LETTER TO THE EDITOR

A mesoscopic field theory of ionic systems versus a collective variable approach

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Abstract
We establish a link between the two functional approaches: a mesoscopic field
theory developed recently by Ciach and Stell (2000 *J. Mol. Liq.* **87** 253) for the
study of ionic models and an exact statistical field theory based on the method
of collective variables.

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Two rigorous scalar field theories were recently developed to describe the phase equilibria
in ionic fluids: the KSSHE (Kac–Siegert–Stratonovich–Hubbard–Edwards) theory [1] and
the approach [2, 3] which is based on the collective variable (CV) method [4, 5]. As was
shown recently [3, 6] both theories are in close relation. Our goal here is to establish a
link between the CV approach and the mesoscopic field theory developed in [7, 8] for the
restricted primitive model with additional short-range interactions presented (RPM + SR) or,
more specifically, to demonstrate how after some approximations in the exact microscopic CV
action $\mathcal{H}[\nu_\alpha, \rho, Q, \omega, \gamma]$ we can arrive at the functional of the grand potential $\Delta\Omega^{\mathrm{MF}}[\eta, \phi]$
considered in [7, 8].

Let us consider a general case of a classical two-component system consisting of N
particles among which there exist N_1 particles of species 1 and N_2 particles of species 2. The
pair interaction potential is assumed to be of the following form:

$$U_{\alpha\beta}(r) = v^{\mathrm{HS}}_{\alpha\beta}(r) + v^C_{\alpha\beta}(r) + v^{\mathrm{SR}}_{\alpha\beta}(r), \tag{1}$$

where $v^{\mathrm{HS}}_{\alpha\beta}(r)$ is the interaction potential between the two additive hard spheres of diameters
$\sigma_{\alpha\alpha}$ and $\sigma_{\beta\beta}$. We call the two-component hard sphere system a reference system (RS).
Thermodynamic and structural properties of RS are assumed to be known. $v^C_{\alpha\beta}(r)$ is the
Coulomb potential: $v^C_{\alpha\beta}(r) = q_\alpha q_\beta v^C(r)$, where $v^C(r) = 1/(Dr)$, D is the dielectric constant,
hereafter we put $D = 1$. The solution is made of both positive and negative ions so that the
electroneutrality is satisfied, $\sum_{\alpha=1}^{2} q_\alpha c_\alpha = 0$, and c_α is the concentration of the species α,

$c_\alpha = N_\alpha/N$. The ions of the species $\alpha = 1$ are characterized by their hard sphere diameter σ_{11} and their electrostatic charge $+q_0$ and those of species $\alpha = 2$, characterized by diameter σ_{22}, bear opposite charge $-zq_0$ (q_0 is elementary charge and z is the parameter of charge asymmetry). $v_{\alpha\beta}^{\text{SR}}(r)$ is the potential of the short-range interaction: $v_{\alpha\beta}^{\text{SR}}(r) = v_{\alpha\beta}^R(r) + v_{\alpha\beta}^A(r)$, where $v_{\alpha\beta}^R(r)$ is used to mimic the soft core asymmetric repulsive interaction, $v_{\alpha\beta}^R(r)$ is assumed to have a Fourier transform; $v_{\alpha\beta}^A(r)$ describes a van der Waals-like attraction.

We consider the grand partition function (GPF) of the system which can be written as follows:

$$\Xi[\nu_\alpha] = \sum_{N_1 \geqslant 0} \sum_{N_2 \geqslant 0} \prod_{\alpha=1,2} \frac{\exp(\nu_\alpha N_\alpha)}{N_\alpha!} \int (\mathrm{d}\Gamma) \exp\left[-\frac{\beta}{2} \sum_{\alpha\beta} \sum_{ij} U_{\alpha\beta}(r_{ij})\right]. \quad (2)$$

Here the following notations are used: ν_α is the dimensionless chemical potential, $\nu_\alpha = \beta\mu_\alpha - 3\ln\Lambda$, μ_α is the chemical potential of the αth species, β is the reciprocal temperature, $\Lambda^{-1} = (2\pi m_\alpha \beta^{-1}/h^2)^{1/2}$ is the inverse de Broglie thermal wavelength and $(\mathrm{d}\Gamma)$ is the element of configurational space of the particles.

Let us introduce operators $\hat{\rho}_{\mathbf{k}}$ and $\hat{Q}_{\mathbf{k}}$: $\hat{\rho}_{\mathbf{k}} = \sum_\alpha \hat{\rho}_{\mathbf{k},\alpha}$ and $\hat{Q}_{\mathbf{k}} = \sum_\alpha q_\alpha \hat{\rho}_{\mathbf{k},\alpha}$, which are combinations of the Fourier transforms of the microscopic number density of the species α: $\hat{\rho}_{\mathbf{k},\alpha} = \sum_i \exp\left(-i\mathbf{k}\mathbf{r}_i^\alpha\right)$. In this case a part of the Boltzmann factor in (2) which does not include the RS interaction can be presented as follows:

$$\exp\left[-\frac{\beta}{2} \sum_{\alpha\beta} \sum_{i,j} \left(U_{\alpha\beta}(r_{ij}) - v_{\alpha\beta}^{\text{HS}}(r_{ij})\right)\right] = \exp\left[-\frac{1}{2}\sum_{\mathbf{k}}(\widetilde{\Phi}_{NN}\hat{\rho}_{\mathbf{k}}\hat{\rho}_{-\mathbf{k}}\right.$$

$$\left. + \widetilde{\Phi}_{QQ}\hat{Q}_{\mathbf{k}}\hat{Q}_{-\mathbf{k}} + 2\widetilde{\Phi}_{NQ}\hat{\rho}_{\mathbf{k}}\hat{Q}_{-\mathbf{k}}) + \frac{1}{2}\sum_\alpha N_\alpha \sum_{\mathbf{k}}\left(\widetilde{\Phi}_{\alpha\alpha}^{\text{SR}}(k) + q_\alpha^2\widetilde{\Phi}^C(k)\right)\right], \quad (3)$$

where

$$\widetilde{\Phi}_{NN}(k) = \frac{1}{(1+z)^2}\left[z^2\widetilde{\Phi}_{11}^{\text{SR}}(k) + 2z\widetilde{\Phi}_{12}^{\text{SR}}(k) + \widetilde{\Phi}_{22}^{\text{SR}}(k)\right],$$

$$\widetilde{\Phi}_{QQ}(k) = \frac{1}{(1+z)^2}\left[\widetilde{\Phi}_{11}^{\text{SR}}(k) - 2\widetilde{\Phi}_{12}^{\text{SR}}(k) + \widetilde{\Phi}_{22}^{\text{SR}}(k)\right] + \widetilde{\Phi}^C(k), \quad (4)$$

$$\widetilde{\Phi}_{NQ}(k) = \frac{1}{(1+z)^2}\left[z\widetilde{\Phi}_{11}^{\text{SR}}(k) + (1-z)\widetilde{\Phi}_{12}^{\text{SR}}(k) - \widetilde{\Phi}_{22}^{\text{SR}}(k)\right]$$

and we use the notations $\widetilde{\Phi}_{\alpha\beta}^{X\cdots}(k) = \frac{\beta}{V}\widetilde{v}_{\alpha\beta}^{X\cdots}(k)$ with $\widetilde{v}_{\alpha\beta}^{X\cdots}(k)$ being a Fourier transform of the corresponding interaction potential.

In order to introduce the collective variables (CVs) we use the identity

$$\exp\left[-\frac{1}{2}\sum_{\mathbf{k}}\widetilde{\Phi}(k)\hat{\xi}_{\mathbf{k}}\hat{\xi}_{-\mathbf{k}}\right] = \int (\mathrm{d}\xi)\delta_{\mathcal{F}}[\xi - \hat{\xi}]\exp\left[-\frac{1}{2}\sum_{\mathbf{k}}\widetilde{\Phi}(k)\xi_{\mathbf{k}}\xi_{-\mathbf{k}}\right], \quad (5)$$

where $\delta_{\mathcal{F}}[\xi - \hat{\xi}]$ denotes the functional delta function.

Taking into account (3)–(5), we can rewrite (2)

$$\Xi[\nu_\alpha] = \int (\mathrm{d}\rho)(\mathrm{d}Q)(\mathrm{d}\omega)(\mathrm{d}\gamma)\exp(-\mathcal{H}[\nu_\alpha, \rho, Q, \omega, \gamma]), \quad (6)$$

where the CV action $\mathcal{H}$ is as follows:

$$\mathcal{H}[\nu_\alpha, \rho, Q, \omega, \gamma] = \frac{1}{2}\sum_{\mathbf{k}}[\widetilde{\Phi}_{NN}(k)\rho_{\mathbf{k}}\rho_{-\mathbf{k}} + \widetilde{\Phi}_{QQ}(k)Q_{\mathbf{k}}Q_{-\mathbf{k}} + 2\widetilde{\Phi}_{NQ}(k)\rho_{\mathbf{k}}Q_{-\mathbf{k}}]$$

$$- i\sum_{\mathbf{k}}(\omega_{\mathbf{k}}\rho_{\mathbf{k}} + \gamma_{\mathbf{k}}Q_{\mathbf{k}}) - \ln\Xi_{\text{HS}}[\bar{\nu}_\alpha; -i\omega, -iq_\alpha\gamma]. \quad (7)$$

In (7) CVs $\rho_{\mathbf{k}}$ and $Q_{\mathbf{k}}$ describe fluctuations of the total number density and charge density, respectively. $\Xi_{\text{HS}}[\bar{v}_\alpha; -i\omega, -iq_\alpha\gamma]$ is the GPF of a two-component system of hard spheres with the renormalized local chemical potential

$$\bar{v}_\alpha = v_\alpha + \frac{1}{2}\sum_{\mathbf{k}}\widetilde{\Phi}^{\text{SR}}_{\alpha\alpha}(k) + \frac{q_\alpha^2}{2}\sum_{\mathbf{k}}\widetilde{\Phi}^C(k) - i\omega(r) - iq_\alpha\gamma(r). \tag{8}$$

In the above integral $(d\ldots)$ is a volume element of the corresponding CV phase space, e.g. $(d\rho) = d\rho_0 \prod'_{\mathbf{k}\neq 0} d\,\text{Re}\,\rho_{\mathbf{k}}\, d\,\text{Im}\,\rho_{\mathbf{k}}$, the prime means that the product over $\mathbf{k}$ is performed in the upper semi-space $(\rho_{-\mathbf{k}} = \rho_{\mathbf{k}}^\star)$.

The MF approximation of functional (6) is defined by

$$\Xi_{\text{MF}}[v_\alpha] = \exp(-\mathcal{H}[v_\alpha, \bar{\rho}, \bar{Q}, \bar{\omega}, \bar{\gamma}]), \tag{9}$$

where $\bar{\rho}, \bar{Q}, \bar{\omega}$ and $\bar{\gamma}$ are the solutions of the saddle point equations:

$$\begin{aligned}
\bar{\rho} &= \langle N[\bar{v}_\alpha; -i\bar{\omega}, -iq_\alpha\bar{\gamma}]\rangle_{\text{HS}}, & \bar{Q} &= 0, \\
\bar{\omega} &= -i\bar{\rho}\widetilde{\Phi}_{NN}(0), & \bar{\gamma} &= -i\bar{\rho}\widetilde{\Phi}_{NQ}(0).
\end{aligned} \tag{10}$$

Now we present CVs $\rho_{\mathbf{k}}$ and $Q_{\mathbf{k}}$ ($\omega_{\mathbf{k}}$ and $\gamma_{\mathbf{k}}$) as

$$\begin{aligned}
\rho_{\mathbf{k}} &= \bar{\rho}\delta_{\mathbf{k}} + \delta\rho_{\mathbf{k}}, & Q_{\mathbf{k}} &= \bar{Q}\delta_{\mathbf{k}} + \delta Q_{\mathbf{k}}, \\
\omega_{\mathbf{k}} &= \bar{\omega}\delta_{\mathbf{k}} + \delta\omega_{\mathbf{k}}, & \gamma_{\mathbf{k}} &= \bar{\gamma}\delta_{\mathbf{k}} + \delta\gamma_{\mathbf{k}},
\end{aligned}$$

where the quantaties with a bar are given by (10) and $\delta_{\mathbf{k}}$ is the Kronecker symbol. Then we write $\ln\Xi_{\text{HS}}[\bar{v}_\alpha; -i\omega, -iq_\alpha\gamma]$ in the form of the cumulant expansion

$$\ln\Xi_{\text{HS}}[\ldots] = \sum_{n\geqslant 0}\frac{(-i)^n}{n!}\sum_{i_n\geqslant 0}\sum_{\mathbf{k}_1,\ldots,\mathbf{k}_n}\mathfrak{M}_n^{(i_n)}(k_1,\ldots,k_n)\delta\gamma_{\mathbf{k}_1}\ldots\delta\gamma_{\mathbf{k}_{i_n}}\delta\omega_{\mathbf{k}_{i_{n+1}}}\ldots\delta\omega_{\mathbf{k}_n}\delta_{\mathbf{k}_1+\cdots+\mathbf{k}_n}, \tag{11}$$

where $\mathfrak{M}_n^{(i_n)}(k_1,\ldots,k_n)$ is the nth cumulant defined by

$$\mathfrak{M}_n^{(i_n)}(k_1,\ldots,k_n) = \left.\frac{\partial^n\ln\Xi_{\text{HS}}[\ldots]}{\partial\delta\gamma_{\mathbf{k}_1}\ldots\partial\delta\gamma_{\mathbf{k}_{i_n}}\partial\delta\omega_{\mathbf{k}_{i_{n+1}}}\ldots\partial\delta\omega_{\mathbf{k}_n}}\right|_{\delta\gamma_{\mathbf{k}}=0,\delta\omega_{\mathbf{k}}=0}. \tag{12}$$

The expressions for the cumulants (for $n \leqslant 4$) are given in [3]. Substituting (11), (12) in (6), (7) we obtain

$$\begin{aligned}
\Xi[v_\alpha] = \Xi_{\text{MF}}[\bar{v}_\alpha]\int(d\delta\rho)(d\delta Q)(d\delta\omega)(d\delta\gamma)\exp\bigg\{&-\frac{1}{2!}\sum_{\mathbf{k}}[\widetilde{\Phi}_{NN}(k)\delta\rho_{\mathbf{k}}\delta\rho_{-\mathbf{k}} \\
&+2\widetilde{\Phi}_{NQ}(k)\delta\rho_{\mathbf{k}}\delta Q_{-\mathbf{k}} + \widetilde{\Phi}_{QQ}(k)\delta Q_{\mathbf{k}}\delta Q_{-\mathbf{k}}] + i\sum_{\mathbf{k}}(\delta\omega_{\mathbf{k}}\delta\rho_{\mathbf{k}} + \delta\gamma_{\mathbf{k}}\delta Q_{\mathbf{k}}) \\
&+\sum_{n\geqslant 2}\frac{(-i)^n}{n!}\sum_{i_n\geqslant 0}\sum_{\mathbf{k}_1,\ldots,\mathbf{k}_n}\mathfrak{M}_n^{(i_n)}(k_1,\ldots,k_n)\delta\gamma_{\mathbf{k}_1}\ldots\delta\gamma_{\mathbf{k}_{i_n}}\delta\omega_{\mathbf{k}_{i_{n+1}}}\ldots\delta\omega_{\mathbf{k}_n} \\
&\times\delta_{\mathbf{k}_1+\cdots+\mathbf{k}_n}\bigg\}.
\end{aligned} \tag{13}$$

Let us make the following approximations. We neglect the k dependence of the cumulants putting $\mathfrak{M}_n^{(i_n)}(k_1,\ldots,k_n) \simeq \mathfrak{M}_n^{(i_n)}(0,\ldots,0)$ and replace the full chemical potentials v_α by their MF values v_α^*. We also limit our consideration to the restricted primitive model ($z = 1$)

supplemented by the same short-range interactions for both species (RPM + SR) $\left(v_{11}^{SR}(r) = v_{22}^{SR}(r) = v_{12}^{SR}(r) = v^{SR}(r)\right)$. The latter means that $\widetilde{\Phi}_{NN}(k) = \widetilde{\Phi}^{SR}(k)$, $\widetilde{\Phi}_{NQ}(k) = 0$ and $\widetilde{\Phi}_{QQ}(k) = \widetilde{\Phi}^C(k)$. In this case we have for the cumulants [2]

$$\mathfrak{M}_n^{(0)} = \widetilde{G}_n, \qquad \mathfrak{M}_n^{(2)} = q_0^2 \widetilde{G}_{n-1}, \qquad \mathfrak{M}_n^{(3)} \equiv 0, \qquad \mathfrak{M}_n^{(4)} = q_0^4(3\widetilde{G}_{n-2} - 2\widetilde{G}_{n-3}),$$
(14)

where $\widetilde{G}_n = \widetilde{G}_n(0, \ldots, 0)$ is the Fourier transform of the n-particle truncated (connected) correlation function [9] of a one-component hard sphere system with the density $\bar{\rho}$ defined by (10). Because both $\mathfrak{M}_2^{(0)}$ and $\mathfrak{M}_2^{(2)}$ are positive and smooth functions in the region under consideration [2], we can integrate in (13) over $\delta\omega_{\mathbf{k}}$ and $\delta\gamma_{\mathbf{k}}$ with the Gaussian density measure as basic one. The integration is performed using the Euler equations. We determine $\delta\omega_{\mathbf{k}}^*$ and $\delta\gamma_{\mathbf{k}}^*$ which provide a maximum for the functional in the exponent of (13). This leads to the expression for Ξ

$$\Xi = \Xi_{MF}\mathcal{C}\int(\mathrm{d}\delta\rho)(\mathrm{d}\delta Q)\exp(-\widetilde{\mathcal{H}}(\delta\rho, \delta Q)),$$
(15)

where

$$\widetilde{\mathcal{H}}(\delta\rho, \delta Q) = \frac{1}{2}\sum_{\mathbf{k}}\left[a_2^{(0)}(k)\delta\rho_{\mathbf{k}}\delta\rho_{-\mathbf{k}} + a_2^{(2)}(k)\delta Q_{\mathbf{k}}\delta Q_{-\mathbf{k}}\right]$$
$$+ \sum_{n\geqslant 3}\frac{1}{n!}\sum_{i_n\geqslant 0}\sum_{\mathbf{k}_1,\ldots,\mathbf{k}_n}a_n^{(i_n)}\delta Q_{\mathbf{k}_1}\ldots\delta Q_{\mathbf{k}_{i_n}}\delta\rho_{\mathbf{k}_{i_{n+1}}}\ldots\delta\rho_{\mathbf{k}_n}\delta_{\mathbf{k}_1+\cdots+\mathbf{k}_n}.$$
(16)

and the following notations are introduced

$$\mathcal{C} = \prod_{\mathbf{k}}\frac{1}{\pi\mathfrak{M}_2^{(0)}}\prod_{\mathbf{k}}\frac{1}{\pi\mathfrak{M}_2^{(2)}},$$
$$a_2^{(0)}(k) = \widetilde{\Phi}^{SR}(k) + 1/\mathfrak{M}_2^{(0)}, \qquad a_2^{(2)}(k) = \widetilde{\Phi}^C(k) + 1/\mathfrak{M}_2^{(2)},$$
(17)

$$a_3^{(0)} = -\mathfrak{M}_3^{(0)}/\left(\mathfrak{M}_2^{(0)}\right)^3, \qquad a_3^{(2)} = -\frac{3\mathfrak{M}_3^{(2)}}{\mathfrak{M}_2^{(0)}\left(\mathfrak{M}_2^{(0)}\right)^2},$$
(18)

$$a_4^{(0)} = -\frac{1}{\left(\mathfrak{M}_2^{(0)}\right)^4}\left[\mathfrak{M}_4^{(0)} - \frac{3\left(\mathfrak{M}_3^{(0)}\right)^2}{\mathfrak{M}_2^{(0)}}\right], \qquad a_4^{(2)} = \frac{12\left(\mathfrak{M}_3^{(2)}\right)^2}{\left(\mathfrak{M}_2^{(0)}\right)^2\left(\mathfrak{M}_2^{(2)}\right)^3}, \quad (19)$$

$$a_4^{(4)} = -\frac{1}{\left(\mathfrak{M}_2^{(2)}\right)^4}\left[\mathfrak{M}_4^{(4)} - \frac{3\left(\mathfrak{M}_3^{(2)}\right)^2}{\mathfrak{M}_2^{(0)}}\right].$$
(20)

Taking into account (14) we rewrite (16)–(20) as follows:

$$\Xi = \Xi_{MF}\mathcal{C}'\int(\mathrm{d}\delta\rho)(\mathrm{d}\delta Q^*)\exp(-\widetilde{\mathcal{H}}(\delta\rho, \delta Q^*)),$$
(21)

where

$$\widetilde{\mathcal{H}}(\delta\rho, \delta Q^*) = \frac{1}{2V}\sum_{\mathbf{k}}\left[\widetilde{a}_2^{(0)}(k)\delta\rho_{\mathbf{k}}\delta\rho_{-\mathbf{k}} + \widetilde{a}_2^{(2)}(k)\delta Q_{\mathbf{k}}^*\delta Q_{-\mathbf{k}}^*\right]$$
$$+ \sum_{n\geqslant 3}\frac{1}{n!}\frac{1}{V^{n-1}}\sum_{i_n\geqslant 0}\sum_{\mathbf{k}_1,\ldots,\mathbf{k}_n}\widetilde{a}_n^{(i_n)}\delta Q_{\mathbf{k}_1}^*\ldots\delta Q_{\mathbf{k}_{i_n}}^*\delta\rho_{\mathbf{k}_{i_{n+1}}}\ldots\delta\rho_{\mathbf{k}_n}\delta_{\mathbf{k}_1+\cdots+\mathbf{k}_n}.$$
(22)

Here

$$\widetilde{a}_2^{(0)}(k) = \beta\widetilde{v}^{\mathrm{SR}}(k) + \frac{1}{\bar\rho\widetilde{S}_2}, \qquad \widetilde{a}_2^{(2)}(k) = \beta\widetilde{v}^{C}(k) + \frac{1}{\bar\rho},$$

$$\widetilde{a}_3^{(0)} = -\frac{\widetilde{S}_3}{\bar\rho^2\widetilde{S}_2^3}, \qquad\qquad \widetilde{a}_3^{(2)} = -\frac{3}{\bar\rho^2},$$

$$\widetilde{a}_4^{(0)} = -\frac{1}{\bar\rho\widetilde{S}_2^4}\left(\widetilde{S}_4 - 3\frac{\widetilde{S}_3^2}{\widetilde{S}_2}\right), \qquad \widetilde{a}_4^{(2)} = \frac{12}{\bar\rho^3}, \qquad \widetilde{a}_4^{(4)} = \frac{2}{\bar\rho^3}$$

with $\delta Q_{\mathbf{k}}^* = \delta Q_{\mathbf{k}}/q_0$ and $\widetilde{S}_n = \widetilde{G}_n/\langle N\rangle$.

After taking into account $\frac{1}{V}\sum_{\mathbf{k}} = (2\pi)^{-3}\int d\mathbf{k}$ and $\delta_{\mathbf{k}_1+\cdots+\mathbf{k}_n} = \frac{1}{V}\int d\mathbf{r}\,\exp i\mathbf{r}(\mathbf{k}_1+\cdots+\mathbf{k}_n)$ in (22) we arrive at the same expression for the action as that obtained in the mesoscopic field theory (see, e.g., equations (44)–(48) in [8]), $\Delta\Omega^{\mathrm{MF}}[\tilde\eta, \tilde\phi]$ with $\widetilde\eta(\mathbf{k}) = \delta\rho_{\mathbf{k}}$ and $\widetilde\phi(\mathbf{k}) = \delta Q_{\mathbf{k}}^*$. In order to demonstrate that corresponding coefficients of both actions coincide i.e.,

$$\widetilde{a}_2^{(0)}(k) = \widetilde{C}_{\eta\eta}^{(0)}(k) = \beta\widetilde{v}^{\mathrm{SR}}(k) + \gamma_{0,2}, \tag{23}$$

$$\widetilde{a}_2^{(2)}(k) = \widetilde{C}_{\phi\phi}^{(0)}(k) = \beta\widetilde{v}^{C}(k) + \gamma_{2,0}, \tag{24}$$

$$\widetilde{a}_3^{(0)} = \gamma_{0,3}, \qquad \widetilde{a}_3^{(2)} = 3\gamma_{2,1}, \qquad \widetilde{a}_4^{(0)} = \gamma_{0,4}, \qquad \widetilde{a}_4^{(2)} = 6\gamma_{2,2}, \qquad \widetilde{a}_4^{(4)} = \gamma_{4,0} \tag{25}$$

($\widetilde{C}_{\eta\eta}^{(0)}(k)$, $\widetilde{C}_{\phi\phi}^{(0)}(k)$ and $\gamma_{2m,n}$ are the notations used in [8]), we consider coefficients $\gamma_{2m,n}$ in detail. To this end we recall that $\gamma_{2m,n}$ denotes the appropriate derivative of the Helmholtz free energy of the hard sphere system f_h (see e.g.[8])

$$\gamma_{2m,n} = \beta\left.\frac{\partial^{2m+n}f_h}{\partial\phi^{2m}\partial\rho^{*n}}\right|_{\phi=0,\rho^*=\bar\rho^*}.$$

For example, when the Carnahan–Starling (CS) form of f_h is adobted in the local-density approximation

$$\beta f_h(\rho^*, \phi) = \frac{\rho^*+\phi}{2}\log\left(\frac{\rho^*+\phi}{2}\right) + \frac{\rho^*-\phi}{2}\log\left(\frac{\rho^*-\phi}{2}\right) - \rho^* + \rho^*\frac{s(4-3s)}{(1-s)^2},$$

we obtain the following explicit expressions for $\gamma_{2m,n}$:

$$\gamma_{0,2} = \frac{1+4s+4s^2-4s^3+s^4}{(1-s)^4\bar\rho^*} = \frac{1}{\bar\rho^*\widetilde{S}_2}, \qquad \gamma_{2,0} = \frac{1}{\bar\rho^*} \tag{26}$$

$$\gamma_{0,3} = -\frac{1-5s-20s^2-4s^3+5s^4-s^5}{\bar\rho^{*2}(1-s)^5} = -\frac{\widetilde{S}_3}{\bar\rho^{*2}\widetilde{S}_2^3}, \qquad \gamma_{2,1} = -\frac{1}{\bar\rho^{*2}}, \tag{27}$$

$$\gamma_{0,4} = -\frac{2(1-6s+15s^2+52s^3+3s^4-6s^5+s^6)}{\bar\rho^{*3}(1-s)^6} = -\frac{1}{\bar\rho^{*3}\widetilde{S}_2^4}\left(\widetilde{S}_4 - 3\frac{\widetilde{S}_3^2}{\widetilde{S}_2}\right), \tag{28}$$

$$\gamma_{2,2} = \frac{2}{\bar\rho^{*3}}, \qquad \gamma_{4,4} = \frac{2}{\bar\rho^{*3}}. \tag{29}$$

In the above equations we use the notations $\rho^* = \bar\rho^* + \delta\rho^*$ and $s = \pi\rho^*/6$ ($\rho^* = \rho\sigma^3$ and $\bar\rho^*$ are the dimensionless total number density and its MF value, respectively). As is seen, expressions (26)–(29) confirm the relations given by (23)–(25).

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