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THE LAPLACE TRANSFORM OF PAIR DISTRIBUTION FUNCTIONS OF THE MULTICOMPONENT MIXTURE OF DIMERIZING HARD SPHERES

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The analytical solution of Wertheim's associative Percus-Yevick approximation for the multicomponent mixture of dimerizing hard spheres is analysed. The Laplace transform is obtained for the pair distribution functions.

The integral equation theory in multidensity formalism [1,2,3] has been successfully used for the studies of associating fluids [4-11] during the last time. The investigations have, however, focused primarily on the using different numerical iteration schemes. More convenient description of the structure should include the analytical expression on particular for the Laplace transform of pair distribution functions which are also very useful for different applications. In particular, the Laplace transform of the pair distribution functions of pure hard-sphere system was successfully utilized by I.O.Vakarchuk, Yu.K.Rudavskii and co-workers in their theory of amorphous and liquid ferromagnets (see, for example, Ref.[20] and references therein) .

In this paper we have obtain general expressions for the Laplace transform of pair distribution function of the M-component system of dimerizing hard spheres. The analytical solution of the associative version of Percus-Yevick (APY) approximation for this model has been done recently in [5]. For the description of this model it was used the two-density version of the Ornstein-Zernike equation [1,4,5]

$$\left[\tilde{h}_{ab}^{mn}(k)\right] = \left[\tilde{c}_{ab}^{mn}(k)\right] + \left[\tilde{h}_{ab}^{mn}(k)\right] * \left[\sigma_{ab}^{mn}\right] * \left[\tilde{c}_{ab}^{mn}(k)\right], \qquad (1)$$

supplemented by APY closure for the partial pair correlation functions $h_{ab}^{mn}(r) = g_{ab}^{mn}(r) - \delta_{m0}\ \delta_{n0}$ and the partial direct correlation functions $c_{ab}^{mn}(r)$,

$$h_{ab}^{mn}(r) = -\delta_{m0}\ \delta_{n0} \qquad \text{for } r < d_{ab} \qquad (2)$$

$$c_{ab}^{mn}(r) = \delta_{1m}\ \delta_{1n}\ B_{ab}\ \delta(r - d_{ab}) \qquad \text{for } r > d_{ab} \qquad (3)$$

where $d_{ab} = \frac{1}{2}(d_a + d_b)$; d_a is the diameter of particle; B_{ab} are the strength parameters of the stickiness; $\delta(r)$ is the Dirac delta function; δ_{mn} denotes the Kroneker delta symbol, $g_{ab}^{mn}(r)$ are the partial pair distribution function.

The square brackets in (1) represent the matrices, the symbol "$*$" denotes the convolution and matrix product. The higher indices in the functions $\tilde{h}_{ab}^{mn}(k)$ and $\tilde{c}_{ab}^{mn}(k)$ denote the degree of association of the corresponding particles and can be equal 0 or 1. The matrix $[\sigma_{ab}^{mn}]$ is diagonal about the component indices

$$\sigma_{ab}^{mn} = \sigma_{a}^{mn}\, \delta_{ab},$$

where

$$\sigma_{a}^{00} = \rho_a, \quad \sigma_{a}^{01} = \sigma_{a}^{10} = \rho_{a}^{0}, \quad \sigma_{a}^{11} = 0.$$

The relation between the densities of particles ρ_a and monomer densities ρ_a^0 has the following form [2,5]

$$\rho_a = \rho_a^0 + 4\pi\, \rho_a^0 \sum_{b=1}^{M} \rho_b^0\, (d_{ab})^2\, g_{ab}^{00}(d_{ab}^{+})\, B_{ab}\ . \tag{4}$$

The method of solution APY approximation relies on the factorization scheme of Wertheim-Baxter [12,13]. As result the solution of equations (1) reduces to the calculation of the corresponding Wertheim-Baxter factor correlation functions which were obtained in [5]. Here we rewrite it in the next compact form

$$Q_{ab}^{mn}(r) = \begin{cases} q_{ab}^{mn}(r), & \text{for} \quad \lambda_{ba} < r < d_{ab} \\ 0 & \text{for} \quad r < \lambda_{ba} \text{ and } r > d_{ab}, \end{cases} \tag{5}$$

where $\lambda_{ba} = \frac{1}{2}(d_b - d_a)$,

$$\begin{aligned} q_{ab}^{mn}(r) &= q_{ab}^{(0)mn} + (r - d_{ab})\, q_{ab}^{(1)mn} + \frac{1}{2}(r - d_{ab})^2\, q_{ab}^{(2)mn}, \\ q_{ab}^{(0)mn} &= 2\pi\, d_{ab}\, \delta_{1m}\, \delta_{1n}\, g_{ab}^{00}(d_{ab}^{+})\, B_{ab}\ , \\ q_{ab}^{(1)mn} &= \left(\frac{2\pi}{\Delta}\, d_{ab} + \frac{\pi^2}{2\Delta^2}\, \xi_2\, d_a\, d_b\right) \delta_{0m}\, \delta_{0n} + \frac{d_a}{2}\, q_{ab}^{(dim)mn}\ , \\ q_{ab}^{(2)mn} &= \left(\frac{2\pi}{\Delta} + \frac{\pi^2}{\Delta^2}\, \xi_2\, d_a\, d_b\right) \delta_{0m}\, \delta_{0n} + q_{ab}^{(dim)mn}\ . \end{aligned} \tag{6}$$

Here

$$\Delta = 1 - \frac{\pi}{6}\, \xi_3, \quad \xi_p = \sum_{a=1}^{M} \rho_a\, (d_a)^p\ ,$$

$$q_{ab}^{(dim)mn} = -\frac{4\pi^2}{\Delta}\, \delta_{0m}\, \delta_{1n} \sum_{c=1}^{M} \rho_c^0\, d_c\, d_{cb}\, g_{cb}^{00}(d_{cb}^{+})\, B_{cb}\ . \tag{7}$$

The problem of calculating the partial pair distribution functions reduces to the solution of the set of convolution integral equations

$$r\ g_{ab}^{mn}(r) \ - \ \sum_{c=1}^{M}\sum_{l=0}^{1}\sum_{k=0}^{1}\sigma_c^{lk}\int\limits_{\lambda_{ba}}^{d_{ab}} \mathrm{d}t\ (r-t) g_{ac}^{ml}(|r-t|)\ Q_{cb}^{kn}(t) \ =$$

$$= \ \frac{1}{2\pi}\left(q_{ab}^{(1)mn} \ + \ (r-d_{ab})\ q_{ab}^{(2)mn}\right) \ , \qquad (8)$$

from which for contact values $g_{ab}^{mn}(d_{ab}^{+})$ we have

$$d_{ab}\ g_{ab}^{0n}(d_{ab}^{+}) \ = \ \frac{1}{2\pi}\ q_{ab}^{(1)0n} \ ,$$

$$d_{ab}\ g_{ab}^{1n}(d_{ab}^{+}) \ = \ \sum_{c=1}^{M}\rho_c^0\ \left(\frac{d_{ac}}{\Delta} \ + \ \frac{\pi}{4\Delta^2}\ \xi_2\ d_a\ d_c\right) Q_{cb}^{0n}(\lambda_{bc}) \ . \qquad (9)$$

By a Laplace transformation, we arrive at the linear algebraic equations

$$\sum_{c=1}^{M}\sum_{l=0}^{1}\hat{G}_{ac}^{ml}(s)\left(\delta_{cb}\delta_{ln}-\sum_{k=0}^{1}\sigma_c^{lk}\hat{Q}_{cb}^{kn}(s)\right) = \frac{\exp(-sd_{ab})}{2\pi s^2}\left(q_{ab}^{(2)mn}+sq_{ab}^{(1)mn}\right), \qquad (10)$$

where

$$\hat{G}_{ab}^{mn}(s) \ = \ \int\limits_0^{\infty}\mathrm{d}r\ r g_{ab}^{mn}(r)\mathrm{e}^{-sr}, \qquad (11)$$

$$\hat{Q}_{ab}^{mn}(s) \ = \ \int\limits_{\lambda_{ba}}^{\infty}\mathrm{d}r\ Q_{ab}^{mn}(r)\mathrm{e}^{-sr} =$$

$$= \ \exp\left(s\lambda_{ab}\right)\left(\phi_0(d_a)q_{ab}^{(0)mn}+\phi_1(d_a)q_{ab}^{(1)mn}+\phi_2(d_a)q_{ab}^{(2)mn}\right), \qquad (12)$$

$$\phi_p(d_a) \ = \ s^{-p-1}\left(\sum_{k=0}^{p}\frac{(-sd_a)^k}{k!}-\exp(-sd_a)\right).$$

Analogically as in [14,15] the solution of eq.(10) reduces in general case to the evaluation of the inverse matrix W^{-1} where the matrix W consists of the element

$$W_{ab}^{mn} \ = \ \delta_{ab}\ \delta_{mn} \ - \ \sum_{k=0}^{1}\sigma_a^{mk}\ \hat{Q}_{ab}^{kn}(s) \ . \qquad (13)$$

We suppose analogically as in [16], that the coefficient $q_{ab}^{(0)mn}$ can be represented in the form

$$q_{ab}^{(0)mn} \ = \ 2\pi\ \sigma_{ab}\ \delta_{1m}\ \delta_{1n}\ g_{ab}^{00}(d_{ab})\ B_{ab} \ \equiv \ (w_a\ w_b \ - \ v_a\ v_b)\ \delta_{1m}\ \delta_{1n}, \quad (14)$$

which is the generalization corresponding condition in [17]. Then the matrix W can be written as the Jacobi matrix

$$W_{ab}^{mn} \;=\; \delta_{ab}\,\delta_{mn} \;-\; \hat{a}_a^m\,\hat{b}_b^n \;-\; \hat{c}_a^m\,\hat{d}_b^n \;-\; \hat{e}_a^m\,\hat{f}_b^n \;-\; \hat{z}_a^m\,\hat{y}_b^n\;, \tag{15}$$

where

$$\hat{a}_a^m \;=\; \frac{\pi}{s\Delta}\,\sigma_a^{m0}\,\Big(\,2\,\phi_1(d_a) \;+\; d_a\,\phi_0(d_a)\,\Big)\;;\quad \hat{b}_a^m \;=\; \delta_{0m}\;; \tag{16}$$

$$\hat{c}_a^m \;=\; \frac{\pi}{2\Delta}\,\xi_2\,\hat{a}_a^m \;+\; \frac{\pi}{\Delta}\,\sigma_a^{m0}\,\phi_1(d_a)\;;\qquad \hat{d}_a^m \;=\; d_a\,\delta_{0m}\;; \tag{17}$$

$$\hat{e}_a^m \;=\; \frac{1}{s}\,\sigma_a^{m1}\,w_a \;-\; P_w\,\hat{a}_a^m\;;\qquad \hat{f}_a^m \;=\; w_a\,\delta_{1m}\;; \tag{18}$$

$$\hat{z}_a^m \;=\; \frac{1}{s}\,\sigma_a^{m1}\,v_a \;-\; P_v\,\hat{a}_a^m\;;\qquad \hat{y}_a^m \;=\; v_a\,\delta_{1m}\;; \tag{19}$$

$$P_w \;=\; \sum_{a=1}^{M}\,\rho_a^1\,d_a\,w_a\;;\qquad P_v \;=\; \sum_{a=1}^{M}\,\rho_a^1\,d_a\,v_a\;. \tag{20}$$

After calculation of the inverse matrix W^{-1} we obtain final expression for the Laplace transform of the partial pair distribution functions

$$\begin{aligned}
&\hat{G}_{ab}^{mn}(s) = \\
&= \frac{\exp(-s\;d_{ab})}{2\pi\;s^2\;D_0}\left\{\left(\frac{2\pi}{\Delta}\;\hat{b}_a^m + \frac{\pi}{\Delta}\;s\;\hat{d}_a^m\right)\Big((1-\hat{c}\hat{d})\left(\hat{b}_a^n + E_1\;\hat{h}_b^n + F_1\;\hat{p}_b^n\right) + \right.\\
&+ (\hat{c}\hat{b})\left(\hat{d}_b^n + E_2\;\hat{h}_b^n + F_2\;\hat{p}_b^n\right)\Big) + \left(\frac{\pi^2}{\Delta^2}\xi_2\hat{b}_a^m + \frac{\pi}{\Delta}s\hat{b}_a^m + \frac{\pi^2}{2\Delta^2}\xi_2 s\hat{b}_a^m\right)\times \\
&\times \left.\Big((1-\hat{a}\hat{b})\left(\hat{d}_b^n + E_2\;\hat{h}_b^n + F_2\;\hat{p}_b^n\right) + (\hat{a}\hat{d})\left(\hat{b}_b^n + E_1\;\hat{h}_b^n + F_1\;\hat{p}_b^n\right)\Big)\right\} + \\
&+ \frac{\exp(-s\;d_{ab})}{2\pi\;s^2\;D_1}\left\{P_v\left(\frac{2\pi}{\Delta}\;\hat{b}_a^m + \frac{\pi}{\Delta}\;s\;\hat{d}_a^m\right)\Big((1-\hat{e}\hat{h})\;\hat{p}_b^n + (\hat{e}\hat{p})\;\hat{h}_b^n\Big) - \right.\\
&- \left.P_w\left(\frac{2\pi}{\Delta}\;\hat{b}_a^m + \frac{\pi}{\Delta}\;s\;\hat{d}_a^m\right)\Big((1-\hat{z}\hat{p})\;\hat{h}_b^n + (\hat{z}\hat{h})\;\hat{p}_b^n\Big)\right\},
\end{aligned} \tag{21}$$

where

$$\begin{aligned}
\hat{h}_a^m \;&=\; \hat{f}_a^m \;+\; \frac{1}{D_0}\left\{(1-\hat{c}\hat{d})(\hat{a}\hat{f}) + (\hat{a}\hat{d})(\hat{c}\hat{f})\right\}\;\hat{b}_a^m \;+ \\
&+\; \frac{1}{D_0}\left\{(1-\hat{a}\hat{b})(\hat{c}\hat{f}) + (\hat{c}\hat{b})(\hat{a}\hat{f})\right\}\;\hat{d}_a^m,
\end{aligned} \tag{22}$$

$$\begin{aligned}
\hat{p}_a^m \;&=\; \hat{y}_a^m \;+\; \frac{1}{D_0}\left\{(1-\hat{c}\hat{d})(\hat{a}\hat{y}) + (\hat{a}\hat{d})(\hat{c}\hat{y})\right\}\;\hat{b}_a^m \;+ \\
&+\; \frac{1}{D_0}\left\{(1-\hat{a}\hat{b})(\hat{c}\hat{y}) + (\hat{c}\hat{b})(\hat{a}\hat{y})\right\}\;\hat{d}_a^m,
\end{aligned} \tag{23}$$

$$E_1 = \frac{1}{D_1}\Big((1-\hat{z}\hat{p})(\hat{e}\hat{b}) + (\hat{e}\hat{p})(\hat{z}\hat{b})\Big), \tag{24}$$

$$E_2 = \frac{1}{D_1}\Big((1-\hat{z}\hat{p})(\hat{e}\hat{d}) + (\hat{e}\hat{p})(\hat{z}\hat{d})\Big), \tag{25}$$

$$F_1 = \frac{1}{D_1}\Big((1-\hat{e}\hat{h})(\hat{z}\hat{b}) + (\hat{z}\hat{h})(\hat{e}\hat{b})\Big), \tag{26}$$

$$F_2 = \frac{1}{D_1}\Big((1-\hat{e}\hat{h})(\hat{z}\hat{d}) + (\hat{z}\hat{h})(\hat{e}\hat{d})\Big), \tag{27}$$

$$D_0 = (1-\hat{a}\hat{b})(1-\hat{c}\hat{d}) - (\hat{a}\hat{d})(\hat{c}\hat{b}), \tag{28}$$

$$D_1 = (1-\hat{z}\hat{p})(1-\hat{e}\hat{h}) - (\hat{e}\hat{p})(\hat{z}\hat{h}), \tag{29}$$

$$(\hat{a}\hat{b}) = \sum_{c=1}^{M} \hat{a}_c \hat{b}_c, \ldots$$

Thus in this letter we have represented the analytical expressions for the Laplace transform of the partial pair distribution functions. From here the expressions for $g_{ab}^{mn}(r)$ can be obtained in explicit form by using zone-zone expansions [18] or Laplace transform can be converted to a Fourier transform for which very efficient and very fast programs for calculating the inverse exist. The total pair distribution functions $g_{ab}(r)$ are the sum of four terms

$$g_{ab}(r) = g_{ab}^{00} + x_a\, g_{ab}^{10}(r) + x_b\, g_{ab}^{01}(r) + x_a\, x_a\, g_{ab}^{11}(r)\,. \tag{30}$$

The generality of considered model allows several application of obtained results. Among these we mention the calculation of intercolloidal mean force for which the knowledge of the Laplace transform of the pair distribution functions is very important (see [19] and further citations therein).

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ЛАПЛАС-ОБРАЗ ПАРНИХ ФУНКЦІЙ РОЗПОДІЛУ БАГАТОКОМПОНЕНТНОЇ СУМІШІ ТВЕРДИХ СФЕР, ЩО ДИМЕРИЗУЮТЬСЯ

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У роботі представлено вираз для лаплас-образів парних функцій розподілу багатокомпонентної суміші димеризуючих твердих сфер. Розрахунки зроблені на основі отриманого нами раніше аналітичного розв'язку інтегральних рівнянь типу Орнштейна-Церніке (теорія асоціативних рідин Вертхайма) в наближенні Перкуса-Йевіка.