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Yukawa fluids: a new solution of the one component case

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In recent work a solution of the Ornstein-Zernike equation for a general Yukawa closure for a single component fluid was found. Because of the complexity of the equations a simplifying assumption was made, namely that the main scaling matrix $\mathbf{\Gamma}$ had to be diagonal. While in principle this is mathematically correct, it is not physical because it will violate symmetry conditions when different Yukawas are assigned to different components. In this work we show that by using the symmetry conditions the off diagonal elements of $\mathbf{\Gamma}$ can be computed explicitly for the case of two Yukawas solving a quadratic equation: There are two branches of the solution of this equation, and the physical one has the correct behavior at zero density. The non-physical branch corresponds to the solution of the diagonal approximation. Although the solution is different from the diagonal case, the excess entropy is formally the same as in the diagonal case.

Key words: *Yukawa fluids, mean spherical approximation, entropy, scaling approximations*

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1. Introduction

There are many problems of practical and academic interest that can be formulated as closures of either a scalar or matrix Ornstein-Zernike (OZ) equation. These closures can always be expressed by a sum of exponentials, which do form a complete basis set if we allow for complex numbers [1–5]. Another interesting application is to fluids with non-spherical molecules, like water [6,7].

While the initial motivation was to study simple approximations like the Mean Spherical (MSA) [8] or Generalized Mean Spherical Approximation (GMSA) [9–13], the availability of closed form scaling solutions [14–16], an equation makes it possible to write down analytical solutions for any given approximation that can be formulated by writing the direct correlation function $c(r)$ outside the hard core as

$$c(r) = \sum_{n=1}^{M} K^{(n)} \frac{\mathrm{e}^{-z_n(r-\sigma)}}{r} = \sum_{n=1}^{M} \mathcal{K}^{(n)} \frac{\mathrm{e}^{-z_n r}}{r}. \tag{1}$$

In this equation $K^{(n)}$ is the interaction/closure constant used in the general solution first found by Blum and Hoye (which we will call BH78) [17], while $\mathcal{K}^{(n)}$ is the definition used in the later general solution by Blum, Vericat and Herrera (BVH92 in what follows) [16]. In this work we will use the more common notation of BVH92. The case of factored interactions discussed by Blum, [14,18] was simplified by Ginoza [15,19,20] for the one Yukawa case.

We have

$$K^{(n)} = K^{(n)}\delta^{(n)}\delta^{(n)}, \qquad \mathcal{K}^{(n)} = K^{(n)}d^{(n)}d^{(n)}, \tag{2}$$

where

$$\delta^{(n)} = d^{(n)}\mathrm{e}^{-z_n\sigma/2}. \tag{3}$$

The general solution of this problem was formulated by Blum, Vericat and Herrera [16] in terms of a scaling matrix $\mathbf{\Gamma}$. The full solution was recently given by Blum et al. [1,2,4]. For only one component the matrix $\mathbf{\Gamma}$ was assumed to be diagonal and explicit expressions for the closure relations for any arbitrary number of Yukawa exponents M were obtained. Then, the solution is remarkably simple in the MSA since explicit formulas for the thermodynamic properties are obtained.

The diagonal assumption is however not correct for mixtures, even if they are of the same hard core diameter. It is also more natural to solve the full problem with no diagonal assumption and compute the nondiagonal terms of the $\mathbf{\Gamma}$ matrix using the symmetry relations: In this work we do precisely the following: the symmetry relations are used to calculate explicitly the off diagonal terms of $\mathbf{\Gamma}$ in the 1 component, 2 Yukawa case.

2. Summary of the previous work

We study the Ornstein-Zernike (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 and $c_{ij}(12)$ is the molecular direct correlation function, ρ_i is the number density of the molecules i, and $i = 1, 2$ is the position $\vec{r}_i, r_{12} = |\vec{r}_1 - \vec{r}_2|$ and σ_{ij} is the distance of the closest approach of two particles (or species) i, j. The direct correlation function is

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

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

$$\left[\mathbf{I} + \rho\tilde{\mathbf{H}}(\mathbf{k})\right]\left[\mathbf{I} - \rho\tilde{\mathbf{C}}(k)\right] = \mathbf{I}, \tag{7}$$

where I is the identity matrix, and we have used the notation

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

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

The matrices J and S have matrix elements

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

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

$$\left[\mathbf{I} - \rho\tilde{\mathbf{C}}(k)\right] \;=\; \left[\mathbf{I} - \rho\tilde{\mathbf{Q}}(k)\right]\left[\mathbf{I} - \rho\tilde{\mathbf{Q}}^T(-k)\right], \tag{12}$$

where $\tilde{\mathbf{Q}}^T(-k)$ is the complex conjugate and transpose of $\tilde{\mathbf{Q}}(k)$. 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

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

where we used the following definitions

$$\sigma_{ji} = \frac{1}{2}(\sigma_j + \sigma_i), \qquad \lambda_{ji} = \frac{1}{2}(\sigma_j - \sigma_i), \tag{14}$$

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

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

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

The general solution is discussed in [3,15,18], and yields

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

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

From here

$$X_i^{(n)} - \sigma_i\phi_0(z_n\sigma_i)\Pi_i^{(n)} = \delta_i^{(n)} - \frac{1}{2}\sigma_i\phi_0(z_n\sigma_i)\sum_\ell \rho_\ell\beta_\ell^0 X_\ell^{(n)} - \sigma_i^3 z_n^2\psi_1(z_n\sigma_i)\Delta^{(n)}, \tag{19}$$

or

$$\sum_\ell \rho_\ell \left\{-\hat{\mathcal{J}}_{j\ell}^{(n)}\Pi_\ell^{(n)} + \hat{\mathcal{I}}_{j\ell}^{(n)}X_\ell^{(n)}\right\} = \delta_j^{(n)}. \tag{20}$$

Here we use the notation of our previous work [3]

$$\beta_\ell^0 = \frac{\pi\sigma_\ell}{\Delta}.$$

2.1. The Laplace transforms

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

$$2\pi\sum_\ell \tilde{g}_{i\ell}(s)[\delta_{\ell j}^{Kr} - \rho_\ell\tilde{q}_{\ell j}(\mathrm{i}s)] = \tilde{q}_{ij}^{0\,\prime}(\mathrm{i}s), \tag{21}$$

where

$$\begin{aligned}\tilde{q}_{ij}^{0\,\prime}(\mathrm{i}s) &= \int_{\sigma_{ij}}^{\infty} \mathrm{d}r\mathrm{e}^{-sr}[q_{ij}^0(r)]' \\ &= \left[\left(1+\frac{s\sigma_i}{2}\right)A_j + s\beta_j\right]\frac{\mathrm{e}^{-s\sigma_{ij}}}{s^2} - \sum_m \frac{z_m}{s+z_m}\mathrm{e}^{-(s+z_m)\sigma_{ij}}C_{ij}^{(m)}. \end{aligned}\tag{22}$$

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

$$\mathrm{e}^{s\lambda_{ji}}\tilde{q}_{ij}(\mathrm{i}s) = \sigma_i^3\psi_1(s\sigma_i)A_j + \sigma_i^2\phi_1(s\sigma_i)\beta_j + \sum_m \frac{1}{s+z_m}[(C_{ij}^{(m)}+D_{ij}^{(m)})\mathrm{e}^{-z_m\lambda_{ji}} - C_{ij}^{(m)}\mathrm{e}^{-z_m\sigma_{ji}}z_m\sigma_i\phi_0(s\sigma_i)C_{ij}^{(m)}\mathrm{e}^{-z_m\sigma_{ji}}]. \tag{23}$$

This result will be used below.

Another important relation deduced from equation [21]by setting $s = z_n$ is

$$-\Pi_j^{(n)} = \sum_m \tilde{M}_{nm}a_j^{(m)}, \tag{24}$$

where

$$\tilde{M}_{nm} = \frac{1}{z_n+z_m}\sum_\ell \rho_\ell\left[X_\ell^{(n)}(z_m X_\ell^{(m)} - \Pi_\ell^{(m)}) + X_\ell^{(m)}\Pi_\ell^{(n)}\right]. \tag{25}$$

3. The general one component closure

The closure relation (BVH92 [16]) is, for only one component

$$\frac{2\pi K^{(n)}\delta^{(n)}}{z_n}+a^{(n)}\mathcal{I}^{(n)} \\ -\sum_m \frac{1}{z_n+z_m}\rho a^{(n)}a^{(m)}\left[\mathcal{J}^{(n)}[\Pi^{(m)}-z_m X^{(m)}]-\mathcal{I}^{(n)}X^{(m)}\right]=0. \tag{26}$$

This simplifies to

$$2\pi K^{(n)}\rho[X^{(n)}]^2+z_n\rho a^{(n)}X^{(n)}+\sum_m \frac{z_n}{z_n+z_m}[\rho a^{(n)}a^{(m)}]\left[\rho X^{(m)}X^{(n)}\right]=0, \tag{27}$$

which is the desired expression. This equation is in a more compact form [1]

$$2\pi\rho K^{(n)}\left[X^{(n)}\right]^2+z_n\beta^{(n)}\left[1+\sum_m \frac{1}{z_n+z_m}\beta^{(m)}\right]=0, \tag{28}$$

where $\beta^{(n)}$ is

$$\beta^{(n)}=\rho X^{(n)}a^{(n)}. \tag{29}$$

4. Symmetry

In this section we will summarize and extend our previous analysis of the most general scaling relation [16] for the multi Yukawa closure of the Ornstein Zernike equation. We have

$$\Pi_i^{(n)}=-\sum_m \Gamma_{nm}X_i^{(m)} \tag{30}$$

where Γ_{mn} is the $M\times M$ matrix of scaling parameters. This matrix is not uniquely defined by the MSA closure relations and must be supplemented by $M(M-1)$ equations obtained from symmetry requirements for the correlations. From the symmetry of the direct correlation function at the origin, equation (15)

$$q_{ij}(\lambda_{ji})=q_{ji}(\lambda_{ij}), \tag{31}$$

we write

$$a_i^{(n)}=\sum_m \Lambda_{nm}X_i^{(m)}, \tag{32}$$

where, as was shown in reference [16], $\mathbf{\Lambda}$ must be a symmetric matrix.

From the symmetry of the contact pair correlation function equation (16) we get

$$\{g_{ij}(\sigma_{ij})=g_{ji}(\sigma_{ij})\}\Longrightarrow\{q_{ij}(\sigma_{ij})'=q_{ji}(\sigma_{ij})'\}, \tag{33}$$

which are

$$\sum_n(\Pi_i^{(n)}-z_nX_i^{(n)})a_j^{(n)}=\sum_n(\Pi_j^{(n)}-z_nX_j^{(n)})a_i^{(n)}, \tag{34}$$

from which we get the scaling relation

$$\Pi_i^{(n)} - z_n X_i^{(n)} = \sum_m \Upsilon_{nm} a_i^{(m)}, \tag{35}$$

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

$$\Upsilon_{mn} = \Upsilon_{nm}. \tag{36}$$

Furthermore, using the scaling relations we get

$$\tilde{\mathbf{M}} \cdot \mathbf{\Lambda} = \mathbf{\Gamma}, \tag{37}$$

where the matrix $\tilde{\mathbf{M}}$ (see equation [25])has elements

$$[\tilde{\mathbf{M}}]_{nm} = \frac{1}{z_n + z_m} \sum_\ell \rho_\ell \left[X_\ell^{(n)} \{ z_m X_\ell^{(m)} - \Pi_\ell^{(m)} \} + X_\ell^{(m)} \Pi_\ell^{(n)} \right]. \tag{38}$$

Solving these equations yields the relations

$$\tilde{\mathbf{M}}^{-1} \cdot \mathbf{\Gamma} = \mathbf{\Lambda} \tag{39}$$

and

$$-\left(\mathbf{I} + \mathbf{z} \cdot \mathbf{\Gamma^{-1}}\right) \cdot \tilde{\mathbf{M}} = \mathbf{\Upsilon}. \tag{40}$$

Both $\mathbf{\Upsilon}$ and $\mathbf{\Lambda}$ must be symmetric matrices. We have, therefore, a total of $M(M-1)$ symmetry relations, which together with the M closure equations give the required equations for the M^2 elements of the matrix $\mathbf{\Gamma}$.
The symmetry requirements are more explicit

$$\mathbf{\Gamma} \cdot \tilde{\mathbf{M}}^T = \tilde{\mathbf{M}} \cdot \mathbf{\Gamma}^T \qquad \tilde{\mathbf{M}}^T \cdot \left[\mathbf{\Gamma}^T\right]^{-1} = \mathbf{\Gamma}^{-1} \cdot \tilde{\mathbf{M}} \qquad SI \tag{41}$$

and

$$\left(\mathbf{I} + \mathbf{z} \cdot \mathbf{\Gamma^{-1}}\right) \cdot \tilde{\mathbf{M}} = \tilde{\mathbf{M}}^T \cdot \left(\mathbf{I} + [\mathbf{\Gamma^{-1}}]^{\mathbf{T}} \cdot \mathbf{z}\right) \qquad SII \tag{42}$$

the matrix $\tilde{\mathbf{M}}$ as

$$\tilde{\mathbf{M}} = \frac{1}{2}\tilde{\mathbf{D}} + \frac{1}{2}\tilde{\mathbf{M}}^{\mathbf{A}} \tag{43}$$

and

$$\begin{aligned} [\tilde{\mathbf{M}}^{\mathbf{A}}]_{nm} &= \frac{-1}{s_{nm}} \sum_\ell \rho_\ell \left[X_\ell^{(n)} (z_m X_\ell^{(m)} - 2\Pi_\ell^{(m)}) - (z_n X_\ell^{(n)} - 2\Pi_\ell^{(n)}) X_\ell^{(m)} \right] \\ &= \frac{-1}{z_n + z_m} \sum_p \rho \Big[X^{(n)} X^{(p)} (z_m \delta_{pm}^{Kr} + 2\Gamma_{mp}) - (z_n \delta_{pn}^{Kr} + 2\Gamma_{np}) X^{(m)} X^{(p)} \Big], \end{aligned} \tag{44}$$

$$[\tilde{\mathbf{M}}^{\mathbf{A}}]_{nm} = -X^{(n)} X^{(m)} \left[\gamma_{nm} + \alpha_{nm} \right], \tag{45}$$

where

$$\alpha_{nm} = -\frac{2\rho}{z_n + z_m} \sum_p \left[\Gamma_{mp} \frac{X^{(p)}}{X^{(m)}} - \Gamma_{np} \frac{X^{(p)}}{X^{(n)}} \right], \tag{46}$$

and

$$\gamma_{nm} = \frac{2\Gamma^{(nn)} + z_n - 2\Gamma^{(mm)} - z_m}{z_m + z_n}. \tag{47}$$

The second symmetry condition in equation (42) is

$$\tilde{\mathbf{M}}^A = \mathbf{\Gamma}^{-1} \cdot \tilde{\mathbf{M}} \cdot \mathbf{z} - \mathbf{z} \cdot \tilde{\mathbf{M}}^{\mathbf{T}} \cdot [\mathbf{\Gamma}^T]^{-1}. \tag{48}$$

5. The two-Yukawa case: symmetric matrix results

We write equation (24) in matrix form [1]

$$-\vec{\mathbf{\Pi}}_i = \tilde{\mathbf{M}} \cdot \vec{\mathbf{a}}_i \tag{49}$$

where

$$\vec{\mathbf{X}}_i = \begin{bmatrix} X_i^{(1)} \\ X_i^{(2)} \end{bmatrix}, \qquad \vec{\mathbf{\Pi}}_i = \begin{bmatrix} \Pi_i^{(1)} \\ \Pi_i^{(2)} \end{bmatrix}, \qquad \vec{\mathbf{a}}_i = \begin{bmatrix} a_i^{(1)} \\ a_i^{(2)} \end{bmatrix}. \tag{50}$$

Using the symmetry relation equation (41) we get

$$\left(\Gamma^{(12)}\frac{X^{(2)}}{X^{(1)}} - \Gamma^{(21)}\frac{X^{(1)}}{X^{(2)}}\right) = \frac{s_{12}}{2}[\chi_{12} - \gamma_{12}] \tag{51}$$

with

$$\chi_{12} = \frac{z_1 - z_2}{z_1 + z_2 + 2\,\Gamma^{(11)} + 2\,\Gamma^{(22)}}, \tag{52}$$

$$\gamma_{12} = \frac{z_1 - z_2 + 2\,\Gamma^{(11)} - 2\,\Gamma^{(22)}}{z_1 + z_2}, \tag{53}$$

in equation (45) we can write

$$\tilde{\mathbf{M}} = \frac{\rho}{2}\begin{bmatrix} X^{(1)} & 0 \\ 0 & X^{(2)} \end{bmatrix}\begin{bmatrix} 1 & 1-\chi_{12} \\ 1+\chi_{12} & 1 \end{bmatrix}\begin{bmatrix} X^{(1)} & 0 \\ 0 & X^{(2)} \end{bmatrix}. \tag{54}$$

We rewrite equation (49) as

$$2\begin{bmatrix} \mathcal{G}^{(1)} \\ \mathcal{G}^{(2)} \end{bmatrix} = \begin{bmatrix} 1 & 1-\chi_{12} \\ 1+\chi_{12} & 1 \end{bmatrix}\begin{bmatrix} \beta^{(1)} \\ \beta^{(2)} \end{bmatrix}. \tag{55}$$

Here we have defined

$$\mathcal{G}^{(1)} = \Gamma^{(11)} + \frac{X^{(2)}}{X^{(1)}}\Gamma^{(12)}, \qquad \mathcal{G}^{(2)} = \Gamma^{(22)} + \frac{X^{(1)}}{X^{(2)}}\Gamma^{(21)}. \tag{56}$$

If we also define

$$2\mathcal{G}^{(s)} = \mathcal{G}^{(1)} + \mathcal{G}^{(2)}, \qquad 2\mathcal{G}^{(12)} = \mathcal{G}^{(1)} - \mathcal{G}^{(2)}, \tag{57}$$

then we can solve equation (55)

$$2\mathcal{G}^{(s)} = 2\beta_s + \beta_{12}\chi_{12}, \qquad 2\mathcal{G}^{(12)} = -\beta_s\chi_{12}, \tag{58}$$

or

$$\beta_s = -2\frac{\mathcal{G}^{(12)}}{\chi_{12}}, \qquad \beta_{12} = \frac{2}{\chi_{12}}\left[\mathcal{G}^{(s)} + \frac{\mathcal{G}^{(12)}}{\chi_{12}}\right]. \tag{59}$$

From the second symmetry condition equation (60) we get

$$\frac{X^{(2)}}{X^{(1)}} z_1 \Gamma^{(12)} - \frac{X^{(1)}}{X^{(2)}} z_2 \Gamma^{(21)} - 2\Gamma^{(12)}\Gamma^{(21)}\chi_{12} + 2\tau_{12} = 0, \tag{60}$$

where

$$\tau_{12} = \left(\frac{z_2\Gamma^{(11)}(z_1 + \Gamma^{(11)}) - z_1\Gamma^{(22)}(z_2 + \Gamma^{(22)})}{z_1 + z_2 + 2\,\Gamma^{(11)} + 2\,\Gamma^{(22)}} \right). \tag{61}$$

We also remark that

$$\tau_{12} = \frac{1}{2}[z_2\Gamma^{(11)}(1 + \chi_{12}) - z_1\Gamma^{(22)}(1 - \chi_{12})] + \chi_{12}\Gamma^{(11)}\Gamma^{(22)}, \tag{62}$$

in equation (60) we get

$$\begin{aligned} &\frac{X^{(2)}}{X^{(1)}} z_1 \Gamma^{(12)} - \frac{X^{(1)}}{X^{(2)}} z_2 \Gamma^{(21)} + 2\chi_{12} D_\Gamma \\ &\quad + [z_2\Gamma^{(11)}(1 + \chi_{12}) - z_1\Gamma^{(22)}(1 - \chi_{12})] = 0. \end{aligned} \tag{63}$$

Using now equation (51)

$$\frac{X_2^2}{X_1^2}\Gamma_{12}^2 - \frac{X_2}{X_1}\Gamma_{12}\left[\frac{s_{12}\chi_{12}}{2} + z_2 + 2\Gamma^{(22)}\right] + \Gamma^{(22)}(z_2 + \Gamma^{(22)}) = 0, \tag{64}$$

and

$$\frac{X_1^2}{X_2^2}\Gamma_{21}^2 - \frac{X_1}{X_2}\Gamma_{21}\left[-\frac{s_{12}\chi_{12}}{2} + z_1 + 2\Gamma^{(11)}\right] + \Gamma^{(11)}(z_1 + \Gamma^{(11)}) = 0, \tag{65}$$

from where

$$\mathcal{G}^{(1)} = \frac{1}{2}\left[\left\{\frac{s_{12}\chi_{12}}{2} + \frac{z_{12}}{\chi_{12}}\right\} - z_1 - \sqrt{\Delta_\Gamma^{(2)}}\right], \tag{66}$$

$$\mathcal{G}^{(2)} = \frac{1}{2}\left[\left\{-\frac{s_{12}\chi_{12}}{2} + \frac{z_{12}}{\chi_{12}}\right\} - z_2 - \sqrt{\Delta_\Gamma^{(1)}}\right], \tag{67}$$

with

$$\Delta_\Gamma^{(2)} = z_2^2 + s_{12}\chi_{12}\left[\frac{s_{12}\chi_{12}}{4} + z_2 + 2\Gamma^{(22)}\right], \tag{68}$$

$$\Delta_\Gamma^{(1)} = z_1^2 + s_{12}\chi_{12}\left[\frac{s_{12}\chi_{12}}{4} - z_1 - 2\Gamma^{(11)}\right], \tag{69}$$

$$\begin{aligned} &\left[2\mathcal{G}^{(1)} - \left\{\frac{s_{12}}{2} + z_{12}\right\}\chi_{12} + z_1\right]^2 - \left[2\mathcal{G}^{(2)} - \left\{-\frac{s_{12}}{2} + z_{12}\right\}\chi_{12} + z_2\right]^2 = \\ &\quad = \Delta_\Gamma^{(2)} - \Delta_\Gamma^{(1)} = 0. \end{aligned} \tag{70}$$

From here we get the equation

$$\left\{\chi_{12} - \frac{2z_{12}}{s_{12} + 2\mathcal{G}_s}\right\}\left\{\chi_{12} - \frac{z_{12} + 2\mathcal{G}^{(12)}}{s_{12}}\right\} = 0, \tag{71}$$

which yields the two solutions

$$\chi_{12} = \frac{2z_{12}}{s_{12} + 2\mathcal{G}_s} \quad \text{(A)}, \qquad \chi_{12} = \frac{z_{12} + 2\mathcal{G}^{(12)}}{s_{12}} \quad \text{(B)}. \tag{72}$$

Notice first that in the zero density limit we get

$$\chi_{12} \Longrightarrow \frac{2z_{12}}{s_{12}}, \qquad \chi_{12} \Longrightarrow \frac{z_{12}}{s_{12}}, \tag{73}$$

and then in equations (66) and (67) we get the correct zero density limit only from the choice (B)

$$\mathcal{G}^{(1)} \simeq \frac{1}{2}\left[\left\{\frac{z_{12}}{2} + s_{12}\right\} - z_1 - \frac{s_{12}}{2}\right] = 0, \tag{74}$$

$$\mathcal{G}^{(2)} \simeq \frac{1}{2}\left[\left\{-\frac{z_{12}}{2} + s_{12}\right\} - z_2 - \frac{s_{12}}{2}\right] = 0. \tag{75}$$

Then

$$\begin{aligned} \beta_s &= -2\mathcal{G}^{(12)}\frac{s_{12}}{(z_{12} + 2\mathcal{G}^{(12)})}, \\ \beta_{12} &= 2\frac{s_{12}}{(z_{12} + 2\mathcal{G}^{(12)})}\left[\mathcal{G}^{(s)} + \frac{2\mathcal{G}^{(12)}s_{12}}{(z_{12} + 2\mathcal{G}^{(12)})}\right]. \end{aligned} \tag{76}$$

These expressions turn out to be identical to those derived by Blum and Ubriaco using the diagonal approximation [2].

6. Thermodynamics by parameter integration

We will use the notation and the results of Blum and Hernando [3]. We recall that

$$\mathcal{J}^{(n)}\Pi^{(n)} = \mathcal{I}^{(n)}X^{(n)} - \delta^{(n)}. \tag{77}$$

Remember that

$$X^{(n)} = \gamma^{(n)} + \hat{\mathcal{J}}^{(n)}\hat{B}(z_n). \tag{78}$$

Here

$$\hat{\mathcal{J}}^{(n)} = \sigma\phi_0(z_n\sigma) - 2\rho\beta^0\sigma^3\psi_1(z_n), \tag{79}$$

and

$$\hat{\gamma}^{(n)} = \delta^{(n)} - \frac{2\beta^0}{z_n^2}\rho\delta^{(n)}(1 + \frac{z_n\sigma}{2}). \tag{80}$$

The total excess internal energy is

$$\frac{E(\beta)}{kTV} = \sum_n K^{(n)}\left\{\rho\delta^{(n)}\hat{B}^{(n)}\right\}. \tag{81}$$

From equation (30) we show that

$$-\Pi^{(n)} = \mathcal{G}^{(n)}X^{(n)}, \tag{82}$$

where $\mathcal{G}^{(n)}$ is a (generally algebraic) function of the coefficients $\boldsymbol{\beta} \equiv \{\beta_1, \beta_2, \cdots\}$. In fact in equation (77)

$$\begin{aligned} \delta^{(n)} &= \sum_m [\mathcal{M}^{nm}] X^{(m)} \\ &= \sum_m \{\mathcal{I}^{(n)} \delta^{Kr}_{nm} + \mathcal{J}^{(n)} \Gamma^{(nm)}\} X^{(m)} \\ &= \mathcal{I}^{(n)} X^{(n)} + \mathcal{J}^{(n)} \sum_m \Gamma^{(nm)}\} X^{(m)} \\ &= \{\mathcal{I}^{(n)} + \mathcal{J}^{(n)} \mathcal{G}^{(n)}\} X^{(n)} \end{aligned} \tag{83}$$

with

$$\mathcal{G}^{(n)} = \sum_m \Gamma^{(nm)} \frac{X^{(m)}}{X^{(n)}}. \tag{84}$$

For the 1 component case we get

$$X^{(n)} = \frac{\delta^{(n)}}{\mathcal{I}^{(n)} + \mathcal{G}^{(n)} \mathcal{J}^{(n)}}. \tag{85}$$

Then, since the “charge” parameters are constants at constant temperature, the derivative of $\hat{B}^{(n)}$ with respect to the scaling parameter $\mathcal{G}^{(n)}$ is

$$\begin{aligned} \left[\frac{\partial \hat{B}^{(n)}}{\partial \mathcal{G}^{(n)}}\right] &= \left[\mathcal{J}^{(n)}\right]^{-1} \left\{\frac{\partial \left(X^{(n)}\right)}{\partial \mathcal{G}^{(n)}}\right\} \\ &= -\left[\mathcal{J}^{(n)}\right]^{-1} \left[\frac{\delta^{(n)} \mathcal{J}^{(n)}}{(\mathcal{I}^{(n)} + \mathcal{G}^{(n)} \mathcal{J}^{(n)})^2}\right], \end{aligned} \tag{86}$$

where we use the fact that $\mathcal{J}^{(n)}$ is independent of $\mathcal{G}^{(n)}$. The desired energy derivative equation (81) is

$$\frac{\partial E}{\partial \mathcal{G}^{(n)}} = -\rho [X^{(n)}]^2 \tag{87}$$

or

$$\begin{aligned} \frac{\partial E}{\partial \mathcal{G}^{(s)}} &= -\sum_n \rho [X^{(n)}]^2, \\ \frac{\partial E}{\partial \mathcal{G}^{(nm)}} &= -\rho \{[X^{(n)}]^2 - [X^{(m)}]^2\}. \end{aligned} \tag{88}$$

The integrability condition is satisfied since

$$\frac{\partial^2 E}{\partial \mathcal{G}^{(n)} \partial \mathcal{G}^{(m)}} = \frac{\partial^2 E}{\partial \mathcal{G}^{(m)} \partial \mathcal{G}^{(n)}} = \delta^{Kr}_{nm} \left[2\rho [X^{(n)}]^2 \frac{\mathcal{J}^{(n)}}{\mathcal{I}^{(n)} + \mathcal{G}^{(n)} \mathcal{J}^{(n)}}\right]. \tag{89}$$

Now we use equation (29) to obtain

$$\frac{\partial E}{\partial \mathcal{G}^{(s)}} = \frac{1}{2} \left[\beta_s^2 + s_{12} \beta_s + z_{12} \beta_{12}\right] = \frac{s_{12} z_{12}}{2(2\mathcal{G}^{(12)} + z_{12})} \left[2\mathcal{G}^{(s)} + s_{12} - \frac{s_{12} z_{12}}{(2\mathcal{G}^{(12)} + z_{12})}\right] \tag{90}$$

and

$$\begin{aligned}\frac{\partial E}{\partial \mathcal{G}^{(12)}} &= \frac{1}{2}\left[\beta_s(\beta_s+s_{12})+z_{12}\beta_s+\frac{z_{12}}{2s_{12}}\{\beta_s^2-\beta_{12}^2\}\right]\\ &= \frac{s_{12}z_{12}}{4(2\mathcal{G}^{(12)}+z_{12})^2}\left[s_{12}^2+z_{12}^2-\left\{2\mathcal{G}^{(s)}+s_{12}-\frac{2s_{12}z_{12}}{(2\mathcal{G}^{(12)}+z_{12})}\right\}^2\right]\\ &\quad -\frac{s_{12}z_{12}}{4}\,. \end{aligned} \tag{91}$$

Thermodynamic integration of these equations leads to

$$\begin{aligned} -\frac{2\pi}{k}\Delta S &= \left(\frac{1}{8}\frac{s_{12}z_{12}}{(z_{12}+2\mathcal{G}^{(12)})}\right)^3\left\{\frac{1}{3}+\left(1-\frac{(z_{12}+2\mathcal{G}^{(12)})(s_{12}+2\mathcal{G}^{(s)})}{s_{12}z_{12}}\right)^2\right\}\\ &\quad -\left(\frac{s_{12}z_{12}}{8}\right)\left(\frac{s_{12}^2+z_{12}^2}{(z_{12}+2\mathcal{G}^{(12)})}-z_{12}+2\mathcal{G}^{(12)}\right)+\frac{s_{12}^3}{12}, \end{aligned} \tag{92}$$

$$\Delta S = -\frac{k}{2\pi}\left[\frac{\beta_s^3}{6}+\frac{\beta_s}{4}[(\beta_s s_{12}+\beta_{12}z_{12}]-\frac{z_{12}^2(\beta_s^2-\beta_{12}^2)}{8(\beta_s+s_{12})}\right]. \tag{93}$$

An interesting point here is that this expression is correct in the zero density limit without any further adjustement. As was shown by Lin et al. [13], the result obtained directly from the diagonal assumption [2] does not automatically satisfy this requirement, and the reason for this is that the wrong branch of the solution is used in this approximation.

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References

1. Blum L., Herrera J.N. // Mol. Phys., 1999, vol. 96, p. 821.
2. Blum L., Ubriaco M. // Mol. Phys., 2000, vol. 98, p. 829.
3. Blum L., Hernando J.A. // J. Phys.: Cond. Matt., 2002, vol. 14, p. 10933.
4. Blum L., Herrera J.N. // Mol. Phys., 1998, vol. 95, p. 425.
5. Blum L., Hernando J.A. Condensed Matter Theories. (Hernandez S., Clark J.W. editors). New York, Nova Publishers, 2001, vol. 16, p. 411.
6. Blum L., Vericat F., Degreve L. // Physica A, 1999, vol. 265, p. 396.
7. Blum L., Vericat F. // J. Phys. Chem., 1996, vol. 100, p. 1197.
8. Waisman E. // Mol. Phys., 1973, vol. 25, p. 45.
9. Waisman E., Stell G., Høye J.S. // Chem. Phys. Letters, 1976, vol. 40, p. 3253.
10. Arrieta E., Jedrzejek C., Marsh K.N. // J. Chem. Phys., 1987, vol. 86, p. 3606.
11. Herrera J.N., Blum L., García-Llanos E. // J. Chem. Phys., 1996, vol. 105, p. 9606.
12. Høye J.S., Stell G. // J. Chem. Phys., 1980, vol. 89, p. 461.
13. Lin Y.Z., Li Y.G., Lu Y.F., Liu Z.P. // Mol. Phys., 2002, vol. 100, p. 3251.

14. Blum L. // Mol. Phys., 1975, vol. 30, p. 1529.
15. Ginoza M. // J. Phys. Soc. Japan, 1986, vol. 55, p. 95,1782.
16. Blum L., Vericat F., Herrera J.N. // J. Stat. Phys., 1992, vol. 66, p. 249.
17. Blum L., Høye J.S. // J. Stat. Phys., 1978, vol. 19, p. 317.
18. Blum L. // J. Stat. Phys., 1980, vol. 22, p. 661.
19. Ginoza M. // Mol. Phys., 1990, vol. 71, p. 145.
20. Ginoza M., Yasutomi M. // J. Stat. Phys., 1998, vol. 90, p. 1475.

Плин Юкави: новий розв’язок однокомпонентного випадку

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В сучасних роботах знайдено розв’язок рівняння Орнштейна-Церніке для простого однокомпонентного плину в рамках узагальнених умов замикання Юкави. У зв’язку зі складністю рівнянь було зроблено припущення про те, що головна скейлінгова матриця $\mathbf{\Gamma}$ має бути діагональною. Хоча це математично правильно, фізично це порушує умови симетрії при співставлянні різних потенціалів Юкави різним компонентам. В цій роботі ми показуємо, що використовуючи умови симетрії, недіагональні елементи матриці $\mathbf{\Gamma}$ можуть бути точно обчислені, розв’язуючи квадратне рівняння для двох потенціалів Юкави. Існують два розв’язки цього рівняння, але тільки один з них має фізично правильну поведінку при нульовій густині. Нефізичний розв’язок відповідає розв’язку з діагональною апроксимацією. І хоча наш розв’язок відрізняється від того, що в діагональному випадку, надлишкова ентропія формально залишається такою ж.

Ключові слова: *плин Юкави, середньо-сферичне наближення, ентропія, скейлінгове наближення*

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