[2–12]

$$\exp(-\beta U(\omega)) = \exp(-\beta U_{\mathrm{HS}}(\omega))\, \exp(N_\alpha v_\alpha^S) \langle \exp(i\beta^{1/2} \langle \hat{\rho}_C\, |\varphi \rangle) \rangle_{v_c}, \tag{2.12}$$

where the brackets $\langle \cdots \rangle_{v_c}$ denote Gaussian averages over the real scalar field $\varphi(\vec{r})$, i.e.,

$$\langle \cdots \rangle_{v_c} \equiv \mathscr{N}_{v_c}^{-1} \int \mathscr{D}\varphi \cdots \exp(-\tfrac{1}{2} \langle \varphi|\, v_c^{-1}\, |\varphi \rangle),$$

$$\mathscr{N}_{v_c} \equiv \int \mathscr{D}\varphi\, \exp(-\tfrac{1}{2} \langle \varphi|\, v_c^{-1}\, |\varphi \rangle), \tag{2.13}$$

where

$$v_c^{-1}(1, 2) = -\frac{1}{4\pi} \, \Delta_1 \delta(1, 2) \tag{2.14}$$

is the inverse of the positive operator $v_c(1, 2)$. Therefore one has, after an integration by parts

$$\mathcal{N}_{v_c} = \int \mathcal{D}\varphi \exp\left(-\frac{1}{8\pi} \int_\Omega d^3\vec{r}(\vec{\nabla}\varphi)^2 \right) \tag{2.15}$$

The functional integrals which enter Eqs. (2.13) and (2.15) can be given a precise meaning when grounded perfect conductor boundary conditions (BC) are adopted; periodic BC's also work if only neutral configurations are considered, we refer the reader to the literature for more details. [2, 11, 20, 23, 24] It will be convenient to write

$$\langle \hat{\rho}_C \mid \varphi \rangle = \langle \hat{\rho}_\alpha \mid \phi_\alpha \rangle, \tag{2.16}$$

where the smeared field ϕ_α is defined as

$$\phi_\alpha(1) \equiv \beta^{1/2} q_\alpha \tau_\alpha(1, 1') \, \varphi(1'). \tag{2.17}$$

The field $i\phi_\alpha(1)$ may thus be seen as an external one-body potential acting on the particles of the species α; indeed, one can rewrite the Boltmann factor (2.12) under the form

$$\exp(-\beta U(\omega)) = \exp(-\beta U_{\mathrm{HS}}(\omega)) \exp(N_\alpha v_\alpha^S) \langle \exp(i\langle \hat{\rho}_\alpha \mid \phi_\alpha \rangle) \rangle_{v_c},$$

$$= \exp(-\beta U_{\mathrm{HS}}(\omega)) \exp(N_\alpha v_\alpha^S) \left\langle \exp\left(\sum_{\alpha=1}^M \sum_{i_\alpha=1}^{N_\alpha} i\phi_\alpha(\vec{r}_{i_\alpha}^\alpha) \right) \right\rangle_{v_c}. \tag{2.18}$$

2.3. The KSSHE Transform of the Grand Partition Function

Henceforward we shall work in the grand canonical (GC) ensemble. We denote by μ_α the chemical potential of the species α and by $\psi_\alpha(\vec{r})$ the external potential with which the particles of the species α interact eventually. According to a terminology due to J. Percus,[25] we shall define the local chemical potential $v_\alpha(\vec{r})$ as $\beta(\mu_\alpha - \psi_\alpha(\vec{r}))$. With these notations, the GC partition function of the system takes the form

$$\Xi[\{v_\alpha\}] = \sum_{N_1=0}^{\infty} \frac{1}{N_1!} \cdots \sum_{N_M=0}^{\infty} \frac{1}{N_M!} \int_\Omega d^3\vec{r}_1^1 \cdots d^3\vec{r}_{N_M}^M \exp(-\beta U(\omega))$$

$$\times \prod_{\alpha=1}^{M} \prod_{i_\alpha=1}^{N_\alpha} \exp(v_\alpha(\vec{r}_{i_\alpha}^\alpha)). \tag{2.19}$$

Grand canonical averages of dynamic variables $\mathscr{A}(\omega)$ will be noted $\langle \mathscr{A}(\omega) \rangle_{GC}$. Inserting the expression (2.18) of the Boltmann factor in Eq. (2.19) one obtains the KSSHE representation of Ξ

$$\Xi[\{v_\alpha\}] = \langle \Xi_{HS}[\{\bar{v}_\alpha + i\phi_\alpha\}] \rangle_{v_c}, \tag{2.20}$$

where $\bar{v}_\alpha = v_\alpha + v_\alpha^S$ and $\Xi_{HS}[\{\bar{v}_\alpha + i\phi_\alpha\}]$ is the GC partition function of a mixture of bare hard spheres in the presence of the local chemical potentials $\bar{v}_\alpha + i\phi_\alpha$. The above result generalizes to the case of the PM the result obtained in paper I for the restricted primitive model. It is also possible to incorporate a part of the Coulomb interaction in the reference potential which yields a more general expression than Eq. (2.20) as detailed in the review of Brydges and Martin (cf. Eq. (2.29) of ref. 11). However, in the liquid domain, the thermodynamics and correlations of this reference system are, by contrast with those of the HS fluid, little known in general. Relations similar to Eq. (2.20) have also been obtained and discussed for neutral fluids.[5, 8, 26, 27]

To make some contact with statistical field theory we introduce the effective Hamiltonian (or action)

$$\mathscr{H}[\varphi] = \tfrac{1}{2} \langle \varphi | v_c^{-1} | \varphi \rangle - \log \Xi_{HS}[\{\bar{v}_\alpha + i\phi_\alpha\}], \tag{2.21}$$

which allows us to recast Ξ under the form

$$\Xi[\{v_\alpha\}] = \mathscr{N}_{v_c}^{-1} \int \mathscr{D}\varphi \exp(-\mathscr{H}[\varphi]). \tag{2.22}$$

It will be important in the sequel to distinguish carefully, besides the GC averages $\langle \cdots \rangle_{GC}$, between two types of statistical field averages: the already defined $\langle \cdots \rangle_{v_c}$ and the $\langle \cdots \rangle_{\mathscr{H}}$ that we define as

$$\langle A[\varphi] \rangle_{\mathscr{H}} \equiv \frac{\int \mathscr{D}\varphi \exp(-\mathscr{H}[\varphi]) A[\varphi]}{\int \mathscr{D}\varphi \exp(-\mathscr{H}[\varphi])}. \tag{2.23}$$

With these definitions in mind one notes that for an arbitrary functional $\mathscr{A}[\varphi]$ one has the relation

$$\langle A[\varphi] \rangle_{\mathscr{H}} = \frac{\langle A[\varphi] \, \Xi_{HS}[\{\bar{v}_\alpha + i\phi_\alpha\}] \rangle_{v_c}}{\langle \Xi_{HS}[\{\bar{v}_\alpha + i\phi_\alpha\}] \rangle_{v_c}}. \tag{2.24}$$

3. CORRELATION FUNCTIONS

3.1. Zoology

The ordinary and truncated (or connected) density correlation functions will be defined in this paper as[28, 29]

$$G_{\alpha_1 \cdots \alpha_n}^{(n)}[\{v_\alpha\}](1,\dots,n) = \left\langle \prod_{1=1}^{n} \hat{\rho}_{\alpha_i}(i) \right\rangle_{GC},$$

$$= \Xi[\{v_\alpha\}]^{-1} \frac{\delta^n \Xi[\{v_\alpha\}]}{\delta v_{\alpha_1}(1) \cdots \delta v_{\alpha_n}(n)}, \tag{3.1}$$

$$G_{\alpha_1 \cdots \alpha_n}^{(n)\,T}[\{v_\alpha\}](1,\dots,n) = \frac{\delta^n \log \Xi[\{v_\alpha\}]}{\delta v_{\alpha_1}(1) \cdots \delta v_{\alpha_n}(n)}.$$

Our notation emphasizes the fact that the $G_{\alpha_1 \cdots \alpha_n}^{(n)}$ (truncated or not) are functionals of the local chemical potentials $v_\alpha(\vec{r})$ and functions of the coordinates $(1,\dots,n) \equiv (\vec{r}_1,\dots,\vec{r}_n)$. Note however that, in the remainder of the paper, we shall frequently omit to quote the functional dependence of $G_{\alpha_1 \cdots \alpha_n}^{(n)}$ upon the v_α when no ambiguity is possible. In standard textbooks of liquid theory[1] the n-body correlation functions are more frequently defined as functional derivatives of Ξ or $\log \Xi$ with respect to the activities $z_\alpha = \exp(v_\alpha)$ rather than with respect to the local chemical potentials. This yields differences involving delta functions. For instance for $n = 2$ and for a homogeneous system one has

$$G_{\alpha\beta}^{(2)}(1, 2) = \rho_\alpha \rho_\beta g_{\alpha\beta}(r_{12}) + \rho_\alpha \delta_{\alpha,\beta} \delta(1, 2),$$

$$G_{\alpha\beta}^{(2)\,T}(1, 2) = \rho_\alpha \rho_\beta h_{\alpha\beta}(r_{12}) + \rho_\alpha \delta_{\alpha,\beta} \delta(1, 2), \tag{3.2}$$

where ρ_α is the equilibrium number density of the species α and $g_{\alpha\beta}(r)$ the usual pair distribution function; finally $h_{\alpha\beta} = g_{\alpha\beta} - 1$.

The charge correlations will play an important role in subsequent developments. They are defined as

$$G_C^{(n)}(1,\dots,n) = \left\langle \prod_{1=1}^{n} \hat{\rho}_C(i) \right\rangle_{GC}. \tag{3.3}$$

It follows from the definition (2.7) of the smeared density of charge $\hat{\rho}_C$ that Eq. (3.3) can be rewritten alternatively

$$G_C^{(n)}(1,\dots,n) = q_{\alpha_1} \cdots q_{\alpha_n} \tau_{\alpha_1}(1, 1') \cdots \tau_{\alpha_n}(n, n') \, G_{\alpha_1 \cdots \alpha_n}^{(n)}(1',\dots,n'). \tag{3.4}$$

Clearly the operator

$$\Theta(1) \equiv i\beta^{1/2}q_\alpha \tau_\alpha(1, 1') \frac{\delta}{\delta v_\alpha(1')} \tag{3.5}$$

is the generator of the charge correlations for we have clearly

$$i^n \beta^{n/2} G_C^{(n)}(1,..., n) = \Xi^{-1}\Theta(1)\cdots\Theta(n)\,\Xi. \tag{3.6}$$

The truncated charge correlations can thus be defined according to

$$i^n \beta^{n/2} G_C^{(n)\,T}(1,..., n) = \Theta(1)\cdots\Theta(n)\log \Xi. \tag{3.7}$$

On the one hand

$$G_C^{(n)\,T}(1,..., n) = q_{\alpha_1}\cdots q_{\alpha_n}\,\tau_{\alpha_1}(1, 1')\cdots\tau_{\alpha_n}(n, n')\,G_{\alpha_1\cdots\alpha_n}^{(n)\,T}(1',..., n'), \tag{3.8}$$

and, in the other hand[23, 28, 29]

$$G_C^{(n)\,T}(1,..., n) = G_C^{(n)\,T}(1,..., n) - \sum_{m<n}\prod G_C^{(m)\,T}(i_1,..., i_m), \tag{3.9}$$

where the sum of products is carried out over all possible partitions of the set $(1,..., n)$ into subsets of cardinality $m < n$.

The functions $G_C^{(n)}$ (resp. $G_C^{(n)\,T}$) are related by a hierarchy of equations most conveniently written with the help of the operator Θ defined at Eq. (3.5). One establishes easily that[22]

$$\Theta(n+1)\,G_C^{(n)\,T}(1,..., n) = i\beta^{1/2}\,G_C^{(n+1)\,T}(1,..., n+1), \tag{3.10}$$

which is valid for all $n \geqslant 0$ with the convention that $G_C^{(n=0)\,T} \equiv \log \Xi$ and that

$$\Theta(n+1)\,G_C^{(n)}(1,..., n) = i\beta^{1/2}[G_C^{(n+1)}(1,..., n+1) - \rho_C(n+1)\,G_C^{(n)}(1,..., n)] \tag{3.11}$$

where $\rho_C \equiv G_C^{(n=1)}$ is the equilibrium charge density. The relations (3.11) are valid for all $n \geqslant 0$ with the convention that $G_C^{(n=0)} \equiv 1$.

In the field theoretical representation of the PM the field correlation functions play a key role. They are defined as

$$G_\varphi^{(n)}(1,..., n) = \langle \varphi(1)\cdots\varphi(n)\rangle_{\mathscr{H}}, \tag{3.12a}$$

$$G_\varphi^{(n)\,T}(1,..., n) = G_\varphi^{(n)\,T}(1,..., n) - \sum_{m<n}\prod G_\varphi^{(m)\,T}(i_1,..., i_m). \tag{3.12b}$$

Of course the $G_\varphi^{(n)}$, as the charge correlation functions, are functionals of the local chemical potentials. The hierarchy for the $G_\varphi^{(n)}$ reads as follows[22]

$$\Theta(n+1) \, G_\varphi^{(n)}(1,..., n)$$
$$= \frac{-\Delta_{n+1}}{4\pi} \left[G_\varphi^{(n+1)}(1,..., n+1) - G_\varphi^{(n)}(1,..., n) \langle \varphi(n+1) \rangle_{\mathscr{H}} \right]$$
$$- \sum_{j=1}^{n} \delta(n+1, j) \, G_\varphi^{(n-1)}(1,..., j-1, j+1,..., n), \tag{3.13}$$

which is valid for all $n \geqslant 1$ with the convention $G_\varphi^{(0)} \equiv 1$. And for the $G_\varphi^{(n)\,T}$ one finds[22]

$$\Theta(2) \, G_\varphi^{(1)}(1) = \frac{-\Delta_2}{4\pi} \, G_\varphi^{(2)\,T}(1, 2) - \delta(1, 2),$$

$$\Theta(n+1) \, G_\varphi^{(n)\,T}(1,..., n) = \frac{-\Delta_{n+1}}{4\pi} \, G_\varphi^{(n+1)\,T}(1,..., n+1) \qquad (n \geqslant 2). \tag{3.14}$$

3.2. Relations between the Charge and Field Correlation Functions

3.2.1. The Density and Charge Correlation Functions as Statistical Field Averages

It follows from the definition (3.1) of $G_{\alpha_1 \cdots \alpha_n}^{(n)}$ and from the KSSHE representation (2.20) of the grand partition function that we have

$$G_{\alpha_1 \cdots \alpha_n}^{(n)}[\{v_\alpha\}](1,..., n)$$
$$= \Xi^{-1} \mathscr{N}_{v_c}^{-1} \int \mathscr{D}\varphi \exp(-\tfrac{1}{2} \langle \varphi| \, v_c^{-1} \, |\varphi \rangle) \frac{\delta^n \Xi_{\mathrm{HS}}[\{\bar{v}_\alpha + i\phi_\alpha\}]}{\delta v_{\alpha_1}(1) \cdots \delta v_{\alpha_n}(n)},$$
$$= \Xi^{-1} \langle \Xi_{\mathrm{HS}} \, G_{\mathrm{HS},\, \alpha_1 \cdots \alpha_n}^{(n)}[\{\bar{v}_\alpha + i\phi_\alpha\}](1,..., n) \rangle_{v_c}, \tag{3.15}$$

where $G_{\mathrm{HS},\, \alpha_1 \cdots \alpha_n}^{(n)}[\{\bar{v}_\alpha + i\phi_\alpha\}](1,..., n)$ denotes the density correlation function of the reference HS fluid in the presence of the local chemical potentials $\{\bar{v}_\alpha + i\phi_\alpha\}$. Thence, making use of Eq. (2.24)

$$G_{\alpha_1 \cdots \alpha_n}^{(n)}[\{v_\alpha\}](1,..., n) = \langle G_{\mathrm{HS},\, \alpha_1 \cdots \alpha_n}^{(n)}[\{\bar{v}_\alpha + i\phi_\alpha\}](1,..., n) \rangle_{\mathscr{H}}. \tag{3.16}$$

Equation (3.16), which extends to ionic mixtures a relation that we derived elsewhere for simple non-charged fluids,[27] although aesthetic is not very useful since the hard sphere correlations $G_{\mathrm{HS},\, \alpha_1 \cdots \alpha_n}^{(n)}$ are complicated

functionals of the field φ. However the case $n = 1$ is of some interest. In that case Eq. (3.16) says that

$$\rho_\beta[\{v_\alpha\}](1) = \langle \rho_{\text{HS},\beta}[\{\bar{v}_\alpha + i\phi_\alpha\}](1) \rangle_{\mathscr{H}}, \tag{3.17}$$

It follows readily from the expression (3.4) of the charge correlation function that we also have

$$G_C^{(n)}[\{v_\alpha\}](1,...,n) = \langle G_{\text{HS},C}^{(n)}[\{\bar{v}_\alpha + i\phi_\alpha\}](1,...,n) \rangle_{\mathscr{H}}, \tag{3.18}$$

where

$$G_{\text{HS},C}^{(n)}(1,...,n) = q_{\alpha_1} \cdots q_{\alpha_n}\, \tau_{\alpha_1}(1,1') \cdots \tau_{\alpha_n}(n,n')\, G_{\text{HS},\alpha_1 \cdots \alpha_n}^{(n)}(1',...,n'). \tag{3.19}$$

Specializing Eq. (3.18) for $n = 1$ we note that

$$\rho_C[\{v_\alpha\}](1) = \langle \rho_{\text{HS},C}[\{\bar{v}_\alpha + i\phi_\alpha\}](1) \rangle_{\mathscr{H}}, \tag{3.20}$$

where

$$\rho_{\text{HS},C}(1) = q_\alpha \tau_\alpha(1,1')\, \rho_{\text{HS},\alpha}(1'). \tag{3.21}$$

3.2.2. Relations between $G_C^{(n)}$ and $G_\varphi^{(n)}$

It follows readily from the expression (3.7) of $G_C^{(n)}$ and from the KSSHE representation (2.20) of the grand partition function that

$$i^n \beta^{n/2} G_C^{(n)}[\{v_\alpha\}](1,...,n) = \Xi^{-1}[\{v_\alpha\}]\, \mathscr{N}_{v_c}^{-1} \int \mathscr{D}\varphi\, \exp(-\tfrac{1}{2} \langle \varphi|\, v_c^{-1}\, |\varphi \rangle)$$
$$\times \Theta(1) \cdots \Theta(n)\, \Xi_{\text{HS}}[\{\bar{v}_\alpha + i\phi_\alpha\}]. \tag{3.22}$$

At this point we make the remark that

$$\frac{\delta \Xi_{\text{HS}}[\{\bar{v}_\alpha + i\phi_\alpha\}]}{\delta\varphi(1)} = \frac{\delta\, i\phi_\alpha(1')}{\delta\varphi(1)} \frac{\delta \Xi_{\text{HS}}[\{\bar{v}_\alpha + i\phi_\alpha\}]}{\delta v_\alpha(1')},$$
$$= \Theta(1)\, \Xi_{\text{HS}}[\{\bar{v}_\alpha + i\phi_\alpha\}]. \tag{3.23}$$

The relation (3.23) enables us to replace the operators $\Theta(i)$ which occur the right hand side (RHS) of Eq. (3.22) by functional derivatives with respect to the field φ. Then, performing n functional integrations by parts[24, 27] yields

$$i^n \beta^{n/2} G_C^{(n)}(1,...,n) = (-)^n \left\langle \frac{\delta^n \exp(-\tfrac{1}{2} \langle \varphi|\, v_c^{-1}\, |\varphi \rangle)}{\delta\varphi(1) \cdots \delta\varphi(n)} \right\rangle_{\mathscr{H}}. \tag{3.24}$$

The relation (3.24) can be used to obtain an explicit representation of $G_C^{(n)}$ in terms of the field correlations as long as n is not too large. Let us first consider the case $n = 1$ in which Eq. (3.24) takes the simple form

$$\Delta_1 \langle \varphi(1) \rangle_{\mathcal{H}} = -4\pi i \beta^{1/2} \rho_C(1). \tag{3.25}$$

We thus obtain the Poisson equation, the solution of which is of course

$$\langle \varphi(1) \rangle_{\mathcal{H}} = i\beta^{1/2} V(1), \tag{3.26}$$

where $V(1)$ is the GC average of the configurational electric potential, i.e., $V(1) = \langle \hat{V}(1) \rangle_{\text{GC}}$.

In the case $n = 2$ Eq. (3.24) says that

$$\beta G_C^{(2)}(1, 2) = \frac{-1}{4\pi} \Delta_1 \delta(1, 2) - \frac{1}{(4\pi)^2} \Delta_1 \Delta_2 G_\varphi^{(2)}(1, 2), \tag{3.27}$$

or, by reverting the equation

$$G_\varphi^{(2)}(1, 2) = v_c(1, 2) - \beta v_c(1, 1') \, G_C^{(2)}(1', 2') \, v_c(2', 2). \tag{3.28}$$

Equations (3.27) and (3.28) extend to electrolyte solutions relations obtained recently for neutral fluids.[27] Equations of this type were also derived by Ciach and Stell in the framework of a heuristic field theory of the RPM.[30]

By combining Eqs. (3.25) and (3.27) one can show easily that the truncated two-body charge correlation function satisfies to a similar relation, i.e.,

$$\beta G_C^{(2)\,T}(1, 2) = \frac{-1}{4\pi} \Delta_1 \delta(1, 2) - \frac{1}{(4\pi)^2} \Delta_1 \Delta_2 G_\varphi^{(2)\,T}(1, 2). \tag{3.29}$$

In the case $n = 3$ Eq. (3.24) yields an awkward expression for $G_C^{(3)}$. However the truncated 3-body charge correlation function takes the simple form

$$i\beta^{3/2} G_C^{(3)\,T}(1, 2, 3) = \frac{1}{(4\pi)^3} \Delta_1 \Delta_2 \Delta_3 G_\varphi^{(3)\,T}(1, 2, 3), \tag{3.30}$$

which can be obtained by brute force calculation. The above result suggests that there are simple relations between $G_C^{(n)\,T}$ and $G_\varphi^{(n)\,T}$ for values of $n \geqslant 3$. Indeed, let us apply the operator $\Theta(2) \cdots \Theta(3)$ ($n \geqslant 3$) to both sides of Eq. (3.25). Then, making use of the hierarchy equations satisfied by the

$G_C^{(n)\,T}$ and the $G_\varphi^{(n)\,T}$ (cf. Eqs. (3.10) and (3.14)) one gets immediately the aesthetic generic formula

$$i^n \beta^{n/2} G_C^{(n)\,T}(1,...,n) = \frac{(-1)^n}{(4\pi)^n}\, \Delta_1 \cdots \Delta_n G_\varphi^{(n)\,T}(1,...,n) \qquad (\forall n \geqslant 3). \quad (3.31)$$

3.2.3. Correlations of the Electric Potential

It is obvious that

$$
\begin{aligned}
\langle \hat{V}(1) \cdots \hat{V}(n) \rangle_{\mathrm{GC}} &= v_c(1, 1') \cdots v_c(n, n')\, G_C^{(n)}(1',...,n'), \\
\langle \hat{V}(1) \cdots \hat{V}(n) \rangle_{\mathrm{GC}}^T &= v_c(1, 1') \cdots v_c(n, n')\, G_C^{(n)\,T}(1',...,n').
\end{aligned}
\tag{3.32}
$$

Combining the above relations with those obtained in Section 3.2.2 one gets

$$i\beta^{1/2}\langle \hat{V}(1) \rangle_{\mathrm{GC}} = \langle \varphi(1) \rangle_{\mathscr{H}}, \tag{3.33a}$$

$$\beta \langle \hat{V}(1)\,\hat{V}(2) \rangle_{\mathrm{GC}}^T = v_c(1, 2) - G_\varphi^{(2)\,T}(1, 2), \tag{3.33b}$$

$$i^n \beta^{n/2}\langle \hat{V}(1) \cdots \hat{V}(n) \rangle_{\mathrm{GC}}^T = G_\varphi^{(n)\,T}(1,...,n) \qquad (\forall n \geqslant 3). \tag{3.33c}$$

What can be learned from the above relations is the subject of the next section.

4. STILLINGER–LOVETT SUM RULES

A salient property of 3D ionic liquids is the screening effect. To paraphrase Ph. Martin, this type of fluid "in thermal equilibrium does not tolerate any charge inhomogeneity over more than a few intermolecular distances."[31] Even at the liquid-vapor critical point where the correlation length associated with the fluctuations of density diverges it is believed, and has been checked by means of numerical simulations in the case of the RPM,[32] that the correlation length associated with the fluctuations of charge remains finite. From the existence of screening it is possible to deduce sum rules for the charge correlation functions for both homogeneous and inhomogeneous systems, the so-called Stillinger–Lovett (SL) sum rules.[18, 19, 33] As pointed out by B. Jancovici, these rules may be rederived under the sole assumption that the system behaves macroscopically as a conductor in the sense that "the laws of macroscopic electrostatics are assumed to be obeyed for length scales large compared to the microscopic characteristic lengths of the model."[34] We examine below how the SL rules can be deduced from simple hypothesis on the behavior of the KSSHE field correlation functions.

Let us first consider a homogeneous system. In this case $\langle \varphi \rangle_{\mathcal{H}}$ is a constant as well as are the densities ρ_α and the smeared density of charge ρ_C. It follows then from Eq. (3.25) that the smeared density $\rho_C = 0$. This is nothing but the usual electroneutrality condition since $\rho_C = \rho_\alpha q_\alpha \tilde{\tau}_\alpha(0)$ can be identified with the usual local charge density for $\tilde{\tau}_\alpha(0) = 1$ (property (2.1b) of the smearing function τ_α). Therefore, in the framework of our formalism, the electroneutrality condition

$$\rho_\alpha q_\alpha = 0 \tag{4.1}$$

is automatically satisfied for an arbitrary set of chemical potentials $\{v_\alpha\}$, a well known property of ionic fluids.[11] Note that Eq. (4.1) implies that there are only $M-1$ independent chemical potentials.

The correlations of the electric potential has been studied by various approaches and asymptotically one has

$$\beta \langle \hat{V}(1)\, \hat{V}(2) \rangle^T_{GC} = v_c(1, 2), \tag{4.2a}$$

$$\langle \hat{V}(1) \cdots \hat{V}(n) \rangle^T_{GC} = 0. \tag{4.2b}$$

It must be stressed that these expressions are valid for relative distances large compared to the microscopic characteristic lengths of the system and if the correlations decay fast enough or, equivalently, if the system behaves as a macroscopic conductor.[11, 31, 34, 35] The comparison of these asymptotic behaviors with the exact relations (3.33) derived in Section 3.2.3 entails that the truncated KSSHE field correlation functions $G_\varphi^{(n)\, T}$ are short range functions; stated otherwise, the KSSHE field is a noncritical field. Conversely, this property being taken as given, we show now that one can infer the SL rules.

We consider now a nonhomogeneous system and we take the Laplacian of Eq. (3.33b). We get

$$\beta \langle \hat{\rho}_C(1)\, \hat{V}(2) \rangle^T_{GC} = \delta(1, 2) + \frac{1}{4\pi} \Delta_1 G_\varphi^{(2)\, T}(1, 2). \tag{4.3}$$

Let us integrate Eq. (4.3) over $\vec{r}_1$. With the hypothesis that $G_\varphi^{(2)\, T}(1, 2)$ is short range the integration of the Laplacian gives zero by an application of Green's theorem. Therefore

$$\beta \int d(1) \langle \hat{\rho}_C(1)\, \hat{V}(2) \rangle^T_{GC} = 1 \tag{4.4}$$

which is the Carnie–Chan sum rule.[19] In the case of a homogeneous system, the Carnie–Chan sum rule is equivalent to the SL sum rule.[34] Let

us retrieve these sum rules in our framework. We start with Eq. (3.29) for a homogeneous system. In this case $G_C^{(2)T}(1, 2) \equiv G_C^{(2)T}(\vec{r} = \vec{r}_1 - \vec{r}_2))$ and we have

$$-4\pi\beta G_C^{(2)T}(\vec{r}) = \Delta\delta(\vec{r}) - \frac{1}{4\pi}\Delta\Delta G_\varphi^{(2)T}(\vec{r}). \tag{4.5}$$

With the hypothesis that $G_\varphi^{(2)T}(1, 2)$ is a short range function the integration over $\vec{r}$ gives zero, i.e.,

$$\int d^3\vec{r}\, G_C^{(2)T}(\vec{r}) = 0 \tag{4.6}$$

which is the first SL rule.[18] Similarly, after integration by parts

$$4\pi\beta \int d^3\vec{r}\, r^2 G_C^{(2)T}(\vec{r}) = -6 + \frac{6}{4\pi}\int d^3\vec{r}\, \Delta G_\varphi^{(2)T}(\vec{r}). \tag{4.7}$$

If $G_\varphi^{(2)T}(\vec{r})$ is a short range function then the integral in the RHS vanishes and we are left with the second SL sum rule

$$\frac{2\pi\beta}{3}\int d^3\vec{r}\, r^2 G_C^{(2)T}(\vec{r}) = -1. \tag{4.8}$$

We want to precise that the results derived in this section are not valid for $2D$ systems which can undergo a Kosterlitz–Thouless transition.[36] In the low-temperature KT phase of a $2D$ PM, the SL rules are violated and the sine-Gordon field should exhibit long range correlations with an algebraic decay. In this case, φ is a critical field and $\langle\varphi\rangle$ is related to the order parameter of the KT transition.[37]

5. THE MEAN FIELD THEORY

5.1. Mean Field Equations

We define the MF level or saddle point approximation of the theory by the equation

$$\Xi_{\mathrm{MF}}[\{v_\alpha\}] \equiv \exp(-\mathscr{H}(\bar{\varphi})), \tag{5.1}$$

where, at $\varphi = \bar{\varphi}$, the action $\mathscr{H}$ is stationary. It follows from the expression (2.21) of $\mathscr{H}$ that the stationarity condition

$$\left.\frac{\delta\mathscr{H}}{\delta\varphi(\vec{r})}\right|_{\bar{\varphi}} = 0 \tag{5.2}$$

may be rewritten as

$$\Delta_1 \bar{\varphi}(1) = -4\pi i \beta^{1/2} \rho_{\mathrm{HS},\,C}[\{\bar{v}_\alpha + i\bar{\phi}_\alpha\}](1), \tag{5.3a}$$

$$\bar{\phi}_\alpha(1) = q_\alpha \tau_\alpha(1, 1') \, \bar{\varphi}(1'). \tag{5.3b}$$

Two comments are in place here. Firstly, it can be pointed out that Eq. (5.3a) is very similar to the well known Poisson–Boltzmann equation.[38] Secondly, it is instructive to compare Eq. (5.3a) with the following exact relation, easily deduced from Eqs. (3.20) and (3.25)

$$\Delta_1 \langle \varphi(1) \rangle_{\mathscr{H}} = -4\pi i \beta^{1/2} \langle \rho_{\mathrm{HS},\,C}[\{\bar{v}_\alpha + i\phi_\alpha\}](1) \rangle_{\mathscr{H}}. \tag{5.4}$$

One notes that Eq. (5.3a) could have been guessed from the exact Eq. (5.4) with the usual assumption of an absence of field correlations at the MF level.

5.2. The Mean Field Grand Canonical Free Energy

The MF grand potential is easily obtained by substituting $\bar{\varphi}$ in Eq. (5.1) with the result

$$\begin{aligned}
\log \, &\Xi_{\mathrm{MF}}[\{v_\alpha\}] \\
&= \log \Xi_{\mathrm{HS}}[\{\bar{v}_\alpha + i\bar{\phi}_\alpha\}] - \frac{1}{2} \langle \bar{\varphi} | \, v_c^{-1} \, | \bar{\varphi} \rangle \\
&= \log \Xi_{\mathrm{HS}}[\{\bar{v}_\alpha + i\bar{\phi}_\alpha\}] + \frac{\beta}{2} \langle \rho_{\mathrm{HS},\,C}[\{\bar{v}_\alpha + i\bar{\phi}_\alpha\}] | \, v_c \, | \rho_{\mathrm{HS},\,C}[\{\bar{v}_\alpha + i\bar{\phi}_\alpha\}] \rangle.
\end{aligned} \tag{5.5}$$

The MF number density of species γ is obtained by taking the functional derivative of $\log \Xi_{\mathrm{MF}}[\{v_\alpha\}]$ with respect to the local chemical potential v_γ. On the one hand we have

$$\begin{aligned}
\frac{\delta \log \Xi_{\mathrm{HS}}[\{\bar{v}_\alpha + i\bar{\phi}_\alpha\}]}{\delta v_\gamma(1)} \\
&= \rho_{\mathrm{HS},\,\gamma}[\{\bar{v}_\alpha + i\bar{\phi}_\alpha\}](1) + \rho_{\mathrm{HS},\,\beta}[\{\bar{v}_\alpha + i\bar{\phi}_\alpha\}](1') \frac{\delta i\bar{\phi}_\beta(1')}{\delta v_\gamma(1)} \\
&= \rho_{\mathrm{HS},\,\gamma}[\{\bar{v}_\alpha + i\bar{\phi}_\alpha\}](1) + i\beta^{1/2} \rho_{\mathrm{HS},\,C}[\{\bar{v}_\alpha + i\bar{\phi}_\alpha\}](1') \frac{\delta \bar{\varphi}(1')}{\delta v_\gamma(1)}, \tag{5.6}
\end{aligned}$$

and, in the other hand

$$\frac{\delta}{\delta v_\gamma(1)} \frac{1}{2} \langle \bar{\varphi} | \, v_c^{-1} \, | \bar{\varphi} \rangle = -\frac{\delta \bar{\varphi}(1')}{\delta v_\gamma(1)} \frac{1}{4\pi} \, \Delta_{1'} \bar{\varphi}(1'). \tag{5.7}$$

Substracting Eqs. (5.6) and (5.7) and making use of the stationarity condition (5.3a) gives us

$$\rho_{\text{MF}, \gamma}(1) = \rho_{\text{HS}, \gamma}[\{\bar{v}_\alpha + i\bar{\phi}_\alpha\}](1), \tag{5.8}$$

from which we infer the expression of the MF charge density:

$$\rho_{\text{MF}, C}(1) = \rho_{\text{HS}, C}[\{\bar{v}_\alpha + i\bar{\phi}_\alpha\}](1). \tag{5.9}$$

In the case of a homogeneous system the MF KSSHE field $\bar{\varphi}$ is uniform and $\bar{\phi}_\alpha$ reduces to $\bar{\phi}_\alpha = \beta^{1/2} q_\alpha \bar{\varphi}$ since $\tilde{\tau}_\alpha(0) = 1$. Moreover, in this case, the MF equation (5.3a) takes the form of the charge neutrality condition

$$\rho_{\text{MF}, C} \equiv q_\alpha \rho_{\text{MF}, \alpha} = 0, \tag{5.10}$$

where $\rho_{\text{MF}, \alpha} = \rho_{\text{HS}, \alpha}[\{\bar{v}_\alpha + i\beta^{1/2} q_\alpha \bar{\varphi}\}]$. Therefore $\bar{\varphi}$ is an imaginary number which adjusts itself in such a way that the charge neutrality condition (5.10) is satisfied. For instance for a RPM with $v_1 = v_2$ one has $\bar{\varphi} = 0$, while for a binary SPM ($M = 2$) one finds, with the same hypothesis on the chemical potentials, that $\bar{\varphi} = -i \sqrt{\beta} \log(|q_2/q_1|)/(q_1 - q_2)$.

The MF grand canonical free energy $\mathscr{A}_{\text{MF}}$ is defined as the Legendre transform of $\log \Xi_{\text{MF}}[\{v_\alpha\}]$ with respect to the local chemical potentials $\{v_\alpha\}$.[25, 28, 39] Therefore one has

$$\beta \mathscr{A}_{\text{MF}} = \langle \rho_{\text{MF}, \alpha} | v_\alpha \rangle - \log \Xi_{\text{MF}}[\{v_\alpha\}]. \tag{5.11}$$

When expressed in terms of its natural variables $\{\rho_{\text{MF}, \alpha}\}$, the functional $\beta \mathscr{A}_{\text{MF}}[\{\rho_{\text{MF}, \alpha}\}]$ reads as

$$\beta \mathscr{A}_{\text{MF}}[\{\rho_{\text{MF}, \alpha}\}] = \beta \mathscr{A}_{\text{HS}}[\{\rho_{\text{MF}, \alpha}\}] - \langle \rho_{\text{MF}, \alpha} | v_\alpha^S \rangle + \frac{\beta}{2} \langle \rho_{\text{MF}, C} | v_c | \rho_{\text{MF}, C} \rangle, \tag{5.12}$$

as a short calculation will show. The functional $\mathscr{A}_{\text{HS}}[\{\rho_\alpha\}]$ which appears in the RHS of Eq. (5.12) is the exact GC free energy of an inhomogeneous hard spheres mixture. As it is well known it is a convex functional of the densities $\{\rho_\alpha\}$.[39, 40] On the other hand the quadratic form $\langle \rho_C | v_c | \rho_C \rangle$ is definite positive, therefore (strictly) convex. The last contribution to $\mathscr{A}_{\text{MF}}$,

i.e., the linear term $\langle \rho_\alpha | v_\alpha \rangle$, will not change our conclusion that $\mathscr{A}_{\mathrm{MF}}[\{\rho_\alpha\}]$ is a convex functional of the densities $\{\rho_\alpha\}$. Thence one has, for all $0 \leqslant \lambda \leqslant 1$

$$\mathscr{A}_{\mathrm{MF}}[\{\lambda \rho_\alpha + (1-\lambda) \rho'_\alpha\}] \leqslant \lambda \mathscr{A}_{\mathrm{MF}}[\{\rho_\alpha\}] + (1-\lambda) \mathscr{A}_{\mathrm{MF}}[\{\rho'_\alpha\}]. \quad (5.13)$$

Since $\mathscr{A}_{\mathrm{MF}}[\{\rho_\alpha\}]$ is convex then its Legendre transform exists and is also convex. Of course, the Legendre transform being involutive, it must be identified with $\log \varXi_{\mathrm{MF}}[\{v_\alpha\}]$. Therefore one has[39]

$$\beta \mathscr{A}_{\mathrm{MF}}[\{\rho_\alpha\}] = \sup_{\{v_\alpha\}} (\langle \rho_\alpha | v_\alpha \rangle - \log \varXi_{\mathrm{MF}}[\{v_\alpha\}]), \quad (5.14a)$$

$$\log \varXi_{\mathrm{MF}}[\{v_\alpha\}] = \sup_{\{\rho_\alpha\}} (\langle \rho_\alpha | v_\alpha \rangle - \beta \mathscr{A}_{\mathrm{MF}}[\{\rho_\alpha\}]). \quad (5.14b)$$

Some comments are in order. Firstly, assuming that a mixture of hard spheres cannot undergo a liquid-liquid transition (liquid-vapor or dimixion)[1] one can safely conclude that $\mathscr{A}_{\mathrm{HS}}[\{\rho_\alpha\}]$ is a strictly convex functional in the fluid region. As the sum of two strictly convex functionals (cf. Eq. (5.12)) the MF free energy functional $\mathscr{A}_{\mathrm{MF}}[\{\rho_\alpha\}]$ is also strictly convex in the fluid region as is the Poisson–Boltzmann functional.[41] In Eq. (5.13) the inequality can thus be replaced by a strict inequality for $0 < \lambda < 1$. An important consequence is that the solution the the MF equation (5.2) is unique for a given set of chemical potential $\{v_\alpha\}$ which rules out the possibility of a fluid–fluid transition of the PM at the MF level. Secondly, the charge neutrality condition (5.10) implies that for a homogeneous system the Helmoltz free energy per unit volume takes the (too much) simple form

$$\beta f_{\mathrm{MF}}(\{\rho_\alpha\}) \equiv \frac{\beta \mathscr{A}_{\mathrm{MF}}}{\Omega} = \beta f_{\mathrm{HS}}(\{\rho_\alpha\}) - \rho_\alpha v_\alpha^s. \quad (5.15)$$

where the charge neutrality condition $\rho_\alpha q_\alpha = 0$ has been imposed (otherwise βf_{MF} diverges to $+\infty$).

5.3. Mean Field Correlation Functions

5.3.1. General Case

It is the place here to recall that a necessary and sufficient condition for the convexity of $\log \varXi_{\mathrm{MF}}[\{v_\alpha\}]$ and $\mathscr{A}_{\mathrm{MF}}[\{\rho_\alpha\}]$ is that their second order functional derivatives are positive operators, i.e.,[25, 39, 40]

$$\left\langle \delta v_\alpha \left| \frac{\delta^{(2)} \log \varXi_{\mathrm{MF}}}{\delta v_\alpha(1)\, \delta v_\beta(2)} \right| \delta v_\beta \right\rangle > 0,$$

$$\left\langle \delta \rho_\alpha \left| \frac{\delta^{(2)} \beta \mathscr{A}_{\mathrm{MF}}}{\delta \rho_\alpha(1)\, \delta \rho_\beta(2)} \right| \delta \rho_\beta \right\rangle > 0.$$

(5.16)

We stress that the inequalities (5.16) are strict in the fluid phase because the two functionals $\log \varXi_{\mathrm{MF}}[\{v_\alpha\}]$ and $\mathscr{A}_{\mathrm{MF}}[\{\rho_\alpha\}]$ are both strictly convex. The second order derivatives of $\log \varXi_{\mathrm{MF}}$ with respect to the local chemical potentials are the density correlation functions at the MF level:

$$G^T_{\mathrm{MF},\,\alpha\beta}[\{v_\alpha\}](1,2) \equiv \frac{\delta^{(2)} \log \varXi_{\mathrm{MF}}}{\delta v_\alpha(1)\, \delta v_\beta(2)}.$$

(5.17)

Note that, since we consider only two-point functions in this section, we have further economized the notation by dropping the subscript (2) in the definition of $G^T_{\mathrm{MF},\,\alpha\beta}$. The second order derivatives of $\beta \mathscr{A}_{\mathrm{MF}}$ with respect to the densities are related to the the two-points direct correlation functions.[25, 29, 39] Define

$$\hat{C}_{\mathrm{MF},\,\alpha\beta}[\{\rho_\alpha\}](1,2) \equiv -\frac{\delta^{(2)} \beta \mathscr{A}_{\mathrm{MF}}}{\delta \rho_\alpha(1)\, \delta \rho_\beta(2)}.$$

(5.18)

In the terminology of statistical field theory $\hat{C}_{\mathrm{MF},\,\alpha\beta}$ is minus the two-point proper vertex; it is related to the usual direct correlation function $c_{\alpha\beta}$ of the theory of liquids by the relation[39]

$$\hat{C}_{\mathrm{MF},\,\alpha\beta}(1,2) = c_{\mathrm{MF},\,\alpha\beta}(1,2) - \frac{1}{\rho_\alpha(1)}\, \delta_{\alpha,\,\beta}\, \delta(1,2).$$

(5.19)

The strict convexity of the functionals $\log \varXi_{\mathrm{MF}}[\{v_\alpha\}]$ and $\beta \mathscr{A}_{\mathrm{MF}}[\{\rho_\alpha\}]$ guarantees the existence and unicity of the functions $G^T_{\mathrm{MF},\,\alpha\beta}$ and $\hat{C}_{\mathrm{MF},\,\alpha\beta}$. Moreover the operators $G^T_{\mathrm{MF},\,\alpha\beta}$ and $-\hat{C}_{\mathrm{MF},\,\alpha\beta}$ are both strictly positive and $-\hat{C}_{\mathrm{MF},\,\alpha\beta}$ is the inverse of $G^T_{\mathrm{MF},\,\alpha\beta}$, i.e.,

$$-\hat{C}_{\mathrm{MF},\,\alpha\beta}(1,2)\, G^T_{\mathrm{MF},\,\beta\gamma}(2,3) = \delta_{\alpha,\,\gamma}\delta(1,3),$$

(5.20)

which, when reexpressed in terms of the functions $h_{\alpha\beta}$ and $c_{\alpha\beta}$, takes the familiar form of the Orstein–Zernike equation[1]

$$h_{\mathrm{MF},\,\alpha\beta}(1,2) = c_{\mathrm{MF},\,\alpha\beta}(1,2) + h_{\mathrm{MF},\,\alpha\gamma}(1,3)\, \rho_\gamma(3)\, c_{\mathrm{MF},\,\gamma\beta}(3,2).$$

(5.21)

$\hat{C}_{\text{MF}, \alpha\beta}(1, 2)$ is obtained readily from the expression (5.12) of the MF free energy functional $\beta \mathscr{A}_{\text{MF}}[\{\rho_\alpha\}]$ with the simple result

$$\hat{C}_{\text{MF}, \alpha\beta}(1, 2) = \hat{C}_{\text{HS}, \alpha\beta}(1, 2) - \beta q_\alpha q_\beta w_{\alpha\beta}(1, 2), \tag{5.22}$$

where $\hat{C}_{\text{HS}, \alpha\beta}(1, 2)$ is minus the exact two-point proper vertex of the reference HS fluid at the mean field densities $\{\rho_{\text{MF}, \alpha}\}$. Equation (5.22) implies that for a homogeneous system and for $r_{12} \geqslant (\bar{\sigma}_\alpha + \bar{\sigma}_\beta)$ the direct MF correlation functions reads as

$$c_{\text{MF}, \alpha\beta}(r_{12}) = c_{\text{HS}, \alpha\beta}(r_{12}) - \beta q_\alpha q_\beta / r_{12}, \tag{5.23}$$

which is nothing but the RPA closure of the theory of liquids.[1, 21]

The calculation of $G_{\beta\gamma}^{\text{MF}, T}(1, 2)$ is more involved. Our starting point will be the equation

$$\begin{aligned} G_{\text{MF}, \alpha\beta}^T(1, 2) &= \frac{\delta \rho_{\text{MF}, \alpha}[\{v_\gamma\}](1)}{\delta v_\beta(2)} \\ &= \frac{\delta \rho_{\text{HS}, \alpha}[\{\bar{v}_\gamma + i\bar{\phi}_\gamma\}](1)}{\delta v_\beta(2)}. \end{aligned} \tag{5.24}$$

Clearly $\rho_{\text{HS}, \alpha}[\{\bar{v}_\gamma + i\bar{\phi}_\gamma\}]$ depends upon v_β directly but also through the smeared mean fields $\bar{\phi}_\gamma$; therefore one has

$$\begin{aligned} G_{\text{MF}, \alpha\beta}^T(1, 2) &= \frac{\delta \rho_{\text{HS}, \alpha}[\{\bar{v}_\gamma + i\bar{\phi}_\gamma\}](1)}{\delta v_\beta(2)}\bigg|_{\bar{\phi}} + \frac{\delta \rho_{\text{HS}, \alpha}[\{\bar{v}_\gamma + i\bar{\phi}_\gamma\}](1)}{\delta \bar{\varphi}(3)}\bigg|_{v_\gamma} \frac{\delta \bar{\varphi}(3)}{\delta v_\beta(2)} \\ &= G_{\text{HS}, \alpha\beta}^T(1, 2) + i\beta^{1/2} G_{\text{MF}, \alpha\gamma}^T(1, 4) \, q_\gamma \tau_\gamma(4, 3) \frac{\delta \bar{\varphi}(3)}{\delta v_\beta(2)}. \end{aligned} \tag{5.25}$$

Now, remarking that the stationarity condition (5.3a) implies that

$$\frac{\delta \bar{\varphi}(3)}{\delta v_\beta(2)} = i\beta^{1/2} v_c(3, 5) \, q_\delta \tau_\delta(5, 6) \, G_{\text{MF}, \delta\beta}^T(6, 2), \tag{5.26}$$

one obtains

$$\begin{aligned} G_{\text{MF}, \alpha\beta}^T(1, 2) = {} & G_{\text{HS}, \alpha\beta}^T(1, 2) \\ & - \beta G_{\text{HS}, \alpha\gamma}^T(1, 4) \, q_\gamma \tau_\gamma(4, 3) \, v_c(3, 5) \, q_\delta \tau_\delta(5, 6) \, G_{\text{MF}, \delta\beta}^T(6, 2), \end{aligned} \tag{5.27}$$

which can be rewritten under a matricial form as

$$\underline{G}^T_{\mathrm{MF}}(1, 2) = \underline{G}^T_{\mathrm{HS}}(1, 2) - \beta \underline{G}^T_{\mathrm{HS}}(1, 3) \, \underline{v}(3, 4) \, \underline{G}^T_{\mathrm{MF}}(4, 2), \qquad (5.28)$$

where $\underline{G}^T_{\mathrm{MF(HS)}}(1, 2)$ denotes the matrix of elements $G^T_{\mathrm{MF(HS)}, \alpha\beta}(1, 2)$ and $\underline{v}(1, 2)$ that of elements $v_{\alpha\beta}(1, 2)$ (cf. Eq. (2.4)) The formal solution of Eq. (5.28) is then

$$\underline{G}^T_{\mathrm{MF}}(1, 2) = (\underline{1} + \beta \, \underline{G}^T_{\mathrm{HS}} * \underline{v})^{-1} * \underline{G}^T_{\mathrm{HS}}, \qquad (5.29)$$

where $\underline{1}_{\alpha\beta}(1, 2) = \delta_{\alpha\beta}\delta(1, 2)$ is the unit operator and the star "$*$" denotes a convolution. One easily checks that $G^T_{\mathrm{MF}, \alpha\beta}$ and $\hat{C}_{\mathrm{MF}, \alpha\beta}$ as given by Eqs. (5.29) and (5.22) respectively do satisfy the OZ equation (5.20).

In the case of a homogeneous system Eq. (5.29) can be simplified considerably. Let us work in Fourier space where we have

$$\underline{\tilde{G}}^T_{\mathrm{MF}}(k) = (\underline{U} - \underline{\tilde{P}}(k))^{-1} \cdot \underline{\tilde{G}}^T_{\mathrm{HS}}(k), \qquad (5.30)$$

where $\underline{U}_{\alpha\beta} = \delta_{\alpha\beta}$ is the unit matrix of rank $M \times M$ and $\underline{\tilde{P}}(k)$ denotes the matrix of elements

$$\tilde{P}_{\alpha\beta} = -\beta \tilde{v}_c(k) \, \tilde{G}^T_{\mathrm{HS}, \alpha\gamma}(k) \, q_\gamma q_\beta \tilde{\tau}_\gamma(k) \, \tilde{\tau}_\beta(k) \quad (\text{no sum over } \beta). \qquad (5.31)$$

$\underline{\tilde{P}}(k)$ has the remarkable property that

$$\underline{\tilde{P}}^2(k) = -\beta \tilde{v}_c(k) \, \tilde{G}^T_{\mathrm{HS}, C}(k) \, \underline{\tilde{P}}(k), \qquad (5.32)$$

which leads us to search the inverse of $\underline{U} - \underline{\tilde{P}}(k)$ under the form $(\underline{U} - \underline{\tilde{P}}(k))^{-1} = \underline{U} + \tilde{\mu}(k) \, \underline{\tilde{P}}(k)$. The identity $(\underline{U} + \tilde{\mu}(k) \, \underline{\tilde{P}}(k)) \cdot (\underline{U} - \underline{\tilde{P}}(k)) = \underline{1}$ when combined with the property (5.32) implies that

$$\mu(k) = \frac{1}{1 + \beta \tilde{v}_c(k) \, \tilde{G}^T_{\mathrm{HS}, C}(k)}. \qquad (5.33)$$

Therefore

$$(\underline{U} - \underline{\tilde{P}}(k))^{-1} = \underline{U} + \frac{\underline{\tilde{P}}(k)}{1 + \beta \tilde{v}_c(k) \, \tilde{G}^T_{\mathrm{HS}, C}(k)}, \qquad (5.34)$$

from which a simple expression for $\tilde{G}^T_{\mathrm{MF}, \alpha\beta}(k)$ is easily obtained

$$\tilde{G}^T_{\mathrm{MF}, \alpha\beta}(k) = \tilde{G}^T_{\mathrm{HS}, \alpha\beta}(k) - \frac{\beta \tilde{v}_c(k) \, \Gamma_\alpha(k) \, \Gamma_\beta(k)}{1 + \beta \tilde{v}_c(k) \, \tilde{G}^T_{\mathrm{HS}, C}(k)}, \qquad (5.35a)$$

$$\Gamma_\alpha(k) = \tilde{G}^T_{\mathrm{HS}, \alpha\gamma}(k) \, q_\gamma \tilde{\tau}_\gamma(k). \qquad (5.35b)$$

The expressions of the Fourier transforms of the usual pair correlations $h_{\mathrm{MF}, \alpha\beta}$ can then be deduced from Eqs. (5.35). One finds

$$\tilde{h}_{\mathrm{MF}, \alpha\beta}(k) = \tilde{h}_{\mathrm{HS}, \alpha\beta}(k) - \frac{\Gamma_\alpha(k)}{\rho_\alpha} \frac{\Gamma_\beta(k)}{\rho_\beta} \frac{\beta \tilde{v}_c(k)}{1 + \beta \tilde{v}_c(k) \, \tilde{G}^T_{\mathrm{HS}, C}(k)}. \tag{5.36}$$

An important comment is in place here. As well known, the fact that the direct correlation functions (5.23) behave as the Coulomb potential at large distances is sufficient to ensure that the SL rules are satisfied.[1, 42] Therefore, the $h_{\mathrm{MF}, \alpha\beta}(r)$, the Fourier transforms of which are given above, automatically satisfy to the SL sum rules.

The two-point MF charge correlation is obtained by taking the convolution of the two members of Eq. (5.27) with $q_\alpha q_\beta \tau_\alpha(1, 1') \, \tau_\beta(2, 2')$ which gives the equation

$$G^T_{\mathrm{MF}, C}(1, 2) = G^T_{\mathrm{HS}, C}(1, 2) - \beta G^T_{\mathrm{HS}, C}(1, 1') \, v_c(1', 2') \, G^T_{\mathrm{MF}, C}(2', 2), \tag{5.37}$$

the formal solution of which is

$$G^T_{\mathrm{MF}, C} = (1 + \beta G^T_{\mathrm{HS}, C} * v_c)^{-1} * G^T_{\mathrm{HS}, C}. \tag{5.38}$$

Therefore, for a homogeneous system, the Fourier transform of $G^T_{\mathrm{MF}, C}(r)$ has the simple expression

$$\tilde{G}^T_{\mathrm{MF}, C}(k) = \frac{k^2 \tilde{G}^T_{\mathrm{HS}, C}(k)}{k^2 + 4\pi\beta \tilde{G}^T_{\mathrm{HS}, C}(k)}. \tag{5.39}$$

Finally the truncated pair correlation function of the KSSHE field is obtained by using Eq. (3.29) which gives us

$$\begin{aligned} G^T_{\mathrm{MF}, \varphi}(1, 2) &= v_c(1, 2) - \beta v_c(1, 1') \, G^T_{\mathrm{MF}, C}(1', 2') \, v_c(2', 2) \\ &= (1 + \beta G^T_{\mathrm{HS}, C} * v_c)^{-1} \, (1, 1') \, v_c(1', 2). \end{aligned} \tag{5.40}$$

For an homogeneous fluid, one thus has in Fourier space

$$\tilde{G}^T_{\mathrm{MF}, \varphi}(k) = \frac{4\pi}{k^2 + 4\pi\beta \tilde{G}^T_{\mathrm{HS}, C}(k)}. \tag{5.41}$$

5.3.2. Application to the Special Primitive Model

In the SPM all the spheres have the same diameter $\sigma_\alpha = \sigma$ and we also assume that all the smearing distributions τ_α are identical with the same τ.

With these assumptions the functions $G_{\mathrm{HS},C}^{(n)\,T}$ are nearly decoupled of the density correlations $G_{\mathrm{HS}}^{(n)\,T}$ of the HS reference fluid. For instance one has for $n=2$

$$\widetilde{G}_{\mathrm{HS},C}^{T}(k) = \rho_{\mathrm{MF},\alpha} q_{\alpha}^{2}\,\widetilde{\tau}^{2}(k), \tag{5.42}$$

which entails considerable simplifications. Indeed the MF pair correlation functions take the simple form

$$\widetilde{h}_{\mathrm{MF},\alpha\beta}(k) = \widetilde{h}_{\mathrm{HS}}(k) - \frac{4\pi\beta q_{\alpha}q_{\beta}\widetilde{\tau}^{2}(k)}{k^{2}+\kappa_{\mathrm{MF}}^{2}\widetilde{\tau}^{2}(k)}, \tag{5.43}$$

where $\kappa_{\mathrm{MF}}^{2} = 4\pi\beta\rho_{\mathrm{MF},\alpha} q_{\alpha}^{2}$ is the squared Debye number and $h_{\mathrm{HS}}(r)$ the truncated pair correlation function of the HS fluid at the density $\rho_{\mathrm{MF}} = \sum \rho_{\mathrm{MF},\alpha}$. Equation (5.43) when combined with the electroneutrality condition implies that the correlations of the (total) density are equal to those of the HS reference fluid which rules out a liquid-vapor transition of the SPM at the MF level. Moreover the charge and KSSHE field correlations of the SPM appear to be completely decoupled from the density fluctuations since one finds

$$\widetilde{G}_{\mathrm{MF},C}^{T}(k) = \frac{1}{4\pi\beta}\frac{\kappa_{\mathrm{MF}}^{2}\widetilde{\tau}^{2}(k)\,k^{2}}{k^{2}+\widetilde{\tau}^{2}(k)\,\kappa_{\mathrm{MF}}^{2}}, \tag{5.44a}$$

$$\widetilde{G}_{\mathrm{MF},\varphi}^{T}(k) = \frac{4\pi}{k^{2}+\widetilde{\tau}^{2}(k)\,\kappa_{\mathrm{MF}}^{2}}. \tag{5.44b}$$

5.4. The Mean Field Free Energy as an Exact Lower Bound of the Free Energy

It can be shown, under quite general conditions, that the logarithm of the grand-partition function $\log \varXi[\{\mu_{\alpha}\}]$ is a convex functional of the local chemical potentials even before the passage to the thermodynamic limit. Similarly, the exact Kohn–Sham free energy $\beta\mathscr{A}[\{\rho_{\alpha}\}]$ is a convex functional of the local densities. Moreover $\log \varXi[\{\mu_{\alpha}\}]$ and $\mathscr{A}[\{\rho_{\alpha}\}]$ constitute a pair of Legendre transforms which can be expressed as[25, 39, 40]

$$\beta\mathscr{A}[\{\rho_{\alpha}\}] = \sup_{\{v_{\alpha}\}}\,(\langle\rho_{\alpha}\,|\,v_{\alpha}\rangle - \log \varXi[\{v_{\alpha}\}]), \tag{5.45a}$$

$$\log \varXi[\{v_{\alpha}\}] = \sup_{\{\rho_{\alpha}\}}\,(\langle\rho_{\alpha}\,|\,v_{\alpha}\rangle - \beta\mathscr{A}[\{\rho_{\alpha}\}]). \tag{5.45b}$$

Recall that the Young inequalities which follow directly from Eqs. (5.45a) and (5.45b) say that

$$\beta \mathscr{A}[\{\rho_\alpha\}] + \log \varXi[\{\nu_\alpha\}] \geqslant \langle \rho_\alpha | \nu_\alpha \rangle \qquad (\forall \{\nu_\alpha\}, \forall \{\rho_\alpha\}). \qquad (5.46)$$

We have seen in Section 5.2 that the MF functionals $\log \varXi_{\mathrm{MF}}[\{\mu_\alpha\}]$ and $\mathscr{A}_{\mathrm{MF}}[\{\rho_\alpha\}]$ are also two convex functionals linked by a Legendre transform. We establish below some rigorous inequalities between the exact and MF free energies and grand potentials which extend to ionic fluids results recently obtained for neutral fluids.[27]

First, we notice that the fundamental Eq. (2.20) rewritten as

$$\varXi[\{\nu_\alpha\}] = \langle \exp(\log \varXi_{\mathrm{HS}}[\{\nu_\alpha + \nu_\alpha^S + i\phi_\alpha\}]) \rangle_{\nu_c} \qquad (\forall \{\nu_\alpha\}), \qquad (5.47)$$

can be inverted in order to give

$$\varXi_{\mathrm{HS}}[\{\nu_\alpha\}] = \langle \exp(\log \varXi[\{\nu_\alpha - \nu_\alpha^S + \phi_\alpha\}]) \rangle_{\nu_c} \qquad (\forall \{\nu_\alpha\}). \qquad (5.48)$$

Then, we apply Young inequality (5.46) to the RHS of Eq. (5.48) which yields

$$\varXi_{\mathrm{HS}}[\{\nu_\alpha\}] \geqslant \exp(-\beta \mathscr{A}[\{\rho_\alpha\}] + \langle \rho_\alpha | \nu_\alpha - \nu_\alpha^S \rangle) \langle \exp(\langle j | \varphi \rangle) \rangle_{\nu_c}$$
$$(\forall \{\nu_\alpha\}, \forall \{\rho_\alpha\}), \qquad (5.49)$$

where it follows from the definition (2.17) of the smeared field ϕ_α that

$$j(1) = \beta^{1/2} q_\alpha \tau_\alpha(1, 1') \rho_\alpha(1'). \qquad (5.50)$$

The field average in the RHS of Eq. (5.49) is computed by making use of Wick's theorem which yields

$$\langle \exp(\langle j | \varphi \rangle) \rangle_{\nu_c} = \exp\left(\frac{\beta}{2} \langle \rho_C | \nu_c | \rho_C \rangle \right). \qquad (5.51)$$

By inserting the above result into Eq. (5.49) we obtain

$$\log \varXi_{\mathrm{HS}}[\{\nu_\alpha\}] \geqslant -\beta \mathscr{A}[\{\rho_\alpha\}] + \langle \rho_\alpha | \nu_\alpha - \nu_\alpha^S \rangle$$
$$+ \frac{\beta}{2} \langle \rho_C | \nu_c | \rho_C \rangle \qquad (\forall \{\nu_\alpha\}, \forall \{\rho_\alpha\}), \qquad (5.52)$$

which implies

$$\beta \mathscr{A}[\{\rho_\alpha\}] \geqslant \sup_{\{v_\alpha\}} \ [\langle \rho_\alpha \,|\, v_\alpha \rangle - \log \varXi_{\mathrm{HS}}[\{v_\alpha\}]]$$

$$+ \frac{\beta}{2} \langle \rho_C |\, v_c \,| \rho_C \rangle - \langle \rho_\alpha \,|\, v_\alpha^S \rangle \qquad (\forall \{\rho_\alpha\}). \qquad (5.53)$$

The sup in the RHS of Eq. (5.53) is the Legendre transform of the exact grand potential $\log \varXi_{\mathrm{HS}}[\{v_\alpha\}]$, i.e., the free energy $\beta \mathscr{A}^{\mathrm{HS}}[\{\rho_\alpha\}]$. It follows then from the expression (5.12) of $\beta \mathscr{A}_{\mathrm{MF}}$ that Eq. (5.53) may be recast under the form

$$\beta \mathscr{A}[\{\rho_\alpha\}] \geqslant \beta \mathscr{A}_{\mathrm{MF}}[\{\rho_\alpha\}] \qquad (\forall \{\rho_\alpha\}). \qquad (5.54)$$

Therefore the MF free energy $\beta \mathscr{A}_{\mathrm{MF}}[\{\rho_\alpha\}]$ is a rigorous lower bound of the exact GC free energy $\beta \mathscr{A}[\{\rho_\alpha\}]$. Moreover since $\beta \mathscr{A}_{\mathrm{MF}}$ and $\log \varXi_{\mathrm{HS}}$ are linked by a Legendre transform (see Eqs. (5.14a) and (5.14b)) we also have

$$\log \varXi_{\mathrm{MF}}[\{v_\alpha\}] = \sup_{\{\rho_\alpha\}} \ [\langle \rho_\alpha \,|\, v_\alpha \rangle - \beta \mathscr{A}_{\mathrm{MF}}[\{\rho_\alpha\}]] \qquad (\forall \{v_\alpha\})$$

$$\geqslant \sup_{\{\rho_\alpha\}} \ [\langle \rho_\alpha \,|\, v_\alpha \rangle - \beta \mathscr{A}[\{\rho_\alpha\}]] \qquad (\forall \{v_\alpha\}), \qquad (5.55)$$

which can be, with help of Eq. (5.45b), rewritten as

$$\log \varXi_{\mathrm{MF}}[\{v_\alpha\}] \geqslant \log \varXi[\{v_\alpha\}] \qquad (\forall \{v_\alpha\}). \qquad (5.56)$$

In other words $\log \varXi_{\mathrm{MF}}[\{v_\alpha\}]$ is a *rigorous upper bound* of the grand potential $\log \varXi[\{v_\alpha\}]$. Recall that, for a homogeneous system in the point-like limit, the Debye–Hückel approximation for the pressure constitutes a *rigorous lower bound* for the pressure (this result can also be proved with the help of the sine-Gordon transform.[43]). Here, in the point-like limit the upper bound $\beta P_{\mathrm{MF}} \equiv \log \varXi_{\mathrm{MF}}[\{v_\alpha\}]/\Omega$ diverges to $+\infty$ since, in this limit $v_S \to +\infty$, leaving us with a much less interesting result.

Let us specialize now to the homogeneous case. We denote by $\beta f(\{\rho_\alpha\})$ the exact free energy per unit volume of the system. It is bounded from below by $\beta f_{\mathrm{MF}}(\{\rho_\alpha\})$ and we have therefore

$$\beta f(\{\rho_\alpha\}) \geqslant \beta f_{\mathrm{HS}}(\{\rho_\alpha\}) - \rho_\alpha v_\alpha^S, \qquad (5.57)$$

where the electroneutrality condition $\rho_C = 0$ has been imposed. It follows from Eq. (5.57) that the "best" or "optimized" MF free energy is obtained by minimizing the functional $K[\{\tau_\alpha\}] = \rho_\alpha v_\alpha^S = \beta \rho_\alpha q_\alpha^2 w_{\alpha\alpha}(0)/2$ with respect

to the variations of the smearing functions $\{\tau_\alpha(\vec{r})\}$. Since these distributions are normalized to unity we introduce M Legendre parameters λ_α and define the functional

$$\bar{K}[\{\tau_\alpha\}] = \tfrac{1}{2}\beta\rho_\alpha q_\alpha^2 w_{\alpha\alpha}(0) - \lambda_\alpha Q_\alpha[\tau_\alpha]$$

$$Q_\alpha[\tau_\alpha] = \int_{r < \bar{\sigma}_\alpha} d^3\vec{r}\, \tau_\alpha(\vec{r}). \tag{5.58}$$

Now, we minimize $\bar{K}[\{\tau_\alpha\}]$ for a given set of λ_α. The constraints $Q_\alpha = 1$ ($\forall\alpha$) will utimately serve to determine the values of the Legendre parameters λ_α. The conditions for an extremum of $\bar{K}$ are

$$\frac{\delta\bar{K}[\{\tau_\alpha\}]}{\delta\tau_\gamma(\vec{r})} = 0 \qquad (\forall\gamma \in (1,...,M), \|\vec{r}\| \leqslant \bar{\sigma}_\gamma). \tag{5.59}$$

Since $w_{\alpha\alpha}(r_{12}) \equiv w_{\alpha\alpha}(1,2) = \tau_\alpha(1,1')\,\tau_\alpha(2,2')\,v_c(1',2')$ we have

$$\frac{\delta w_{\alpha\alpha}(0)}{\delta\tau_\gamma(\vec{r})} = 2\delta_{\alpha\gamma}V_\gamma(\vec{r}), \tag{5.60}$$

where V_γ is the electrostatic potential created by the charge distribution τ_γ (i.e., $V_\gamma(r_{12}) \equiv V_\gamma(1,2) = \tau_\gamma(1,2')\,v_c(2',2)$). The stationarity condition (5.59) takes thus the form

$$V_\gamma(\vec{r}) = \lambda_\gamma \qquad (\forall\gamma \in (1,...,M), \|\vec{r}\| \leqslant \bar{\sigma}_\gamma). \tag{5.61}$$

The potential V_γ created by the distribution τ_γ must therefore be constant inside the sphere of radius $\bar{\sigma}_\alpha$. From elementary electrostatics we conclude that $\tau_\gamma(\vec{r})$ must be an uniform surface distribution of charge of radius $\bar{\sigma}_\alpha$. In order to satisfy the constraint $Q_\gamma = 1$ one must have

$$\tau_\gamma(\vec{r}) = \delta(\|\vec{r}\| - \bar{\sigma}_\gamma)\frac{1}{\pi\sigma_\gamma^2}. \tag{5.62}$$

Note that the solution (5.62) is indeed a minimum of $\bar{K}$ since its second order functional derivative with respect to τ_α is the Coulomb potential $v_c(1,2)$ which is a positive operator. The simple form of the Fourier transform of $\tau_\gamma(\vec{r})$ which is found to be

$$\tilde{\tau}_\gamma(k) = \frac{\sin(k\bar{\sigma}_\gamma)}{k\bar{\sigma}_\gamma} \tag{5.63}$$

allows us to compute explicitly the pair potentials $w_{\alpha\beta}(r)$ as the inverse Fourier transforms of the functions $\tilde{w}_{\alpha\beta}(k) = 4\pi\tilde{\tau}_\alpha(k)\,\tilde{\tau}_\beta(k)/k^2$ with the result

$$r > \bar{\sigma}_\alpha + \bar{\sigma}_\beta \Rightarrow w_{\alpha\beta}(r) = \frac{1}{r} \tag{5.64a}$$

$$\bar{\sigma}_\alpha - \bar{\sigma}_\beta < r < \bar{\sigma}_\alpha + \bar{\sigma}_\beta \Rightarrow w_{\alpha\beta}(r) = \frac{\sigma_\alpha + \sigma_\beta - r}{\sigma_\alpha \sigma_\beta} + \frac{1}{2r} - \frac{1}{4r}\frac{\sigma_\alpha^2 + \sigma_\beta^2}{\sigma_\alpha \sigma_\beta} \tag{5.64b}$$

$$0 < r < \bar{\sigma}_\alpha - \bar{\sigma}_\beta \Rightarrow w_{\alpha\beta}(r) = \frac{2}{\sigma_\alpha}, \tag{5.64c}$$

where it was assumed that $\sigma_\alpha \geqslant \sigma_\beta$. As a subproduct of these equations we obtain the self-energies $v_\alpha^S = \beta q_\alpha^2/\sigma_\alpha$ and thus the expression of the optimized MF free energy

$$\beta f_{\mathrm{MF}}(\{\rho_\alpha\}) = \beta f_{\mathrm{HS}}(\{\rho_\alpha\}) - \frac{\beta q_\alpha^2}{\sigma_\alpha}\,\rho_\alpha. \tag{5.65}$$

Note that the corresponding excess internal energy per unit volume $\beta u_{\mathrm{MF}} = \partial(\beta f_{\mathrm{MF}})/\partial\beta = -\beta\rho_\alpha q_\alpha^2/\sigma_\alpha$ coincides with the Onsager lower bound.[44] We note that the MF approximation is thermodynamically inconsistent in the sense that the MF energy u_{MF} is obviously not equal to that which can be obtained by the integration of $g_{\mathrm{MF},\,\alpha\beta}(r)\,w_{\alpha\beta}(r)$.

Reporting the expressions (5.64) of the pair potentials $w_{\alpha\beta}(r)$ in the equations (5.18) one obtains the MF direct correlation functions. We shall discuss only the case of the SPM where all the radii σ_α are equal to the same σ. In this case one finds

$$r > \sigma \Rightarrow c_{\mathrm{MF},\,\alpha\beta}(r) = c_{\mathrm{HS}}(r) - \beta q_\alpha q_\beta/r \tag{5.66a}$$

$$0 < r < \sigma \Rightarrow c_{\mathrm{MF},\,\alpha\beta}(r) = c_{\mathrm{HS}}(r) - \beta q_\alpha q_\beta\,\frac{2\sigma - r}{\sigma^2}, \tag{5.66b}$$

where $c_{\mathrm{HS}}(r)$ is the exact direct correlation function of the HS fluid at the density $\rho = \sum_\alpha \rho_\alpha$. The expressions (5.66) of the $c_{\alpha\beta}$ are very similar to that obtained in the framework of the MSA approximation, i.e.,[42, 45]

$$r > \sigma \Rightarrow c_{\mathrm{MSA},\,\alpha\beta}(r) = c_{\mathrm{HS}}^{\mathrm{PY}}(r) - \beta q_\alpha q_\beta/r \tag{5.67a}$$

$$0 < r < \sigma \Rightarrow c_{\mathrm{MSA},\,\alpha\beta}(r) = c_{\mathrm{HS}}^{\mathrm{PY}}(r) - \beta q_\alpha q_\beta\,\frac{2B\sigma - B^2 r}{\sigma^2}, \tag{5.67b}$$

where $c_{\mathrm{HS}}^{\mathrm{PY}}(r)$ denotes the direct correlation function of the HS fluid in the Percus–Yevick approximation which is an excellent approximation of the exact $c_{\mathrm{HS}}(r)$ especially at low or moderate densities.[1] The main difference between Eqs. (5.66) and. (5.67) is the occurrence of a parameter B in the MSA solution. Clearly the MF and MSA solutions coincide for $B = 1$. Since we have[42, 45]

$$B = \frac{\kappa^2 \sigma^2}{(\kappa\sigma)^2 + \kappa\sigma - \kappa\sigma(1 + 2\kappa\sigma)^{1/2}}, \tag{5.68}$$

where κ is the Debye number, it happens only in the limit $\kappa \to \infty$. For a finite κ, $B(\kappa)$ is positive and comprised between 0 and 1. Obviously the electrostatic contribution to $c_{\alpha\beta}^{\mathrm{MSA}}(r)$ in the core (i.e., the second term in the RHS of Eq. (5.67b)) may be seen as the interaction energy $w_{\alpha\beta}(r)$ of two surface distributions of charge of equal radii $\bar{\sigma}' = \bar{\sigma}/B$. However, since $B < 1 \Rightarrow \bar{\sigma}' > \bar{\sigma}$, this interaction energy is not equal to $1/r$ outside the core. Consequently the MSA solution cannot be interpreted as a MF KSSHE theory except in the limiting case $B = 1$.

6. THE GAUSSIAN APPROXIMATION

6.1. The General Case

Let us define the Gaussian approximation of the KSSHE theory in the following way.[20] We write $\varphi = \bar{\varphi} + \delta\varphi$ where $\bar{\varphi}$ is the mean field solution and $\delta\varphi$ a real scalar field and we expand functionally the action $\mathscr{H}[\varphi]$ (cf. Eq. (2.21)) up to second order in $\delta\varphi$ around the MF solution. In this way the exact action $\mathscr{H}[\varphi]$ is replaced by an approximate action $\mathscr{H}_G[\varphi]$ given by

$$\mathscr{H}_G[\varphi] = \mathscr{H}[\bar{\varphi}] + \tfrac{1}{2}\langle \delta\varphi | \, \Delta^{-1} \, | \delta\varphi \rangle, \tag{6.1}$$

where the terms linear in $\delta\varphi$ are absent as a consequence of the stationarity condition (5.2), and the inverse of the propagator Δ is given by:

$$\Delta^{-1}(1, 2) = v_c^{-1}(1, 2) + \beta G_{\mathrm{HS}, C}^T(1, 2). \tag{6.2}$$

A comparison of Eq. (6.2) with Eq. (5.40) yields the expected result[20]

$$\Delta(1, 2) = G_{\mathrm{MF}, \varphi}^T(1, 2). \tag{6.3}$$

In the Gaussian approximation, the grand partition function is therefore given by

$$\Xi_G[\{v_\alpha\}] = \exp(-\mathscr{H}[\bar{\varphi}]) \frac{\int \mathscr{D}\varphi \exp(-\frac{1}{2} \langle\varphi| \Delta^{-1} |\varphi\rangle)}{\int \mathscr{D}\varphi \exp(-\frac{1}{2} \langle\varphi| v_c^{-1} |\varphi\rangle)}. \tag{6.4}$$

From now we specialize to the case of a homogeneous system for which an explicit expression of Ξ_G can be obtained, i.e.,

$$\Xi_G[\{v_\alpha\}] = \exp(-\mathscr{H}[\bar{\varphi}]) \frac{\mathscr{N}_\Delta}{\mathscr{N}_{v_c}}, \tag{6.5}$$

where the normalization constants $\mathscr{N}_\Delta$ and $\mathscr{N}_{v_c}$ are defined according to Eq. (2.13). A well known property of functional integrals of Gaussian functionals gives us[20, 23, 24]

$$\log \frac{\mathscr{N}_\Delta}{\mathscr{N}_{v_c}} = \frac{\Omega}{2} \int d^\vee k \log \frac{\tilde{\Delta}(k)}{\tilde{v}_c(k)}$$
$$= -\frac{\Omega}{2} \int d^\vee k \log \left(1 + \frac{4\pi\beta}{k^2} \tilde{G}_{HS, C}^T(k) \right). \tag{6.6}$$

Taking the logarithm of Eq. (6.5) and taking into account the relation (6.6) we thus obtain the pressure of the ionic solution at the Gaussian level:

$$\beta P_G[\{v_\alpha\}] = \beta P_{HS}[\{\bar{v}_\alpha + i\beta^{1/2}\bar{\varphi}\}]$$
$$- \frac{1}{2} \int d^\vee k \log \left(1 + \frac{4\pi\beta}{k^2} q_\alpha q_\beta \tilde{\tau}_\alpha(k) \tilde{\tau}_\beta(k) \tilde{G}_{HS, \alpha\beta}^T(k) \right), \tag{6.7}$$

where we have expanded the HS charge correlation function in oder to make explicit the dependence of the result upon the smearing functions $\tilde{\tau}_\alpha(k)$. Note that the HS truncated pair correlation functions $\tilde{G}_{HS, \alpha\beta}^T(k)$ must be evaluated at the chemical potentials $\{\bar{v}_\alpha + i\beta^{1/2}\bar{\varphi}\}$. As a short examination reveals, the integral in the RHS of Eq. (6.7) is convergent at large k for any reasonable smearing function τ_α (i.e., surface, volume distributions etc) but diverges for point charge distributions ($\tilde{\tau}_\alpha(k) = 1$).

Some words on the field correlation functions at the Gaussian level. Following Ma[20] we define

$$G_{G, \varphi}^{(n)}(1,...,n) = \frac{\int \mathscr{D}\varphi \exp(-\mathscr{H}_G[\varphi]) \varphi(1)\cdots\varphi(n)}{\int \mathscr{D}\varphi \exp(-\mathscr{H}_G[\varphi])} \tag{6.8}$$

which entails the relations

$$\langle \delta \varphi \rangle_{\mathscr{H}_G} = 0, \tag{6.9a}$$

$$G_{G,\varphi}^{(2)T}(1, 2) = \Delta(1, 2) \equiv G_{\mathrm{MF},\varphi}^{(2)T}(1, 2), \tag{6.9b}$$

$$G_{G,\varphi}^{(n)T}(1,\ldots, n) = 0 \qquad \text{for} \quad n \geqslant 3. \tag{6.9c}$$

In particular, Eq. (6.9a) says that the number densities in the Gaussian approximation coincide with their MF values. The Legendre transform of βP_G is therefore easily obtained and reads as

$$\beta f_G[\{\rho_\alpha\}] = \beta f_{\mathrm{HS}}[\{\rho_\alpha\}] - \rho_\alpha v_\alpha^S + \frac{1}{2} \int d^\vee k \, \log\left(1 + \frac{4\pi\beta}{k^2} \, \widetilde{G}_{\mathrm{HS}, C}^T(k)\right), \tag{6.10}$$

where the truncated charge correlation function $G_{\mathrm{HS}, C}^T$ of the reference HS fluid must be evaluated at the densities $\{\rho_\alpha\}$. Replacing the self energy v_α^S by its expression (2.6), βf_G can be recast under the form

$$\beta f_G[\{\rho_\alpha\}] = \beta f_{\mathrm{HS}}[\{\rho_\alpha\}] + \frac{\beta}{2} \, \rho_\alpha \rho_\beta q_\alpha q_\beta \int d^3\vec{r} \, h_{\mathrm{HS}, \alpha\beta}(r) \, w_{\alpha\beta}(r)$$
$$+ \frac{1}{2} \int d^\vee k \left\{ \log\left(1 + \frac{4\pi\beta}{k^2} \, \widetilde{G}_{\mathrm{HS}, C}^T(k)\right) - \frac{4\pi\beta}{k^2} \, \widetilde{G}_{\mathrm{HS}, C}^T(k) \right\}. \tag{6.11}$$

As in the case of neutral fluids,[27] the expression (6.11) of the free energy at the Gaussian level can be shown[22] to coincide with that obtained in the framework of the random phase approximation (RPA) of the theory of liquids.[1, 21, 38]

It must be stressed that in the RPA the pair potential $v_{\alpha\beta}$ between two ions is arbitrary in the core (i.e., for $0 < r < \bar{\sigma}_\alpha + \bar{\sigma}_\beta$). In the optimized RPA (ORPA) the pair potentials in the core are chosen in such a way to ensure that the radial pair correlations $g_{\mathrm{ORPA}, \alpha\beta}(r)$ vanish for $0 < r < \bar{\sigma}_\alpha + \bar{\sigma}_\beta$.[21] Chandler and Andersen have shown that this condition corresponds to an extremum of βf_{RPA} considered as a functional of the core potentials. There is no analytical solution to this variational problem as far as the author knows, and the solution must be sought numerically. It is however quite certain that this solution cannot be interpreted as the interaction of two smeared charges as suggested by the discussion on the MSA integral equation of Section 5.4 (the MSA is identical with the ORPA if the HS reference fluid is described in the framework of the PY theory). Therefore, with

smeared electrostatic potentials one can never ensure that the $g_{G,\alpha\beta}(r)$ vanish in the core.

6.2. The SPM

We conclude this section by specializing to the case of the SPM. In this model all the hard spheres have the same diameter σ and all the smearing distributions τ_α are equal to the same τ. It follows from the expression (5.42) of $G_{HS,C}^{(2)T}$ that the Gaussian free energy of the SPM takes then the very simple form:

$$\beta f_G[\{\rho_\alpha\}] = \beta f_{HS}[\{\rho_\alpha\}] + \frac{1}{2}\int d^\vee k \left\{ \log\left(1 + \frac{\kappa^2}{k^2}\tilde\tau^2(k)\right) - \frac{\kappa^2}{k^2}\tilde\tau^2(k) \right\}. \tag{6.12}$$

Several comments on Eq. (6.12) are in order at this point.

(a)   As it is well known,[38] and as a direct calculation will show, Eq. (6.12) reduces to the Debye–Hückel free energy $\beta f_{DH} = \beta f_{HS} - \kappa^3/12\pi$ in the limit of point-like distributions (i.e., when $\tilde\tau(k) = 1$ for all k). Recall that in the point-like limit, the MF free energy diverges. Therefore the first order term in the loopwise expansion of the free energy makes the final result finite.

(b)   The expression (6.12) shows no sign of a hidden "RPA catastrophe"[47] which would be the case if the argument of the logarithm happened to be negative for some k. This happy circumstance is a consequence of the regularization by "smearing" of the Coulomb potential which was adopted in this paper. Other types of regularization can however lead to such a RPA catastrophe. For instance, adopting the Weeks–Chandler–Andersen (WCA) recipe[48] one could set the potential constant in the core, i.e., $v_{\alpha\beta}(r) = q_\alpha q_\beta/\sigma$ for $0 < r < \sigma$. Clearly, one has in fact $v_{\alpha\beta}(r) = q_\alpha q_\beta w(r)$ ($\forall r$) where $w(r)$ can be interpreted as the electric potential created by the surface distribution of charge $\tau_S(r) = \delta(r - \bar\sigma)/\pi\sigma^2$. Thus $w(1,2) = \tau_S(1,1')v_c(1',2)$. As a consequence, one must replace the term $\tilde\tau^2(k)$ by $\tilde\tau_S(k) = \sin(k\bar\sigma)/k\bar\sigma$ (*not* squared) in Eq. (6.12), with the annoying consequence that the argument of the log can become negative for some k yielding a "RPA catastrophe." The mathematical origin of this catastrophe is that, within the WCA framework, the energy is not a positive definite quadratic form and the KSSHE transform is ill-defined. It has been suggested that this instability of the RPA theory could possibly be related to the order-disorder transition of the lattice-version of the RPM.[30,49] Note that this transition is not present in the continuous version of the

model although the RPA catastrophe for the WCA-RPA free energy is still there. In all cases, one cannot be comfortable with a theory the ability of which to predict a possible transition depends on the way the regularization of the interaction is performed.

7. A TWO-LOOP ORDER CALCULATION

7.1. The Cumulant Expansion

We adopt the same decomposition $\varphi = \bar{\varphi} + \delta\varphi$ of the KSSHE field as that considered in the section on the Gaussian approximation but, this time, we do not truncate the action at the second order in $\delta\varphi$ and consider rather the full functional Taylor expansion of $\mathscr{H}[\varphi]$ about the saddle point

$$\mathscr{H}[\varphi] = \mathscr{H}[\bar{\varphi}] + \frac{1}{2}\langle\delta\varphi|\,\Delta_{\bar{\varphi}}^{-1}\,|\delta\varphi\rangle + \Delta\mathscr{H}[\delta\varphi], \tag{7.1a}$$

$$\Delta\mathscr{H}[\delta\varphi] = \sum_{n=3}^{\infty}\frac{1}{n!}\,\mathscr{H}^{(n)}[\bar{\varphi}](1,...,n)\,\delta\varphi(1)\cdots\delta\varphi(n), \tag{7.1b}$$

where the free propagator $\Delta_{\bar{\varphi}}$ defined at Eq. (6.2) must be evaluated at the saddle point $\bar{\varphi}$ and the integral kernels are given by

$$\begin{aligned}
\mathscr{H}^{(n)}[\bar{\varphi}](1,...,n) &= -(i\beta^{1/2})^n\,q_{\alpha_1}\cdots q_{\alpha_n}\,\tau_{\alpha_1}(1,1')\cdots\tau_{\alpha_n}(n,n')\\
&\quad\times G_{\mathrm{HS},\,\alpha_1\cdots\alpha_n}^{(n)\,T}[\{\bar{\nu}_\alpha + i\bar{\phi}_\alpha\}](1',...,n'),\\
&\equiv -(i\beta^{1/2})^n\,G_{\mathrm{HS},\,C}^{(n)\,T}[\bar{\varphi}](1,...,n). \tag{7.2}
\end{aligned}$$

With these notations, the grand partition function can be recast under the form

$$\Xi[\{\nu_\alpha\}] = \exp(-\mathscr{H}[\bar{\varphi}])\,\frac{\mathscr{N}_{\Delta_{\bar{\varphi}}}}{\mathscr{N}_{\nu_c}}\,\langle\exp(-\Delta\mathscr{H}[\delta\varphi])\rangle_{\Delta_{\bar{\varphi}}}, \tag{7.3}$$

yielding the cumulant expansion[20, 50, 51]

$$\log\Xi = -\mathscr{H}[\bar{\varphi}] + \log\frac{\mathscr{N}_{\Delta_{\bar{\varphi}}}}{\mathscr{N}_{\nu_c}} - \langle\Delta\mathscr{H}\rangle_{\Delta_{\bar{\varphi}}} + \frac{1}{2!}\langle\Delta\mathscr{H}^2\rangle_{\Delta_{\bar{\varphi}}}^T - \frac{1}{3!}\langle\Delta\mathscr{H}^3\rangle_{\Delta_{\bar{\varphi}}}^T + \cdots. \tag{7.4}$$

The two first terms in the RHS of Eq. (7.4) correspond the MF and Gaussian approximations respectively, the other terms are Gaussian

averages which can be computed with the help of Wick's theorem. Reordering these additional terms in powers of some small parameter yields various types of expansions. Low fugacity and high temperature expansions of the pressure and the free energy of the RPM where obtained in this way in papers I and II, yielding to a rediscovery of old results derived years ago by Mayer graphs expansion technics.[13, 14] In both cases the "small parameter" has a physical origin and thus each order of the expansion should be independent of the pair potentials in the core and therefore of the smearing functions τ_α. This point was checked carefully in I and II for the RPM by considering surface distributions of radius $\bar{a} < \bar{\sigma}$ and by showing that the first terms of the fugacity and temperature expansions were indeed independent of $\bar{a}$.

Here we consider a loopwise expansion. The small parameter λ of this expansion is defined by rewriting[50, 51]

$$\delta\varphi \to \lambda^{1/2}\, \delta\varphi,$$

$$\mathcal{H}[\varphi] \to \frac{1}{\lambda}\, \mathcal{H}[\bar{\varphi} + \lambda^{1/2}\, \delta\varphi], \tag{7.5}$$

$$\log \varXi \to \lambda \log \varXi.$$

An expansion of Eq. (7.4) in powers of λ yields the loopwise expansion of $\log \varXi$; at the end of the calculation one set $\lambda = 1$. The "small" parameter λ ($\equiv \hbar$!!) is not a physical parameter but serves mainly to keep track of different classes of Feynman diagrams; therefore each term of the loop expansion can *a priori* depend on the smearing functions τ_α. One can only hope that the larger the number of terms is retained in the expansion the "smaller" this dependence will be. In a sense, the fact that the MF free energy diverges for point charge distributions but remains finite in the Gaussian (one-loop) approximation confirms this hope. Henceforth we shall retain for τ_α the distributions (5.63) which lead to the best MF free energy. Finally, we note that it follows from Eqs. (2.20), (2.17), and (7.5) that a high-temperature expansion of the loop-expansion of $\log \varXi$ at order λ^k obviously yields the correct high-temperature expansion of $\log \varXi$ at order β^k.

7.2. The Two-Loop Expansion of log $\varXi$

The loop expansion of $\log \varXi$ for the general Hamiltonian (7.1) can be found in the literature.[50, 51] Taking into account the form (7.2) of the kernels $\mathcal{H}^{(n)}$ one finds, at the two-loop order

$$\log \varXi[\{v_\alpha\}] = \log \varXi_{\mathrm{MF}}[\{v_\alpha\}] + \lambda \log \frac{\mathcal{N}_{\varDelta_{\bar\varphi}}}{\mathcal{N}_{v_c}}$$

$$+ \frac{\lambda^2 \beta^2}{8} G_{\mathrm{HS},C}^{(4)\,T}[\bar\varphi](1,2,3,4)\,\varDelta_{\bar\varphi}(1,2)\,\varDelta_{\bar\varphi}(3,4) \quad (\equiv \mathrm{D_a})$$

$$- \frac{\lambda^2 \beta^3}{8} G_{\mathrm{HS},C}^{(3)\,T}[\bar\varphi](X_1,X_2,X_3)\,G_{\mathrm{HS},C}^{(3)\,T}[\bar\varphi](Y_1,Y_2,Y_3)$$

$$\times \varDelta_{\bar\varphi}(X_1,X_2)\,\varDelta_{\bar\varphi}(Y_1,Y_2)\,\varDelta_{\bar\varphi}(X_3,Y_3) \quad (\equiv \mathrm{D_b})$$

$$- \frac{\lambda^2 \beta^3}{12} G_{\mathrm{HS},C}^{(3)\,T}[\bar\varphi](X_1,X_2,X_3)\,G_{\mathrm{HS},C}^{(3)\,T}[\bar\varphi](Y_1,Y_2,Y_3)$$

$$\times \varDelta_{\bar\varphi}(X_1,Y_1)\,\varDelta_{\bar\varphi}(X_2,Y_2)\,\varDelta_{\bar\varphi}(X_3,Y_3) \quad (\equiv \mathrm{D_c})$$

$$+ \mathcal{O}(\lambda^3), \tag{7.6}$$

where the diagrams corresponding to the two-loop order terms of the RHS of Eq. (7.6) have been sketched in Fig. 1.

Some remarks. In general the loop-expansion (7.6) does not converge notably in the critical region as a consequence of the singular behavior of the correlation functions.[50,51] Here however, we deal with a noncritical field φ the correlation functions of which were shown to be short range in Section 4; Eq. (7.6) is thus expected to be an asymptotic expansion. The second remark is that the expression (7.6) is horribly intricate in the general case since, *a priori*, it involves the 2, 3-body and 4-body density correlation functions of the reference HS fluid. However it turns out that Eq. (7.6) can be considerably simplified for the SPM since, in this case, only the 2-body correlation functions survive, yielding tractable expressions.

Before specializing to the case of the SPM let us introduce some notations. All the thermodynamic quantities of interest will be expanded in powers of λ. We shall note, for intance for the density of species α

$$\rho_\alpha = \sum_{n=0}^{\infty} \lambda^n \rho_\alpha^{(n)}, \tag{7.7}$$

with, of course $\rho_\alpha^{(0)} \equiv \rho_{\mathrm{MF},\alpha} = \rho_{\mathrm{HS},\alpha}[\{\bar{v}_\alpha + i q_\alpha \bar\varphi\}]$. As it is well known, the two-loop order expansion of the free energy requires the densities at the
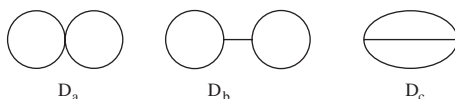

Fig. 1.   Two-loop diagrams contributing to log $\varXi$. The lines represent the bare propagator $\varDelta_{\bar\varphi}$.

one-loop order only.[50, 51] We have checked in the general case that the one-loop order correction to the densities preserves the electroneutrality; the detailed calculation can be found in ref. 22.

Henceforth we consider only the homogeneous SPM. All the ions have the same diameter σ and all the smearing functions are equal to $\tilde{\tau}(k) = \sin(k\bar{\sigma})/k\bar{\sigma}$. With this assumption the charge neutrality condition at the MF level ($\rho_C^{(0)} = 0$) kills most of the terms involved in the expressions of $G_{\text{HS}, C}^{(n) T}[\bar{\varphi}]$, it is easy to show that the only surviving terms are[22]

$$G_{\text{HS}, C}^{(2) T}[\bar{\varphi}](1, 2) = \rho_\alpha^{(0)} q_\alpha^2 \, \tau(1, 1') \, \tau(2, 1') \quad (\equiv D_2)$$

$$G_{\text{HS}, C}^{(3) T}[\bar{\varphi}](1, 2, 3) = \rho_\alpha^{(0)} q_\alpha^3 \, \tau(1, 1') \, \tau(2, 1') \, \tau(3, 1') \quad (\equiv D_3)$$

$$\begin{aligned}
G_{\text{HS}, C}^{(4) T}[\bar{\varphi}](1, 2, 3, 4) &= \rho_\alpha^{(0)} q_\alpha^4 \, \tau(1, 1') \, \tau(2, 1') \, \tau(3, 1') \, \tau(4, 1') \quad (\equiv D_{4a}) \\
&\quad + (\rho_\alpha^{(0)} q_\alpha^2)^2 \\
&\quad \times \{\tau(1, 1') \, \tau(2, 1') \, h_{\text{HS}}(1', 2') \, \tau(2', 4) \, \tau(2', 3) \quad (\equiv D_{4b}) \\
&\quad + \tau(1, 1') \, \tau(3, 1') \, h_{\text{HS}}(1', 2') \, \tau(2', 4) \, \tau(2', 2) \quad (\equiv D_{4c}) \\
&\quad + \tau(1, 1') \, \tau(4, 1') \, h_{\text{HS}}(1', 2') \, \tau(2', 2) \, \tau(2', 3) \quad (\equiv D_{4d})\},
\end{aligned}$$
$$(7.8)$$

where $h_{\text{HS}}(r) \equiv g_{\text{HS}}(r) - 1$ is the pair distribution of the reference HS fluid at the total MF density $\rho^{(0)} = \sum_\alpha \rho_\alpha^{(0)}$. Diagrammatic representations of the various terms of the RHS of Eq. (7.8) have been sketched in Fig. 2.

Replacing either algebraically or graphically the kernels $G_{\text{HS}, C}^{(n) T}[\bar{\varphi}]$ by their expressions (7.8) in Eq. (7.6) yields the expression for the pressure $\beta P = \log \Xi / \Omega$ at the two-loop order, i.e., $P = P^{(0)} + \lambda P^{(1)} + \lambda^2 P^{(2)} + \mathcal{O}(\lambda^3)$ with of course

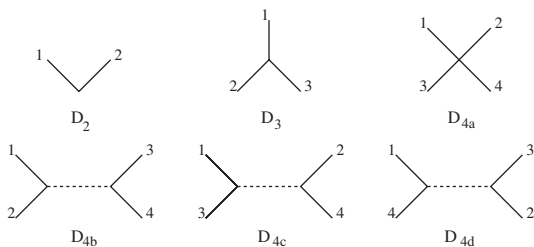$$\beta P^{(0)}[\{\nu_\alpha\}] = \beta P_{\text{MF}}[\{\nu_\alpha\}], \quad (7.9)$$

Fig. 2. Diagrams representing $G_{\text{HS}, C}^{(n) T}$ ($n = 2, 3, 4$). Dashed lines represent $h_{\text{HS}}(1, 2)$ and solid lines the smearing function $\tau(1, 2)$.

and

$$\beta P^{(1)}[\{v_\alpha\}] = -\frac{1}{2} \int d^\vee k \log\left(1 + \frac{\kappa^{(0)\,2}}{k^2}\, \tilde{\tau}^2(k)\right), \qquad (7.10)$$

(where $\kappa^{(0)\,2} \equiv \kappa_{\mathrm{MF}}^2 = 4\pi\beta\rho_\alpha^{(0)}q_\alpha^2$ is the squared Debye number at the 0-loop order) as we already know, and

$$\begin{aligned}
\beta P^{(2)}[\{v_\alpha\}] = \frac{\beta^2}{8} \Bigg\{ &\rho_\alpha^{(0)}q_\alpha^4\, [\Delta_\tau^{(0)}(0)]^2 \qquad (\equiv \mathrm{D}_1) \\
&+ [\Delta_\tau^{(0)}(0)]^2\, [\rho_\alpha^{(0)}q_\alpha^2]^2 \int d^3\vec{r}\, h_{\mathrm{HS}}(r) \qquad (\equiv \mathrm{D}_2) \\
&+ 2[\rho_\alpha^{(0)}q_\alpha^2]^2 \int d^3\vec{r}\, h_{\mathrm{HS}}(r)[\Delta_\tau^{(0)}(r)]^2 \qquad (\equiv \mathrm{D}_3) \Bigg\} \\
&- \frac{\beta^3}{8}\, [\rho_\alpha^{(0)}q_\alpha^3]^2\, [\Delta_\tau^{(0)}(0)]^2\, \tilde{\Delta}_\tau^{(0)}(0) \qquad (\equiv \mathrm{D}_4) \\
&- \frac{\beta^3}{12}\, [\rho_\alpha^{(0)}q_\alpha^3]^2 \int d^3\vec{r}\, [\Delta_\tau^{(0)}(r)]^3 \qquad (\equiv \mathrm{D}_5), \qquad (7.11)
\end{aligned}$$

where the ''smeared'' propagator $\Delta_\tau^{(0)}$ which enters the RHS of Eq. (7.11) is given by the convolution

$$\Delta_\tau^{(0)}(1, 2) = \tau(1, 1')\, \Delta_{\bar{\varphi}}(1', 2')\, \tau(2', 2) \qquad (7.12)$$

or, in Fourier space

$$\tilde{\Delta}_\tau^{(0)}(k) = \frac{4\pi\tilde{\tau}^2(k)}{k^2 + \kappa^{(0)\,2}\,\tilde{\tau}^2(k)}. \qquad (7.13)$$

We have already met the function $\Delta_\tau^{(0)}(r)$ (under the name $X_\tau(r)$) in papers I and II. Recall its high temperature, or low $\kappa^{(0)}$, behavior

$$r \leqslant \sigma \Rightarrow \Delta_\tau^{(0)}(r) = \frac{2}{\sigma} - \frac{r}{\sigma^2} - \kappa^{(0)} + \mathcal{O}(\kappa^{(0)\,2}), \qquad (7.14a)$$

$$r \geqslant \sigma \Rightarrow \Delta_\tau^{(0)}(r) = \frac{\sinh^2(\kappa^{(0)}\bar{\sigma})}{(\kappa^{(0)}\bar{\sigma})^2} \frac{\exp(-\kappa^{(0)}r)}{r} + \mathcal{O}(\kappa^{(0)\,2}). \qquad (7.14b)$$

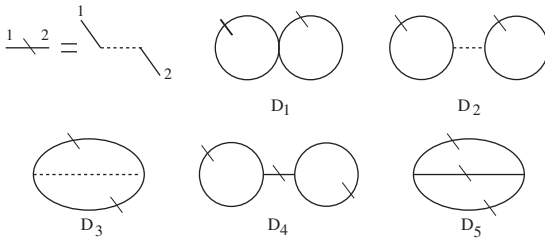Diagrammatic representations of the various terms of the RHS of Eq. (7.11) have been sketched in Fig. 3.

Fig. 3. Two-loop diagrams contributing to the pressure (cf. Eq. (7.11)). The smeared propagator $\Delta_\tau^{(0)}(1, 2)$ has been represented by a solid line plus a slash. As for the diagrams of Fig. 2 the dashed lines represent $h_{HS}(1, 2)$.

7.3. The Two-Loop Expansion of the Free Energy

As it is well known from statistical field theory, the reducible diagram D_b of Fig. 1 should disappear after a Legendre transform of the pressure yielding a simple expression for the free energy.[50, 51] However in statistical field theory one is interested with the Legendre transform of βP with respect to the mean value of the field $\langle \varphi \rangle_{\mathscr{H}}$; by contrast, in our case, the quantity of interest is rather the Helmoltz free energy βf defined as the Legendre Transform of the pressure with respect to the M densities ρ_α (cf. Eqs. (5.45a) and (5.45b)). These two Legendre transforms do not coincide *a priori* and a direct calculation of βf at the two-loop order is therefore necessary.

We have first to compute the densities at the one-loop order since the terms $\lambda^2 \rho_\alpha^{(2)}$ and of higher order do not contribute to βf at order $\mathcal{O}(\lambda^2)$ (included) as a consequence of the stationarity condition (this point will emerge in subsequent developments). Equations (7.9) and (7.10) entail that

$$\rho_\alpha = \frac{\partial \beta P[\{v_\alpha\}]}{\partial v_\alpha}$$

$$= \rho_\alpha^{(0)} - \frac{\lambda}{2} \frac{\Delta_\tau^{(0)}(0)}{4\pi} \frac{\partial \kappa^{(0)\,2}}{\partial v_\alpha} + \mathcal{O}(\lambda^2), \tag{7.15}$$

where we recall that $\rho_\alpha^0 = \rho_{HS, \alpha}[\{\bar{v}_\alpha + i\beta^{1/2} q_\alpha \bar{\varphi}\}]$ is the 0-loop order (or MF) density of species α. We note that

$$\frac{\partial \kappa^{(0)\,2}}{\partial v_\alpha} = 4\pi\beta\, q_\gamma^2 (\partial \rho_\gamma^{(0)} / \partial v_\alpha) = 4\pi\beta\, q_\gamma^2 \widetilde{G}_{MF,\,\alpha\gamma}^T(k=0), \tag{7.16}$$

where $\widetilde{G}^T_{\mathrm{MF},\,\alpha\gamma}$ can be computed from Eq. (5.43). After some algebra one finds finally

$$\rho_\alpha^{(1)} = -\frac{\beta\varDelta_\tau(0)}{2}\left([\rho_\gamma^{(0)}q_\gamma^2]\,\tilde{h}_{\mathrm{HS}}(0)\,\rho_\alpha^{(0)} + \rho_\alpha^{(0)}q_\alpha^2 - \frac{[\rho_\gamma^{(0)}q_\gamma^3]}{[\rho_\gamma^{(0)}q_\gamma^2]}\rho_\alpha^{(0)}q_\alpha\right). \quad (7.17)$$

(no summation over α in the RHS). We have already pointed out that the electroneutrality is satisfied at the MF level (i.e., $\rho_\alpha^{(0)}q_\alpha = 0$) and we note with satisfaction that Eq. (7.17) implies that it is also satisfied at the one-loop order (i.e., $\rho_\alpha^{(1)}q_\alpha = 0$; see also ref. 22 for a thorough treatment in the general case). As a subproduct of Eq. (7.17) we obtain the one-loop order corrections to the total density and Debye number

$$\rho^{(1)} = -\frac{\beta\varDelta_\tau^{(0)}(0)}{2}[\rho_\gamma^{(0)}q_\gamma^2](1+\rho^{(0)}\tilde{h}_{\mathrm{HS}}(0)) \quad (7.18a)$$

$$\kappa^{2\,(1)} \equiv 4\pi\beta\rho_\alpha^{(1)}q_\alpha^2$$

$$= -2\pi\beta^2\varDelta_\tau^{(0)}(0)\left([\rho_\gamma^{(0)}q_\gamma^2]^2\,\tilde{h}_{\mathrm{HS}}(0) + [\rho_\gamma^{(0)}q_\gamma^4] - \frac{[\rho_\gamma^{(0)}q_\gamma^3]^2}{[\rho_\gamma^{(0)}q_\gamma^2]}\right). \quad (7.18b)$$

The free energy at the two-loop order is obtained by reexpressing

$$\beta f = \rho_\alpha v_\alpha - \beta P^{(0)} - \lambda\beta P^{(1)} - \lambda^2\beta P^{(2)} + \mathcal{O}(\lambda^3) \quad (7.19)$$

in terms of the densities

$$\rho_\alpha = \rho_\alpha^{(0)} + \varDelta\rho_\alpha$$
$$\varDelta\rho_\alpha = \lambda\rho_\alpha^{(1)} + \lambda^2\rho_\alpha^{(2)} + \mathcal{O}(\lambda^3). \quad (7.20)$$

Let us first evaluate

$$\rho_\alpha v_\alpha - \beta P^{(0)}[\{v_\alpha\}] = \beta f^{(0)}[\{\rho_\alpha^{(0)}\}] + v_\alpha\,\varDelta\rho_\alpha. \quad (7.21)$$

We have already obtained the leading term of βf (i.e., at the MF or 0-loop order) in sec (5.2) as a functions of the densities, i.e., for the homogeneous system considered here

$$\beta f^{(0)}[\{\rho_\alpha\}] \equiv \beta f_{\mathrm{MF}}[\{\rho_\alpha\}] = \beta f_{\mathrm{HS}}[\{\rho_\alpha\}] - \rho_\alpha v_\alpha^S. \quad (7.22)$$

At this point we remark that

$$\beta f^{(0)}[\{\rho_\alpha + \varDelta\rho_\alpha\}] = \beta f^{(0)}[\{\rho_\alpha\}] + v_\alpha\,\varDelta\rho_\alpha - \frac{1}{2\Omega}\langle\varDelta\rho_\alpha|\,\hat{C}_{\alpha\beta}^{(0)}\,|\varDelta\rho_\beta\rangle + \mathcal{O}(\lambda^3), \quad (7.23)$$

where $\hat{C}_{\alpha\beta}^{(0)}$ is the two-body MF proper vertex. In the case of the SPM the expression (5.22) of $\hat{C}_{\alpha\beta}^{(0)}$ takes the form

$$\hat{C}_{\alpha\beta}^{(0)}(1, 2) = c_{\text{HS}}^{(0)}(r_{12}) - \frac{\delta_{\alpha\beta}}{\rho_{\alpha}^{(0)}} \delta(1, 2), \qquad (7.24)$$

where $c_{\text{HS}}^{(0)}$ is the usual direct correlation function of the HS fluid at the density $\rho^{(0)}$. Reporting the expression (7.24) of $\hat{C}_{\alpha\beta}^{(0)}$ in Eq. (7.23) and taking into account the electroneutrality condition at the MF level one finds

$$\beta f^{(0)}[\{\rho_\alpha + \Delta\rho_\alpha\}] = \beta f^{(0)}[\{\rho_\alpha\}] + \nu_\alpha \Delta\rho_\alpha - \frac{\lambda^2}{2} \tilde{c}_{\text{HS}}^{(0)}(0) \rho^{(1)2}$$
$$+ \frac{\lambda^2}{2} \sum_\alpha \frac{\rho_\alpha^{(1)2}}{\rho_\alpha^{(0)}} + \mathcal{O}(\lambda^3). \qquad (7.25)$$

Reporting now the expression (7.17) of $\rho_\alpha^{(1)}$ in the above equation one obtains

$$\beta f^{(0)}[\{\rho_\alpha + \Delta\rho_\alpha\}]$$
$$= \beta f^{(0)}[\{\rho_\alpha\}] + \nu_\alpha \Delta\rho_\alpha$$
$$+ \frac{\lambda^2\beta^2}{8} \Delta_\tau^{(0)2}(0) \left\{ [\rho_\alpha^{(0)}q_\alpha^2]^2 \tilde{h}_{\text{HS}}^{(0)}(0) + \rho_\alpha^{(0)}q_\alpha^4 - \frac{[\rho_\alpha^{(0)}q_\alpha^3]^2}{\rho_\alpha^{(0)}q_\alpha^2} \right\} + \mathcal{O}(\lambda^3), \qquad (7.26)$$

where we have made use of the OZ equation for the reference HS fluid $\tilde{c}_{\text{HS}}^{(0)}(0) = \tilde{h}_{\text{HS}}^{(0)}(0)/(1 + \rho^{(0)}\tilde{h}_{\text{HS}}^{(0)}(0))$. The first contribution (7.21) of βf can thus be recast under the form

$$\rho_\alpha \nu_\alpha - \beta P^{(0)}[\{\nu_\alpha\}] = \beta f^{(0)}[\{\rho_\alpha\}]$$
$$- \frac{\lambda^2\beta^2}{8} \Delta_\tau^2(0) \left\{ [\rho_\alpha q_\alpha^2]^2 \tilde{h}_{\text{HS}}(0) + \rho_\alpha q_\alpha^4 - \frac{[\rho_\alpha q_\alpha^3]^2}{\rho_\alpha q_\alpha^2} \right\} + \mathcal{O}(\lambda^3), \qquad (7.27)$$

where the smeared propagator Δ_τ as well as the pair correlation h_{HS} of the HS fluid can be evaluated at the total density $\rho = \sum_\alpha \rho_\alpha$ (rather than $\rho^{(0)}$) at this order in λ.

The second step in the calculation of βf is to reexpress $\beta P^{(1)}$ in terms of the densities ρ_α. We note that

$$\lambda \beta P^{(1)} = -\frac{\lambda}{2} \int d^\vee k \log\left(1 + \frac{\kappa^{(0)2}}{k^2} \tilde{\tau}^2(k) \right) \qquad (7.28)$$

which shows that $\beta P^{(1)}$ is a function of the sole squared Debye number κ^2. Defining the increment $\Delta\kappa^2 = \kappa^2 - \kappa^{(0)\,2}$ and performing a Taylor expansion of $\beta P^{(1)}$ around $\kappa^{(0)\,2}$ yields

$$\lambda\beta P^{(1)} = -\frac{\lambda}{2}\int d^{\vee}k \log\left(1+\frac{\kappa^2}{k^2}\,\tilde{\tau}^2(k)\right) + \frac{\lambda}{8\pi}\,\Delta_\tau(0)\,\Delta\kappa^2 + \mathcal{O}(\lambda^3), \quad (7.29)$$

which, after substitution of the expression of $\Delta\kappa^2$ at order $\mathcal{O}(\lambda)$ (cf. Eq. (7.18b) allows us to write

$$\lambda\beta P^{(1)} = -\frac{\lambda}{2}\int d^{\vee}k \log(1+\frac{\kappa^2}{k^2}\tilde{\tau}^2(k))$$

$$-\frac{\lambda^2\beta^2}{4}\,\Delta_\tau^2(0)\left\{[\rho_\alpha q_\alpha^2]^2\,\tilde{h}_{\mathrm{HS}}(0) + \rho_\alpha q_\alpha^4 - \frac{[\rho_\alpha q_\alpha^3]^2}{\rho_\alpha q_\alpha^2}\right\} + \mathcal{O}(\lambda^3), \quad (7.30)$$

where, once again, the smeared propagator Δ_τ as well as the pair correlation h_{HS} of the HS fluid can be evaluated at the total density $\rho = \sum_\alpha \rho_\alpha$ (rather than $\rho^{(0)}$) at this order in λ.

It remains to reexpress $\beta P^{(2)}$ in terms of the densities ρ_α, which is done readily, and to gather all the intermediate results. After doing this job, one finds that the free energy at the second order in the loop expansion reads as

$$\beta f[\{\rho_\alpha\}] = \beta f_{\mathrm{HS}}[\{\rho_\alpha\}] + \frac{1}{2}\int d^{\vee}k \left(\log\left(1+\frac{\kappa^2}{k^2}\,\tilde{\tau}^2(k)\right) - \frac{\kappa^2}{k^2}\,\tilde{\tau}^2(k)\right)$$

$$-\frac{\beta^2}{4}\,[\rho_\alpha q_\alpha^2]^2\int d^3\vec{r}\, h_{\mathrm{HS},\,\rho}(r)\,\Delta_{\tau,\kappa}^2(r)$$

$$+\frac{\beta^3}{12}\,[\rho_\alpha q_\alpha^3]^2\int d^3\vec{r}\,\Delta_{\tau,\kappa}^3(r), \quad (7.31)$$

where a subscript ρ has been added to the function $h_{\mathrm{HS},\,\rho}(r)$ to emphasize that it has to be computed at the density $\rho = \sum_\alpha \rho_\alpha$. There are good theories for the HS pair correlations $h_{\mathrm{HS}}(r)$, for instance one could try $h_{\mathrm{HS}}(r) = h_{\mathrm{PY}}(r)$, which makes the two-loop expression for the free energy manageable. Similarly the smeared propagator in the RHS of Eq. (7.31) must be computed from (7.13) with $\kappa^2 = 4\pi\beta\rho_\alpha q_\alpha^2$.

Several comment are in order at this point.

(a) We note that only the irreducible diagrams D_3 and D_5 of Fig. 3 have survived to the Legendre transform; note that, moreover, the symmetry factor of D_3 has changed as the result of many compensations of equal terms. Diagram D_3 is interesting because it can be interpreted as the

contribution of an effective attractive interaction $-\Delta_{\tau,\kappa}^2(r)$ to the free energy. Such a term should play an important role in the description of the liquid-vapor transition of the SPM.

(b)   Digging the literature we have found that the expression (7.31) when specialized to the case of the RPM (i.e., with the last term of the right hand side set to zero) is not new and has been obtained more than thirty years ago by Chandler and Andersen[15] in the framework of the mode expansion formalism. According to the numerical study performed by these authors Eq. (7.31) gives reasonable results in the liquid regime.

(c)   Recent developments of the theory of collective variables (in its modern formulation[52, 53]) yield, in the case of the RPM, to an expression for βf that disagrees with Eq. (7.31). As far as I understand the details of ref. 49 one can reconciliate the two points of view by replacing $h_{HS,\rho}(r)$ by its Fourier transform at $k=0$ in Eq. (7.31). This approximation is correct if the correlation length associated to charge fluctuations (i.e., $\xi_C \sim 1/\kappa$) is large compared to the correlation length associated with the HS fluid which does not seem to be fully justified in general.

(d)   We have checked in the case of the RPM that, expanding the expression (7.31) of βf in powers of β with the help of Eq. (7.14) gives back the high-T expansion discussed in ref. 3, i.e., in reduced units ($x = r/\sigma$, $\beta^* = \beta q^2/\sigma$, and $\rho^* = \rho\sigma^3$)

$$\beta^* f_{RPM}(\rho^*) = \beta^* f_{HS}(\rho^*) - \rho^* \log 2 - \frac{2\pi^{1/2}}{3}(\rho^*\beta^*)^{3/2}$$

$$-\frac{(\rho^*\beta^*)^2}{4} \int d^3\vec{x} \frac{h_{HS,\rho^*}(x)}{x^2}$$

$$+\pi^{1/2}(\rho^*\beta^*)^{5/2} \int d^3\vec{x} \frac{h_{HS,\rho^*}(x)}{x} + \mathcal{O}(\beta^{*3}). \qquad (7.32)$$

This result corroborates the conclusions of Stell in his study of the relation between the γ-ordering and the mode expansion.[54]

8. CONCLUSION

The KSSHE field theoretical representation of liquids provides a general framework for studying either neutral atomic liquids[27] or ionic solutions, as in this series of papers. It is taylor made for building perturbation theories with respect to a reference fluid chosen conveniently in general as the HS fluid. The technics is roughly always the same, i.e., an ordering of the cumulant expansion of the grand potential in ascending

powers of some small parameter. The latter can be either a physical parameter such as the fugacity or the inverse temperature as considered in papers I and II or, as in the present work, an abstract one related to the numbers of loops of the Feynman diagrams retained in the expansion. The salient features of this loop expansion can be summarized as follows.

• The zero-loop order approximation of the free energy $\beta \mathscr{A}_{\mathrm{MF}}$ constitutes a rigorous lower bound for the exact GC free energy $\beta \mathscr{A}$. An optimized MF theory can be obtained by maximizing $\beta \mathscr{A}_{\mathrm{MF}}$ with respect to the smearing distribution functions in the cores. The MF grand potential $\log \varXi_{\mathrm{MF}}$ constitutes a rigorous upper bound for the exact grand potential. Both functionals $\beta \mathscr{A}_{\mathrm{MF}}[\{\rho_\alpha\}]$ and $\log \varXi_{\mathrm{MF}}[\{v_\alpha\}]$ are strictly convex in the fluid phase which rules out a fluid–fluid phase transition at the MF level.

• At the MF level (or in the Gaussian approximation) the pair correlation functions coincide with those of the RPA theory. The direct correlation functions of the PM in the optimized MF theory are very similar to those considered in the ORPA (or MSA) approximation of the theory of liquids, however the pair correlation functions $g_{\mathrm{MF},\,\alpha\beta}(r)$, which have simple analytical expressions, do not vanish in the cores, except in limit cases.

• The one-loop free energy is identical with that obtained in the RPA theory of liquids.[1, 21, 38]

• An explicit and manageable expression of the two-loop order free energy can be written for the SPM; in the case of the RPM it coincides with a result obtained by Chandler and Andersen in the framework of the mode expansion theory.[15] However the expression (7.11) of the pressure seems to be a new result even for the RPM.

The homogeneous specific free energy βf of the PM can be used to study the critical point (CP) of the PM at the MF level. Recently, the one-loop order expression of βf in the WCA scheme was considered to study the CP of the RPM.[30, 49] We have performed a similar study for the SPM with the one- and two-loop order expressions of βf derived in this paper. These results will be discussed elsewhere.

ACKNOWLEDGMENTS

REFERENCES

1. J.-P. Hansen and I. R. Mc Donald, *Theory of Simple Liquids* (Academic Press, London, 1986).

2. J.-M. Caillol and J.-L. Raimbault, *J. Stat. Phys.* **103**:753 (2001).
3. J.-L. Raimbault and J.-M. Caillol, *J. Stat. Phys.* **103**:777 (2001).
4. M. Kac, *Phys. Fluids* **2**:8 (1959).
5. A. J. F. Siegert, *Physica* **26**:530 (1960).
6. R. L. Stratonovich, *Sov. Phys. Solid State* **2**:1824 (1958).
7. J. Hubbard, *Phys. Rev. Lett.* **3**:77 (1954).
8. J. Hubbard and P. Schofield, *Phys. Lett. A* **40**:245 (1972).
9. S. F. Edwards, *Phil. Mag.* **4**:1171 (1959).
10. S. Samuel, *Phys. Rev. D* **18**:1916 (1978).
11. D. C. Brydges and Ph. Martin, *J. Stat. Phys* **96**:1163 (1999).
12. R. R. Netz, and H. Orland, *Eur. Phys. J. E* **1**:67 (2000).
13. J. E. Mayer, *J. Chem. Phys.* **18**:1426 (1950).
14. G. R. Stell and J. Lebowitz, *J. Chem. Phys.* **49**:3706 (1968).
15. H. C. Andersen and D. Chandler, *J. Chem. Phys.* **53**:547 (1970); *ibid.* **55**:1497 (1971); D. Chandler and H. C. Andersen, *J. Chem. Phys.* **54**:26 (1971).
16. I. R. Iukhnoviskii, *Sov. Phys. JETP* **7**:263 (1958).
17. K. B. Eisenthal and W. G. McMillan, *J. Chem. Phys.* **42**:3766 (1965); *ibid.* **44**:2542 (1966).
18. F. H. Stillinger and R. Lovett, *J. Chem. Phys.* **49**:1991 (1968).
19. S. L. Carnie and D. Y. C. Chan, *Chem. Phys. Lett.* **77**:437 (1981).
20. K. Ma, *Modern Theory of Critical Phenomena* (Addison–Wesley, 1982).
21. H. C. Andersen and D. Chandler, *J. Chem. Phys.* **57**:1918 (1972).
22. J.-M. Caillol, arXiv: cond-mat/0305465.
23. J. J. Binney, N. J. Dowrick, A. J. Fisher, and M. E. J. Newman, *The Theory of Critical Phenomena* (Clarendon Press, Oxford, 1992).
24. G. Parisi, *Statistical Field Theory* (Addison–Wesley, 1988).
25. J. K. Percus, in *The Liquid State of Matter*, E. W. Montroll and J. L. Lebowitz, eds. (North-Holland, Amsterdam, 1982).
26. N. V. Brilliantov, *Phys. Rev. E* **58**:2628 (1998).
27. J.-M. Caillol, *Mol. Phys.* **101**:1617 (2003).
28. G. Stell, in *The Equilibrium Theory of Classical Fluids*, H. L. Frisch and J. L. Lebowitz, eds. (Benjamin, New York, 1964).
29. G. Stell, in *Phase Transitions and Critical Phenomena*, Vol. 5b, C. Domb and J. L. Lebowitz, eds. (Academic Press, New York, 1973).
30. A. Ciach and G. Stell, *J. Mol. Phys. Liq.* **87**:255 (2000); *J. Chem. Phys.* **114**:382 (2001); *ibid* **114**:3617 (2001); *Physica A* **306**:220 (2002).
31. Ph. A. Martin, *Rev. Mod. Phys.* **60**:1075 (1988).
32. J.-M. Caillol and J.-J. Weis, *J. Chem. Phys.* **102**:7610 (1995).
33. B. Jancovici, in *Strongly Plasma Physics*, F. J. Rogers and H. E. DeWitt, eds. (Plenum, New York, 1987).
34. B. Jancovici, *J. Stat. Phys.* **80**:445 (1995).
35. J. L. Lebowitz and Ph. A. Martin, *J. Stat. Phys.* **34**:287 (1984).
36. J. M. Kosterlitz and D. J. Thouless, *J. Phys. C* **6**:1181 (1973).
37. A. Diehl, M. C. Barbosa, and Y. Levin, *Phys. Rev. E* **56**:619 (1997).
38. C. W. Outhwaite, in *Statistical Mechanics*, Vol. 2, K. Singer, ed. (The Chemical Society, London, 1975).
39. J.-M. Caillol, *J. Phys. A: Math. Gen.* **35**:4189 (2002).
40. J. T. Chayes and L. Chayes , *J. Stat. Phys.* **36**:471 (1984).
41. E. Trizac, *Phys. Rev. E* **62**:R1465 (2000).
42. L. Blum, in *Theoretical Chemistry: Advances and Perspectives*, Vol. 5 (Academic Press, New York, 1980).

43. T. Kennedy, *J. Stat. Phys.* **28**:633 (1982).

44. L. Onsager, *J. Chem. Phys.* **43**:189 (1939).

45. E. Waisman and J. L. Lebowitz, *J. Chem. Phys.* **56**:3086 (1972); *ibid* **56**:3093 (1972).

46. V. I. Smirnov, *Linear Algebra and Group Theory* (McGraw–Hill, New York, 1961).

47. J. C. Wheeler and D. Chandler, *J. Chem. Phys.* **55**:1645 (1971).

48. J. D. Weeks, D. Chandler, and H. C. Andersen, *J. Chem. Phys.* **54**:5237 (1971).

49. O. V. Patsahan, arXiv: cond-mat/0301039.

50. D. Amit, *Field Theory, the Renormalization Group and Critical Phenomena*, 2nd edn. (World Scientific, Singapore, 1984).

51. J. Zinn-justin, *Quantum Field Theory and Critical Phenomena* (Clarendon Press, Oxford, 1989).

52. I. R. Yukhnovskii, *Physica A* **168**:999 (1990).

53. I. R. Yukhnovskii and O. V. Patsahan, *J. Stat. Phys.* **81**:647 (1995).

54. G. Stell, *J. Chem. Phys.* **55**:1485 (1971).