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Yukawa fluids in the mean scaling approximation: I. The general solution*

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Abstract

A new general form of the multi-Yukawa, multicomponent closure of the Ornstein–Zernike equation for factored interactions is derived. The general solution is given in terms of an $M \times M$ scaling matrix $\mathbf{\Gamma}$ obtained by solving M (equal to the number of Yukawa terms in the closure) equations together with $M(M-1)$ symmetry conditions

$$2\pi K^{(n)} \sum_j \rho_j X_j^{(n)} \hat{B}_j(z_n) + z_n \sum_k \rho_k a_k^{(n)} \Pi_k^{(n)} + \sum_m \frac{z_n}{z_n + z_m} \left\{ \sum_k \rho_k a_k^{(n)} a_k^{(m)} \right\} \sum_j \rho_j X_j^{(m)} \Pi_j^{(n)} = \tilde{\tilde{\mathbf{\Delta}}}^{(n)}$$

where $\tilde{\tilde{\mathbf{\Delta}}}^{(n)}$ is of higher order in the density, and all quantities are algebraic functions of $\mathbf{\Gamma}$.

Explicit formulae for the thermodynamic properties are also provided.

1. Introduction

The density functional developed by Yasha Rosenfeld [1, 2] is, no doubt, a great advance in the treatment of fluid systems. The extension of these methods to systems with general soft interactions such as Coulomb [3] and screened Coulomb interactions is still an open problem.

There is an enormous wealth of problems, ranging from engineering applications to biological research, polymers, colloidal systems, water and ionic solutions, which can be formulated as closures of some kind of either a scalar or matrix Ornstein–Zernike (OZ)

* We dedicate this paper to Yasha Rosenfeld, a giant in condensed matter physics.
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equation. These closures can always be expressed by a sum of exponentials, which form a complete basis set if we allow for complex numbers [4, 5].

The discussion of numerical examples such as the equation of state for simple fluids [6] and the ' YUKAGUA' model of water [7] is left for future publications. The YUKAGUA model is the octupole model of water with the Yukawa closure. The analytic solution of the sticky octupole model was discussed in a paper by Blum and Vericat [8].

While the initial motivation was to study simple approximations such as the mean spherical approximation (MSA) [9] or generalized mean spherical approximation (GMSA)[10], the availability of closed-form solutions for the general closure of the hard-core OZ equation makes it possible to write down analytical solutions for any given approximation that can be formulated by writing the direct correlation function $c_{ij}(r)$ outside the hard core as

$$c_{ij}(r) = \sum_{n=1}^{M} K_{ij}^{(n)} \mathrm{e}^{-z_n(r-\sigma_{ij})}/r = \sum_{n=1}^{M} \mathcal{K}_{ij}^{(n)} \mathrm{e}^{-z_n r}/r. \tag{1}$$

This is the most general form of the closure of the OZ equation. As was discussed elsewhere by us [11], the first $M_0 \leqslant M$ terms correspond to the interaction energy and the remainder to a parametrized form of the closure. We have called this approximation the mean scaling approximation (MESCA). Clearly when $M_0 = M$, then the MESCA is identical to the MSA. In this equation $K_{ij}^{(n)}$ is the interaction/closure constant used in the general solution first found by Blum and Høye (which we will call BH78) [12], while $\mathcal{K}_{ij}^{(n)}$ is the definition used in the later general solution by Blum, Vericat and Herrera (BVH92 in what follows) [13]. In this work we shall use the more common notation of BVH92. The case of factored interactions discussed by Blum [14] was simplified by Ginoza [15–18], who found that, as in the case of electrolytes [19], the solution of the one-exponent case could be expressed in terms of a single scaling parameter Γ. In the factorizable case we have

$$K_{ij}^{(n)} = K^{(n)} \delta_i^{(n)} \delta_j^{(n)} \qquad \mathcal{K}_{ij}^{(n)} = K^{(n)} d_i^{(n)} d_j^{(n)} \tag{2}$$

where we have defined

$$\delta_i^{(n)} = d_i^{(n)} \mathrm{e}^{-z_n \sigma_i/2}. \tag{3}$$

The general solution of this problem was formulated by Blum *et al* [13] in terms of a scaling matrix $\mathbf{\Gamma}$. The full solution was given recently by Blum *et al* [4, 20, 21]. For only one component the matrix $\mathbf{\Gamma}$ is assumed diagonal and explicit expressions for the closure relations for any arbitrary number of Yukawa exponents M are obtained. The solution is remarkably simple in the MSA since then explicit formulas for the thermodynamic properties are obtained.

In the next section we review and upgrade our previous work. In section 3 we discuss the closure, and derive new formulae for the general case. In section 4 we review briefly the symmetry conditions, in section 5 we derive general expressions for the thermodynamic properties and finally in section 6 we show that our equations reduce correctly to the 1-Yukawa case.

2. Summary of previous work

We study the OZ equation

$$h_{ij}(12) = c_{ij}(12) + \sum_k \int \mathrm{d}3\, h_{ik}(13)\rho_k c_{kj}(32) \tag{4}$$

where $h_{ij}(12)$ is the molecular total correlation function, $c_{ij}(12)$ is the molecular direct correlation function, ρ_i is the number density of the molecules i, $i = 1, 2$ is the position

$\vec{r}_i$, $r_{12} = |\vec{r}_1 - \vec{r}_2|$ and σ_{ij} is the distance of closest approach of two particles i, j. The direct correlation function is

$$c_{ij}(r) = \sum_{n=1}^{M} K_{ij}^{(n)} \mathrm{e}^{-z_n(r-\sigma_{ij})} \big/ r, \qquad r > \sigma_{ij} \tag{5}$$

and the pair correlation function is

$$h_{ij}(r) = g_{ij}(r) - 1 = -1, \qquad r \leqslant \sigma_{ij}. \tag{6}$$

We use the Baxter–Wertheim (BW) factorization of the OZ equation

$$[\boldsymbol{I} + \rho\tilde{\boldsymbol{H}}(\boldsymbol{k})][\boldsymbol{I} - \rho\tilde{\boldsymbol{C}}(k)] = \boldsymbol{I} \tag{7}$$

where $\boldsymbol{I}$ is the identity matrix, and we have used the notation

$$\tilde{\boldsymbol{H}}(k) = 2\int_0^\infty \mathrm{d}r \cos(kr)\boldsymbol{J}(r) \tag{8}$$

$$\tilde{\boldsymbol{C}}(k) = 2\int_0^\infty \mathrm{d}r \cos(kr)\boldsymbol{S}(r). \tag{9}$$

The matrices J and S have matrix elements

$$J_{ij}(r) = 2\pi \int_r^\infty \mathrm{d}s\, s h_{ij}(s) \tag{10}$$

$$S_{ij}(r) = 2\pi \int_r^\infty \mathrm{d}s\, s c_{ij}(s) \tag{11}$$

$$[\boldsymbol{I} - \rho\tilde{\boldsymbol{C}}(k)] = [\boldsymbol{I} - \rho\tilde{\boldsymbol{Q}}(k)][\boldsymbol{I} - \rho\tilde{\boldsymbol{Q}}^{\mathrm{T}}(-k)] \tag{12}$$

where $\tilde{\boldsymbol{Q}}^{\mathrm{T}}(-k)$ is the complex conjugate and transpose of $\tilde{\boldsymbol{Q}}(k)$. The first matrix is non-singular in the upper half complex k-plane, while the second is non-singular in the lower half complex k-plane.

It can be shown that the factored correlation functions must be of the form

$$\tilde{\boldsymbol{Q}}(k) = \boldsymbol{I} - \rho\int_{\lambda_{ji}}^\infty \mathrm{d}r\, \mathrm{e}^{\mathrm{i}kr}\tilde{\boldsymbol{Q}}(r) \tag{13}$$

where we used the following definition:

$$\lambda_{ji} = \tfrac{1}{2}(\sigma_j - \sigma_i) \tag{14}$$

$$\boldsymbol{S}(r) = \boldsymbol{Q}(r) - \int \mathrm{d}r_1\, \boldsymbol{Q}(r_1)\rho\boldsymbol{Q}^{\mathrm{T}}(r_1 - r). \tag{15}$$

Similarly, from equations (12) and (7) we obtain, using the analytical properties of Q and Cauchy's theorem,

$$\boldsymbol{J}(r) = \boldsymbol{Q}(r) + \int \mathrm{d}r_1\, \boldsymbol{J}(r - r_1)\rho\boldsymbol{Q}(r_1). \tag{16}$$

The general solution is discussed in [14, 15], and yields

$$q_{ij}(r) = q_{ij}^0(r) + \sum_{n=1}^{M} D_{ij}^{(n)}\mathrm{e}^{-z_n r} \qquad \lambda_{ji} < r \tag{17}$$

$$q_{ij}^0(r) = (1/2)A_j[(r - \sigma_j/2)^2 - (\sigma_i/2)^2] + \beta_j[(r - \sigma_j/2) - (\sigma_i/2)] + \sum_{n=1}^{M} C_{ij}^{(n)}\mathrm{e}^{-z_n\sigma_j/2}[\mathrm{e}^{-z_n(r-\sigma_j/2)} - \mathrm{e}^{-z_n\sigma_i/2}] \qquad \lambda_{ji} < r < \sigma_{ij}. \tag{18}$$

From here

$$q_{ij}(\lambda_{ji}) = -\sigma_i\beta_j - \sum_{m=1}^{M}\big[(C_{ij}^{(m)} + D_{ij}^{(m)})(1-\mathrm{e}^{-z_m\sigma_i}) + D_{ij}^{(m)}\mathrm{e}^{-z_m\sigma_i}\big]\mathrm{e}^{-z_m\lambda_{ji}} \tag{19}$$

$$q'_{ij}(\sigma_{ji}) = A_j(\sigma_i/2) + \beta_j - \sum_{m=1}^{M} z_m(C_{ij}^{(m)} + D_{ij}^{(m)})\mathrm{e}^{-z_m\sigma_{ji}} \tag{20}$$

which will be used below in connection with the symmetry requirements for the factor functions. Furthermore the coefficients of all the exponentials must satisfy equation (16)

$$C_{ij}^{(n)} + D_{ij}^{(n)} = \frac{2\pi}{z_n}\sum_k \rho_k \tilde{g}_{ik}^{(n)} D_{kj}^{(n)} \tag{21}$$

where

$$D_{ij}^{(n)} = -\delta_j^{(n)} a_j^{(n)} \mathrm{e}^{z_n\sigma_{ij}}. \tag{22}$$

The solution of this system of equations [13] yields in the factored case

$$A_j = A_j^0 + \frac{\pi}{\Delta}\sum_n a_j^{(n)} P^{(n)} \tag{23}$$

$$\beta_j = \beta_j^0 + \sum_n a_j^{(n)}\Delta^{(n)} \tag{24}$$

where

$$A_j^0 = \frac{2\pi}{\Delta}\left[1 + (1/2)\zeta_2\frac{\pi}{\Delta}\sigma_j\right] \tag{25}$$

$$\beta_j^0 = \frac{\pi}{\Delta}\sigma_j \tag{26}$$

and

$$\left(\frac{\pi}{\Delta}\right)P^{(n)} = \frac{1}{z_n}\sum_\ell \rho_\ell\big[A_\ell^0 X_\ell^{(n)} + 2\beta_\ell^0\big(z_n X_\ell^{(n)} - \Pi_\ell^{(n)}\big)\big]. \tag{27}$$

Alternatively

$$P^{(n)} = \left(\zeta_2 - \frac{\Delta z_n}{\pi}\right)\Delta^{(n)} + \sum_\ell \rho_\ell\big[\sigma_\ell^2\phi_0(\sigma_\ell z_n)\hat{B}_\ell(z_n) + \sigma_\ell\delta_\ell^{(n)}\big] \tag{28}$$

$$\Delta^{(n)} = -\frac{1}{z_n^2}\sum_\ell \rho_\ell[X_\ell^{(n)}A_\ell^0 + \beta_\ell^0(z_n X_\ell^{(n)} - 2\Pi_\ell^{(n)})]. \tag{29}$$

Also

$$\Delta^{(n)} = -\frac{2\pi}{z_n^2\Delta}\sum_\ell \rho_\ell\big[(1 + z_n\sigma_\ell/2)\delta_\ell^{(n)}\big] - \frac{2\pi}{\Delta}\sum_\ell \rho_\ell\sigma_\ell^3\psi_1(z_n\sigma_\ell)\hat{B}_\ell(z_n). \tag{30}$$

We notice that

$$P^{(n)} = \sum_\ell \rho_\ell\beta_\ell^0 X_\ell^{(n)} - z_n\Delta^{(n)}. \tag{31}$$

We recall that

$$\Pi_j^{(n)} = \hat{B}_j(z_n) + (1 + \sigma_j z_n/2)\Delta^{(n)} + \tfrac{1}{2}\sigma_j\sum_\ell \rho_\ell\beta_\ell^0 X_\ell^{(n)} \tag{32}$$

$$X_i^{(n)} = \delta_i^{(n)} + \sigma_i\hat{B}_i(z_n)\phi_0(z_n\sigma_i) + \sigma_i\Delta^{(n)} \tag{33}$$

which now read

$$\Pi_j^{(n)} = \hat{\xi}_j^{(n)} + \sum_\ell \hat{\mathcal{I}}_{j\ell}^{(n)} \hat{B}_\ell(z_n) \tag{34}$$

where

$$\hat{\mathcal{I}}_{j\ell}^{(n)} = \delta_{j\ell} + \rho_\ell \left[\beta_\ell^0 \frac{\sigma_j^2}{2} \phi_0(z_n\sigma_j) - (A_\ell^0 + z_n\beta_\ell^0)\sigma_j^3 \psi_1(z_n\sigma_j)) \right] \tag{35}$$

and

$$\hat{\xi}_j^{(n)} = -\frac{1}{z_n^2} \sum_\ell \rho_\ell \delta_\ell^{(n)} \left[z_n\beta_j^0 + A_j^0 \left(1 + \frac{z_n\sigma_\ell}{2} \right) \right]. \tag{36}$$

Furthermore

$$X_j^{(n)} = \gamma_j^{(n)} + \sum_\ell \hat{\mathcal{J}}_{j\ell}^{(n)} \hat{B}_\ell(z_n). \tag{37}$$

Here

$$\hat{\mathcal{J}}_{j\ell}^{(n)} = \delta_{j\ell}\sigma_j\phi_0(z_n\sigma_\ell) - 2\rho_\ell\beta_\ell^0\sigma_j^3\psi_1(z_n\sigma_j) \tag{38}$$

and

$$\hat{\gamma}_j^{(n)} = \delta_j^{(n)} - \frac{2\beta_j^0}{z_n^2} \sum_\ell \rho_\ell \delta_\ell^{(n)} \left(1 + \frac{z_n\sigma_\ell}{2} \right). \tag{39}$$

Remember also that

$$\zeta_n = \sum_k \rho_k \sigma_k^n \tag{40}$$

$$\Delta = 1 - \pi\zeta_3/6 \tag{41}$$

$$\tilde{g}_{ij}(s) = \int_0^\infty \mathrm{d}r\, r g_{ij}(r) \mathrm{e}^{-sr} \tag{42}$$

$$\hat{B}_j(z_n) = 2\pi \sum_i \rho_i \delta_i^{(n)} \tilde{g}_{ij}(z_n) \mathrm{e}^{z_n\sigma_{ij}}. \tag{43}$$

Also

$$\psi_1(x) = [1 - x/2 - (1 + x/2)\mathrm{e}^{-x}]/(x^3) = [-1 + (1 + x/2)\phi_0(x)]/x^2 \tag{44}$$

$$\phi_1(x) = [1 - x - \mathrm{e}^{-x}]/(x^2) = x\psi_1(x) - \phi_0(x)/2 \tag{45}$$

$$\phi_0(x) = [1 - \mathrm{e}^{-x}]/(x). \tag{46}$$

Furthermore from equations (33) and (32) we obtain by eliminating $\hat{B}_i(z_n)$

$$X_i^{(n)} - \sigma_i\phi_0(z_n\sigma_i)\Pi_i^{(n)} = \delta_i^{(n)} - \tfrac{1}{2}\sigma_i\phi_0(z_n\sigma_i) \sum_\ell \rho_\ell\beta_\ell^0 X_\ell^{(n)} - \sigma_i^3 z_n^2 \psi_1(z_n\sigma_i)\Delta^{(n)} \tag{47}$$

or

$$\sum_\ell \left\{ \frac{\rho_\ell}{\rho_j} \right\} \hat{J}_{\ell j}^{(n)} \Pi_\ell^{(n)} = \sum_\ell \left\{ \frac{\rho_\ell}{\rho_j} \right\} \hat{I}_{\ell j}^{(n)} X_\ell^{(n)} - \delta_j^{(n)} \tag{48}$$

which can be rewritten as

$$\sum_\ell \rho_\ell \{ \Pi_\ell^{(n)} \hat{\gamma}_\ell^{(n)} - X_\ell^{(n)} \hat{\xi}_\ell^{(n)} \} = \mathcal{E}^{(n)} \tag{49}$$

where

$$\mathcal{E}^{(n)} = \sum_\ell \rho_\ell \hat{B}_\ell(z_n) \hat{\delta}_\ell^{(n)}. \tag{50}$$

2.1. The Laplace transforms

From equation (16) we obtain the Laplace transform of the pair correlation function

$$2\pi \sum_{\ell} \tilde{g}_{\ell}(s)[\delta_{\ell j} - \rho_{\ell}\tilde{q}_{\ell j}(\mathrm{i}s)] = \tilde{q}^{0'}_{ij}(\mathrm{i}s) \tag{51}$$

where

$$\tilde{q}^{0'}_{ij}(\mathrm{i}s) = \int_{\sigma_{ij}}^{\infty} \mathrm{d}r\, \mathrm{e}^{-sr}[q^0_{ij}(r)]' = [(1 + s\sigma_i/2)A_j + s\beta_j]\mathrm{e}^{-s\sigma_{ij}}/s^2 - \sum_m \frac{z_m}{s + z_m}\mathrm{e}^{-(s+z_m)\sigma_{ij}} C^{(m)}_{ij}. \tag{52}$$

The Laplace transform of equations (17) and (18) yields

$$\mathrm{e}^{s\lambda_{ji}}\tilde{q}_{ij}(\mathrm{i}s) = \sigma_i^3\psi_1(s\sigma_i)A_j + \sigma_i^2\phi_1(s\sigma_i)\beta_j + \sum_m \frac{1}{s + z_m} \times \left[(C^{(m)}_{ij} + D^{(m)}_{ij})\mathrm{e}^{-z_m\lambda_{ji}} - C^{(m)}_{ij}\mathrm{e}^{-z_m\sigma_{ji}} - z_m\sigma_i\phi_0(s\sigma_i)C^{(m)}_{ij}\mathrm{e}^{-z_m\sigma_{ji}}\right]. \tag{53}$$

This result will be used below.

3. The closure

The MSA closure condition obtained from equation (5) is

$$2\pi K^{(n)}\delta^{(n)}_i\delta^{(n)}_j/z_n = \sum_{\ell} D^{(n)}_{i\ell}[\delta_{\ell j} - \rho_{\ell}\tilde{q}_{j\ell}(\mathrm{i}z_n)]. \tag{54}$$

Using the results of the last section we obtain the result of BVH92 [13]

$$2\pi K\delta^{(n)}_j/z_n + \sum_{\ell} a^{(n)}_{\ell}\mathcal{I}^{(n)}_{j\ell} - \sum_m \frac{1}{z_n + z_m}\left\{\sum_k \rho_k a^{(n)}_k a^{(m)}_k\right\} \left[\sum_{\ell}\mathcal{J}^{(n)}_{j\ell}[\Pi^{(m)}_{\ell} - z_m X^{(m)}_{\ell}] - \mathcal{I}^{(n)}_{j\ell}X^{(m)}_{\ell}\right] = 0 \tag{55}$$

where we are using the new symbols

$$\mathcal{I}^{(n)}_{j\ell} = \hat{\mathcal{I}}^{(n)}_{\ell j}\frac{\rho_{\ell}}{\rho_j}; \qquad \mathcal{J}^{(n)}_{j\ell} = \hat{\mathcal{J}}^{(n)}_{\ell j}\frac{\rho_{\ell}}{\rho_j}. \tag{56}$$

We multiply now equation (55) by

$$\rho_j\hat{B}^{(n)}_j\delta^{(n)}_j \tag{57}$$

and sum over the index j. Then, using equations (34) and (37) we obtain

$$2\pi\frac{K^{(n)}}{z_n}\sum_j \rho_j\delta^{(n)}_j\hat{B}^{(n)}_j - \sum_{\ell}\rho_{\ell}a^{(n)}_{\ell}\hat{\xi}^{(n)}_{\ell} + \sum_m \frac{1}{z_n + z_m}\left\{\sum_k \rho_k a^{(n)}_k a^{(m)}_k\right\}\left[\sum_{\ell}[\Pi^{(m)}_{\ell} - z_m X^{(m)}_{\ell}]\hat{\gamma}^{(n)}_{\ell} - X^{(m)}_{\ell}\hat{\xi}^{(n)}_{\ell}\right] = 0. \tag{58}$$

This can be written in the form

$$\sum_j \rho_j\delta^{(n)}_j\left[2\pi\frac{K^{(n)}}{z_n}\hat{B}^{(n)}_j + \sum_m \frac{1}{z_n + z_m}\left\{\sum_k \rho_k a^{(n)}_k a^{(m)}_k\right\}[\Pi^{(m)}_j - z_m X^{(m)}_j]\right] - \sum_{\ell}\rho_{\ell}a^{(n)}_{\ell}\hat{\xi}^{(n)}_{\ell} + \sum_m \frac{1}{z_n + z_m}\left\{\sum_k \rho_k a^{(n)}_k a^{(m)}_k\right\} \times \sum_{\ell}\rho_{\ell}([\Pi^{(m)}_{\ell} - z_m X^{(m)}_{\ell}](\hat{\gamma}^{(n)}_{\ell} - \hat{\delta}^{(n)}_{\ell}) - X^{(m)}_{\ell}\hat{\xi}^{(n)}_{\ell}) = 0. \tag{59}$$

3.1. The alternative closure

Combining equation (5) with (51), we now obtain an expression for the excess MSA energy parameter due to the interaction n

$$\frac{2\pi}{z_n}\sum_\ell \rho_\ell \tilde{g}_{j\ell}(z_n)K_{i\ell}^{(n)} = \frac{1}{2\pi}\sum_\ell \rho_\ell D_{i\ell}^{(n)}\tilde{q}_{j\ell}^{0\prime}(\mathrm{i}z_n). \tag{60}$$

For the factored case we obtain, also using equation (43),

$$\frac{K^{(n)}}{z_n}\hat{B}_j(z_n) = -\frac{1}{2\pi}\sum_\ell \rho_\ell a_\ell^{(n)}\mathrm{e}^{z_n\sigma_{j\ell}}\tilde{q}_{j\ell}^{0\prime}(\mathrm{i}z_n). \tag{61}$$

Using the results of the previous subsection we obtain

$$2\pi K^{(n)}\hat{B}_j(z_n) = z_n\sum_\ell \rho_\ell a_\ell^{(n)}\left\{-\frac{1}{z_n^2}\left[A_\ell\left(1+\frac{z_n\sigma_j}{2}\right)+z_n\beta_\ell\right]+\sum_m\frac{z_m}{z_n+z_m}\mathrm{e}^{-z_m\sigma_{j\ell}}C_{j\ell}^{(m)}\right\}. \tag{62}$$

After some algebra

$$2\pi K^{(n)}\hat{B}_j(z_n) = \sum_m\frac{z_n}{z_n+z_m}\left\{\sum_k\rho_k a_k^{(n)}a_k^{(m)}\right\}[-\Pi_j^{(m)}+z_mX_j^{(m)}]+\tilde{\Delta}_j(z_n) \tag{63}$$

where

$$\begin{aligned}\tilde{\Delta}_j(z_n) = {}&-\sum_\ell\rho_\ell a_\ell^{(n)}\left\{\frac{1}{z_n}A_\ell^0\left(1+\frac{z_n\sigma_j}{2}\right)+\beta_\ell^0\right\}\\ &-\sum_m\sum_\ell\rho_\ell a_\ell^{(n)}a_\ell^{(m)}\left\{\frac{\pi}{z_n\Delta}P^{(m)}+\frac{z_m}{z_n+z_m}\left[\Delta^{(m)}+\frac{\sigma_j\pi}{2\Delta}P^{(m)}\right]\right\}.\end{aligned} \tag{64}$$

This equation is equal to equation (75) of BVH92 [13] (which had two typos)

$$\begin{aligned}2\pi K^{(n)}\hat{B}_j^{(n)}/z_n = {}&-\frac{2\pi}{\Delta z_n^2}\sum_\ell\rho_\ell a_\ell^{(n)}\left[1+z_n\sigma_\ell/2+\sigma_\ell\left[\left(1+\zeta_2\frac{\pi}{2\Delta}\sigma_j\right)\frac{z_n}{2}+\zeta_2\frac{\pi}{2\Delta}\right]\right]\\ &-\sum_m\frac{1}{z_n+z_m}\left\{\sum_k\rho_k a_k^{(n)}a_k^{(m)}\right\}\left[\Pi_j^{(m)}-z_mX_j^{(m)}+\frac{z_m}{z_n}\Delta^{(m)}\right.\\ &\left.+\frac{\pi}{\Delta z_n^2}P^{(m)}(z_n+z_m+\sigma_jz_nz_m/2)\right]\end{aligned} \tag{65}$$

and can be written as

$$\begin{aligned}2\pi K^{(n)}\hat{B}_j^{(n)} = {}&\sum_m\left\{\sum_k\rho_k a_k^{(n)}a_k^{(m)}\right\}\left[\frac{z_n}{z_n+z_m}(z_m\delta_j^{(m)}-\hat{B}_j^{(m)}\mathrm{e}^{-z_m\sigma_j})+\Delta^{(m)}\right.\\ &\left.+\frac{\pi}{z_n\Delta}P^{(m)}\left(1+\frac{z_n\sigma_j}{2}\right)\right]-\sum_\ell\rho_\ell a_\ell^{(n)}\left\{\frac{1}{z_n}A_\ell^0\left(1+\frac{z_n\sigma_j}{2}\right)+\beta_\ell^0\right\}.\end{aligned} \tag{66}$$

The closure of our problem can also be obtained from equation (63) by contracting this equation with $\rho_jX_j^{(n)}$: we obtain

$$\begin{aligned}2\pi K^{(n)}\sum_j\rho_jX_j^{(n)}\hat{B}_j(z_n) = {}&\sum_m\frac{1}{z_n+z_m}\left\{\sum_k\rho_k a_k^{(n)}a_k^{(m)}\right\}\sum_j\rho_jX_j^{(n)}[-\Pi_j^{(m)}+z_mX_j^{(m)}]\\ &+\sum_j\rho_jX_j^{(n)}\tilde{\Delta}_j(z_n)\end{aligned} \tag{67}$$

which can be expressed as

$$2\pi K^{(n)}\sum_j \rho_j X_j^{(n)}\hat{B}_j(z_n) = -z_n\sum_k \rho_k a_k^{(n)}\Pi_k^{(n)} - \sum_m \frac{z_n}{z_n+z_m}\left\{\sum_k \rho_k a_k^{(n)} a_k^{(m)}\right\}\sum_j \rho_j X_j^{(m)}\Pi_j^{(n)} + \tilde{\tilde{\mathbf{\Delta}}}^{(n)} \tag{68}$$

with

$$\tilde{\tilde{\mathbf{\Delta}}}^{(n)} = \sum_j \rho_j X_j^{(n)}\tilde{\Delta}_j(z_n)$$

or also as

$$2\pi K^{(n)}\sum_j \rho_j X_j^{(n)}\Pi_j^{(n)} = -z_n\sum_k \rho_k a_k^{(n)}\Pi_k^{(n)} - \sum_m \frac{z_n}{z_n+z_m}\left\{\sum_k \rho_k a_k^{(n)} a_k^{(m)}\right\}\sum_j \rho_j X_j^{(m)}\Pi_j^{(n)} + \tilde{\tilde{\mathbf{\Delta}}}_p^{(n)} \tag{69}$$

with

$$\tilde{\tilde{\mathbf{\Delta}}}_p^{(n)} = \sum_j \rho_j X_j^{(n)}\left\{\tilde{\Delta}_j(z_n) + 2\pi K^{(n)}\left[(1+\sigma_j z_n/2)\Delta^{(n)} + \tfrac{1}{2}\beta_j^0\sum_\ell \rho_\ell \beta_\ell^0 X_\ell^{(n)}\right]\right\}. \tag{70}$$

This yields a new set of M equations for the scaling matrix $\mathbf{\Gamma}$ [11, 13]. The remaining $M(M-1)$ parameters are obtained from the symmetry relations that we shall discuss in the next section. This equation will be used below to compute various physical quantities of interest, such as the pair distribution functions and excess thermodynamic properties. We notice that in all of the equations of this section the variable z_n is completely interchangeable with the Laplace variable s. For example, instead of equation (63) we could have written

$$2\pi K^{(n)}\hat{B}_j(s) = \sum_m \frac{s}{s+z_m}\left\{\sum_k \rho_k a_k^{(n)} a_k^{(m)}\right\}[-\Pi_j^{(m)} + z_m X_j^{(m)}] + \tilde{\Delta}_j(s). \tag{71}$$

4. Symmetry

A full solution of the multi-Yukawa, multicomponent mixture requires the introduction of a scaling parameter. The most general scaling relation is obtained comparing equations (32) and (33)

$$\Pi_i^{(n)} = -\sum_m \Gamma_{nm} X_i^{(m)} \tag{72}$$

where Γ_{mn} is an $M \times M$ matrix of scaling parameters. From the symmetry of the direct correlation function at the origin, equation (15),

$$q_{ij}(\lambda_{ji}) = q_{ji}(\lambda_{ij}) \tag{73}$$

which from equations (17) and (18) is equivalent to

$$\sum_n X_i^{(n)} a_j^{(n)} = \sum_n X_j^{(n)} a_i^{(n)} \tag{74}$$

which in turn implies that

$$a_i^{(n)} = \sum_m \Lambda_{nm} X_i^{(m)} \tag{75}$$

and also that there are $M(M-1)/2$ symmetry relations

$$\Lambda_{mn} = \Lambda_{nm}. \tag{76}$$

From the symmetry of the contact pair correlation function equation (16) we obtain, using equations (17) and (18),

$$g_{ij}(\sigma_{ij}) = g_{ji}(\sigma_{ij}) \qquad q_{ij}(\sigma_{ij})' = q_{ji}(\sigma_{ij})' \tag{77}$$

which from equations (32) and (33) are

$$\sum_n (\Pi_i^{(n)} - z_n X_i^{(n)}) a_j^{(n)} = \sum_n (\Pi_j^{(n)} - z_n X_j^{(n)}) a_i^{(n)} \tag{78}$$

from which we obtain the scaling relation

$$\Pi_i^{(n)} - z_n X_i^{(n)} = \sum_m \Upsilon_{nm} a_i^{(m)} \tag{79}$$

and a new set of $M(M-1)/2$ symmetry relations

$$\Upsilon_{mn} = \Upsilon_{nm}. \tag{80}$$

The three scaling matrices $\mathbf{\Gamma}$, $\mathbf{\Lambda}$ and $\mathbf{\Upsilon}$ are related to each other. From equations (72), (76) and (79) we obtain by substitution

$$-(\mathbf{\Gamma} + \boldsymbol{z} \cdot \boldsymbol{I}) = \mathbf{\Upsilon} \cdot \mathbf{\Lambda} \tag{81}$$

where $\boldsymbol{z}$ is a diagonal matrix of elements z_n, and $\boldsymbol{I}$ is the unit matrix.

Furthermore, using the scaling relations we obtain

$$\tilde{\boldsymbol{M}} \cdot \mathbf{\Lambda} = \mathbf{\Gamma} \tag{82}$$

where the matrix $\tilde{\boldsymbol{M}}$ has elements

$$[\tilde{\boldsymbol{M}}]_{nm} = \frac{1}{z_n + z_m} \sum_\ell \rho_\ell [z_m X_\ell^{(n)} X_\ell^{(m)} + X_\ell^{(m)} \Pi_\ell^{(n)} - X_\ell^{(n)} \Pi_\ell^{(m)}]. \tag{83}$$

Solving these equations yields

$$\tilde{\boldsymbol{M}}^{-1} \cdot \mathbf{\Gamma} = \mathbf{\Lambda} \tag{84}$$

and

$$-(\boldsymbol{I} + \boldsymbol{z} \cdot \mathbf{\Gamma}^{-1}) \cdot \tilde{\boldsymbol{M}} = \mathbf{\Upsilon}. \tag{85}$$

The symmetry requirements are then

$$\tilde{\boldsymbol{M}}^{-1} \cdot \mathbf{\Gamma} = \mathbf{\Gamma}^{\mathrm{T}} \cdot [\tilde{\boldsymbol{M}}^{-1}]^{\mathrm{T}} \tag{86}$$

and

$$(\boldsymbol{I} + \boldsymbol{z} \cdot \mathbf{\Gamma}^{-1}) \cdot \tilde{\boldsymbol{M}} = \tilde{\boldsymbol{M}}^{\mathrm{T}} \cdot (\boldsymbol{I} + [\mathbf{\Gamma}^{-1}]^{\mathrm{T}} \cdot \boldsymbol{z}) \tag{87}$$

where the superscript T indicates that the transpose of the matrix is taken. We have therefore a total of $M(M-1)$ symmetry relations, which together with the M closure equations gives the required equations for the M^2 elements of the matrix $\mathbf{\Gamma}$.

5. Thermodynamic properties

We compute the excess thermodynamic properties of the mixture using the equations of Blum and Høye [12, 22, 23]. While most of the discussion is that of BVH92, we shall use here the notation of the earlier work BH78 [12].

The energy density ΔE is (see for example [12, 22])

$$\frac{\beta \Delta E}{V} = -2\pi \sum_{ij} \rho_i \rho_j \sum_n \tilde{g}_{ij}^{(n)} K_{ij}^{(n)}. \tag{88}$$

We remember that in the factored case using equation (2) for $K_{ij}^{(n)}$, we obtain an expression for the configurational energy in terms of $\hat{B}_i(z_n)$ defined in equation (43).

The excess energy density is

$$\frac{\beta \Delta E}{V} = -\sum_{i,n} \rho_i \delta_i^{(n)} K^{(n)} \hat{B}_i(z_n). \tag{89}$$

The excess virial pressure P^v is the expression

$$\beta \Delta P^v = \frac{2\pi}{3} \sum_{ij} \rho_i \rho_j \sigma_{ij}^3 \{g_{ij}(\sigma_{ij} - g_{ij}^0(\sigma_{ij}))\} + J. \tag{90}$$

The excess energy pressure P^E is

$$\beta \Delta P^E = \frac{\pi}{3} \sum_{ij} \rho_i \rho_j \sigma_{ij}^3 \{[g_{ij}(\sigma_{ij})]^2 - [g_{ij}^0(\sigma_{ij})]^2\} + J. \tag{91}$$

It is possible to write J in terms of $\hat{B}_i(s)$ (see equation (43)) and $\beta \Delta E$ (see [12, 22]):

$$\begin{aligned} J &= \frac{1}{3} \sum_{j,n} \rho_j \delta_j^{(n)} K^{(n)} \left[z_n \frac{\partial \hat{B}_j(s)}{\partial s} - \hat{B}_j(s) \right]_{s=z_n} \\ &= \frac{1}{3} \sum_{j,n} \rho_j \delta_j^{(n)} K^{(n)} \left[z_n \frac{\partial \hat{B}_j(s)}{\partial s} \right]_{s=z_n} - \frac{\beta \Delta E}{3V}. \end{aligned} \tag{92}$$

For factored interactions we obtain using equation (71)

$$2\pi K^{(n)} \hat{B}_j(s) = \sum_m \frac{s}{s+z_m} \left\{ \sum_k \rho_k a_k^{(n)} a_k^{(m)} \right\} \left[-\Pi_j^{(m)} + z_m X_j^{(m)} \right] + \tilde{\Delta}_j(s). \tag{93}$$

The excess Helmholtz free energy is

$$\frac{\beta \Delta A}{V} = \frac{\beta \Delta E}{V} - \beta \Delta P^E + \frac{1}{8\pi^2} \sum_j \rho_j \{[A_j]^2 - [A_j^0]^2\}. \tag{94}$$

The excess entropy is then

$$\frac{\Delta S}{kV} = \frac{\pi}{3} \sum_{ij} \rho_i \rho_j \sigma_{ij}^3 \{[g_{ij}(\sigma_{ij})]^2 - [g_{ij}^0(\sigma_{ij})]^2\} + J - \frac{1}{8\pi^2} \sum_j \rho_j \{[A_j]^2 - [A_j^0]^2\}. \tag{95}$$

The excess energy pressure P^E is

$$\beta \Delta P^E = \frac{\pi}{3} \sum_{ij} \rho_i \rho_j \sigma_{ij}^3 \{[g_{ij}(\sigma_{ij})]^2 - [g_{ij}^0(\sigma_{ij})]^2\} + J. \tag{96}$$

6. The 1-Yukawa limit

Using the results of section [6, 17, 18], we recover the simple analytic expressions [16] for the internal energy E, the Helmholtz free energy F and the scaled entropy S per particle and per unit volume. In addition we have a simple form of the equation of state.

From equation (89), we obtain the excess internal energy:

$$\frac{\beta\Delta E}{V} = -\sum_i \rho_i\delta_i K\hat{B}_i(z). \tag{97}$$

For the 1-Yukawa case we have the explicit solution for $\hat{B}_i$, the excess energy parameter

$$\hat{B}_i = \sum_j [\mathcal{J}_{ij}]^{-1}\left\{X_j - \sum_j\left[\delta_{jk} - \frac{2\pi\sigma_j}{\Delta z^2}\left(1+\frac{z\sigma_k}{2}\right)\right]\delta_k\right\}. \tag{98}$$

Now we observe that

$$X_i = \sum_k [\mathcal{M}_{ik}]^{-1}\delta_k \qquad [\mathcal{M}_{ij}] \equiv \mathcal{I}_{ij}\delta_{nm} + \mathcal{J}_{ij}\Gamma. \tag{99}$$

The radial distribution function at contact is [13, 18]

$$g_{ij}(\sigma_{ij}) - 2\pi\sigma_{ij}g^0_{ij}(\sigma_{ij}) = 2\pi K X_i X_j = -2\Gamma(z+\Gamma)\frac{X_i X_j}{D_2} = -(z+\Gamma)X_i a_j \tag{100}$$

where $g^0_{ij}(\sigma_{ij})$ is the contact radial distribution function for a hard-sphere mixture, X_j is given by equation (22) and

$$D_2 = \sum_k \rho_k X_k^2. \tag{101}$$

We have used $\beta = 1/(k_B T)$, where k_B is Boltzmann's constant and T is the absolute temperature.

The excess entropy density ΔS is given by [6, 16]

$$\frac{\Delta S}{kV} = -\left(\frac{\Gamma^3}{3\pi} + \frac{z\Gamma^2}{2\pi}\right). \tag{102}$$

Notice also that

$$\frac{1}{2}(\chi^{-1} - \chi_0^{-1}) = \frac{1}{2}\left[\sum_k \rho_k\left[\frac{A_k}{2\pi}\right]^2 - \chi_0^{-1}\right]. \tag{103}$$

In fact

$$\begin{aligned}\sum_k \frac{\rho_k}{8\pi^2}[(A_k)^2 - (A_k^0)^2] &= \sum_k \frac{\rho_k}{8\Delta\pi}a_k P_n\left\{2A_k^0 + \frac{\pi}{\Delta}a_k P_n\right\}\\ &= \frac{P_n}{4\pi\Delta}\sum_k \rho_k a_k A_k^0 + \frac{P_n^2}{8\Delta^2}\sum_k \rho_k a_k^2 \frac{P_n}{4\pi\Delta}\sum_k \rho_k a_k A_k^0 + \frac{P_n^2}{8\Delta^2}\sum_k \rho_k a_k^2\\ &= \frac{\pi K}{2\Delta^2}P_n\left[P_n + \frac{z}{2}\Delta_n\right] = -\frac{\Gamma(z+\Gamma)}{4D_2\Delta^2}P_n\left[P_n + \frac{z}{2}\Delta_n\right]\end{aligned} \tag{104}$$

where we have used

$$\frac{1}{\pi}\sum_k \rho_k a_k A_k^0 = \frac{z\pi K}{\Delta}\Delta_n$$

$$\sum_k \rho_k a_k^2 = 4\pi K.$$

Finally the excess pressure is

$$\frac{\Delta P^E}{\rho k_B T} = -\left(\frac{\Gamma^3}{3\pi} + \frac{z\Gamma^2}{2\pi}\right) + \frac{\pi K}{2\Delta^2}P_n\left\{P_n + \frac{z}{2}\Delta_n\right\}. \tag{105}$$

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