

Solution of the Ornstein–Zernike Equation for a Soft-Core Yukawa Fluid

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A model for simple fluids is proposed in which the radial distribution function has a parametric form appropriate to a soft-core fluid for interparticle separation $r \leq R$, where R is some range parameter. For $r > R$, the direct correlation function is assumed to be of Yukawa form. The Ornstein–Zernike equation is solved for this system, yielding the radial distribution and the total correlation function for the entire range of interparticle separation. Methods of relating the model fluid to a real fluid by assigning values to the parameters are discussed.

KEY WORDS: Ornstein–Zernike equation; Baxter’s factorization; soft-core; Yukawa closure.

1. INTRODUCTION

In a recent paper Perram and Wright⁽¹⁾ introduced a method for describing the correlation functions for a fluid with soft-core repulsions. The Ornstein–Zernike equation⁽²⁾

$$h(|\mathbf{r}|) = c(|\mathbf{r}|) + \rho \int ds c(|\mathbf{r} - \mathbf{s}|)h(|\mathbf{s}|) \quad (1)$$

where ρ is the number density, $h(r)$ is the total correlation function, and $c(r)$ is the direct correlation function, was solved for $h(r)$ having the parametric form

$$h(x) = -1 + \sum_{i=1}^M \frac{\alpha_i \lambda_i^2}{\cosh \lambda_i} \left[\frac{\sinh \lambda_i x}{\lambda_i x} - 1 \right], \quad 0 < x < 1 \quad (2)$$

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and the direct correlation satisfying

$$c(x) = 0, \quad x > 1 \quad (3)$$

Equations (2) and (3) may be considered to be appropriate to the Percus–Yevick approximation for a purely repulsive potential whose range R is here set to be 1 for convenience. Viewed in this way, Eq. (2) may be regarded as an ansatz for $h(x)$ on the domain $0 < x < 1$. The motivation for this model fluid was the need to describe more adequately correlations in fluids whose intermolecular potential has a soft-core component, typically softer than, for example, the repulsive part of the Lennard-Jones potential. The latter has been adequately described in terms of hard-sphere repulsions via the WCA perturbation theory.⁽³⁾ However, for softer potentials, such as those relevant to liquid metals^(4,5) and argon,⁽⁶⁾ a reference potential less harsh than hard spheres is desirable.

In addition to these considerations of the inadequacy of the treatment of the soft core, some attention must be given to including a more realistic form of the direct correlation function for $x > 1$ than that assumed in Eq. (3). Despite the convenience of assuming Eq. (3), it is nonetheless incorrect even for the case of noninteracting hard spheres.⁽⁷⁾ Much recent work on hard-core fluids has centered around assuming that $c(x)$ has a Yukawa form for $x > 1$.⁽⁸⁾ This may be regarded as a mean spherical approximation for fluids interacting with an attractive Yukawa potential⁽⁹⁾ or as an ansatz for the real $c(x)$ outside the hard core, resulting in a generalized mean spherical approximation (GMSA).⁽¹⁰⁾ The success of the GMSA and the recent suggestion of Høye and Stell regarding the use of the Yukawa form of $c(x)$ to enforce self-consistency on the Ornstein–Zernike equation⁽¹¹⁾ implies that a more appropriate form for $c(x)$ is given by

$$c(x) = \sum_{j=1}^N \frac{K_j e^{-z_j(x-1)}}{x}, \quad x > 1 \quad (4)$$

In Section 2 we solve the Ornstein–Zernike equation with closure relations given by Eqs. (2) and (4). This model combines the desirable features of soft-core repulsions and a form of direct correlation relevant to a realistic intermolecular potential. In Section 3 we discuss methods of assigning the $2 \times (N + M)$ parameters (α_i , λ_i , K_j , and z_j) in such a way as to model the behavior of real fluids.

2. METHOD OF SOLUTION

The method of solution used is that of Baxter's factorization technique.⁽¹²⁾ The Fourier transform of the Ornstein–Zernike equation may be written as

$$[1 - \rho \hat{c}(k)][1 + \rho \hat{h}(k)] = 1 \quad (5)$$

where $\hat{c}(k)$ and $\hat{h}(k)$ are the Fourier transforms of the direct correlation function and total correlation function, respectively. Following Baxter,⁽¹²⁾ we find that

$$\hat{A}(k) = 1 - \rho\hat{c}(k) = \hat{Q}(k)\hat{Q}(-k) \tag{6}$$

where $\hat{Q}(k)$ is related to a real-space function $q(r)$ by the pair of relations

$$\hat{Q}(k) = 1 - 2\pi\rho \int_0^\infty dx e^{ikx}q(x) \tag{7}$$

$$2\pi\rho q(x) = \frac{1}{2\pi} \int_{-\infty}^\infty dk e^{-ikx}[1 - \hat{Q}(k)] \tag{8}$$

Using the condition contained in Eq. (4) and closing the integral in Eq. (8) around the upper half-plane for $x < 0$, and around the lower half-plane for $x > 1$, we find that

$$q(x) = \begin{cases} 0, & x < 0 \\ \sum_{j=1}^N \beta_j e^{-z_j(x-1)}, & x > 1 \end{cases} \tag{9}$$

where

$$\beta_j = \frac{K_j}{z_j} \frac{1}{\hat{Q}(iz_j)}, \quad j = 1, \dots, N \tag{10}$$

We now define a function $q_0(x)$ by the relation

$$q(x) = q_0(x) + \sum_{j=1}^N \beta_j e^{-z_j(x-1)}, \quad x > 0 \tag{11}$$

so that

$$q_0(x) = 0, \quad x \geq 1$$

Inversion of the Ornstein–Zernike relation [Eq. (5)] and Eq. (6) yields

$$-q(x) + H(x) - 12\eta \int_0^\infty dt q(t)H(|x-t|) = 0 \tag{12}$$

$$S(x) = q(x) - 12\eta \int_x^\infty dt q(t)q(t-x) \tag{13}$$

where

$$H(x) = \int_x^\infty th(t) dt \tag{14}$$

$$S(x) = \int_x^\infty tc(t) dt \tag{15}$$

and

$$\eta = (\pi/6)\rho \quad (16)$$

Equations (12) and (13) are quite often used in their differentiated form, viz.

$$xh(x) = -q'(x) + 12\eta \int_0^\infty dt q(t)(x-t)h(|x-t|) \quad (17)$$

$$xc(x) = -q'(x) + 12\eta \int_x^\infty dt q'(t)q(t-x) \quad (18)$$

It can be seen that a knowledge of $q_0(x)$ would represent a complete resolution of the problem, since once $q(x)$ is known, $h(x)$ and $c(x)$ may be evaluated for arbitrary x by means of Eqs. (17) and (18).

From Eq. (2) we have that

$$H(x) = H_0 + \frac{1}{2}\gamma x^2 - \sum_{i=1}^M \Delta_i [\cosh \lambda_i x - 1], \quad 0 < x < 1 \quad (19)$$

where

$$\gamma = 1 + \sum_{i=1}^M (\alpha_i \lambda_i^2 / \cosh \lambda_i) \quad (20)$$

$$\Delta_i = \alpha_i / \cosh \lambda_i \quad (21)$$

and

$$H_0 = \int_0^\infty th(t) dt \quad (22)$$

For $0 < x < 1$, on substitution of Eq. (19) into Eq. (12), we find

$$\begin{aligned} & H_0 + \frac{1}{2}\gamma x^2 - \sum_{i=1}^M \Delta_i [\cosh \lambda_i x - 1] \\ &= q_0(x) + \sum_{j=1}^N \beta_j e^{-z_j(x-1)} \\ &+ 12\eta \int_0^1 q_0(t) \left\{ H_0 + \frac{1}{2}\gamma(x-t)^2 \right. \\ &- \sum_{i=1}^M \Delta_i [\cosh \lambda_i(x-t) - 1] \left. \right\} dt \\ &+ 12\eta \int_0^\infty \sum_{j=1}^N \beta_j e^{-z_j(t-1)} H(|x-t|) dt \end{aligned}$$

Solving this equation for $q_0(x)$, we find that

$$q_0(x) = \frac{1}{2}Q_2(x^2 - 1) + Q_1(x - 1) + \sum_{j=1}^N \beta_j d_j [1 - e^{-z_j(x-1)}] + \sum_{i=1}^M [Q_{i1}(\cosh \lambda_i x - \cosh \lambda_i) + Q_{i2}(\sinh \lambda_i x - \sinh \lambda_i)] \tag{23}$$

$$0 < x < 1$$

where

$$Q_2 = \gamma \left[1 - 12\eta \int_0^1 q_0(t) dt - 12\eta \sum_{j=1}^N \frac{\beta_j e^{z_j}}{z_j} \right] \tag{24}$$

$$Q_1 = 12\eta\gamma \left[\int_0^1 q_0(t) t dt + \sum_{j=1}^N \frac{\beta_j e^{z_j}}{z_j^2} \right] \tag{25}$$

$$d_j = 1 - \frac{12\eta}{z_j} \left[\tilde{g}(z_j) + \frac{\gamma - 1}{z_j^2} - \sum_{i=1}^M \frac{\Delta_i \lambda_i^2}{z_j^2 - \lambda_i^2} \right] \tag{26}$$

$$Q_{i1} = \Delta_i \left[-1 + 12\eta \int_0^1 q_0(t) \cosh \lambda_i t dt + 12\eta \sum_{j=1}^N \frac{\beta_j z_j e^{z_j}}{z_j^2 - \lambda_i^2} \right] \tag{27}$$

$$Q_{i2} = -12\eta \Delta_i \left[\int_0^1 q_0(t) \sinh \lambda_i t dt + \left(\sum_{j=1}^N \frac{\beta_j e^{z_j}}{z_j^2 - \lambda_i^2} \right) \lambda_i \right] \tag{28}$$

and $\tilde{g}(s)$ is the Laplace transform of $xg(x)$,

$$\tilde{g}(s) = \int_0^\infty e^{-sx} xg(x) dx \tag{29}$$

The solution for $q(x)$ has generated $2 \times (N + M + 1)$ variables, namely $\beta_j, d_j (j = 1, \dots, N), Q_{i1}, Q_{i2} (i = 1, \dots, M)$ and Q_1, Q_2 , for which we require $2 \times (N + M + 1)$ independent equations. Of these equations, N are provided by Eq. (10), which we note from the form of $q(x)$ is linear in the variables d_j . Also, substitution of the form of $q_0(x)$ from Eq. (23) into Eqs. (24), (25), (27), and (28) yields $2M + 2$ equations which are linear in the variables Q_1, Q_2, Q_{i1} , and Q_{i2} . Hence linear inversion of the $2M + 2 + N$ equations given above will yield expressions for these variables in terms of the β_j . We therefore require an independent equation for $\tilde{g}(s)$ to obtain the

remaining N nonlinear equations for the quantities β_j . We note that Eq. (17) may be rewritten in terms of $g(x)$ as

$$\begin{aligned}
 xg(x) = & x \left[1 - 12\eta \int_0^\infty q(t) dt \right] + 12\eta \int_0^\infty q(t)t dt \\
 & - q'(x) + 12\eta \int_0^x dt q(t)(x-t)g(x-t) \\
 & + 12\eta \int_x^\infty dt q(t)(x-t)g(t-x)
 \end{aligned} \tag{30}$$

Using the definitions of Eqs. (24) and (35), we find for $x > 1$

$$\begin{aligned}
 xg(x) = & (Q_2/\gamma)x + (Q_1/\gamma) + \sum_{j=1}^N \beta_j c_j z_j e^{-z_j(x-1)} \\
 & + 12\eta \int_0^x dt q(t)(x-t)g(x-t)
 \end{aligned} \tag{31}$$

where

$$c_j = 1 - \frac{12\eta}{z_j} \tilde{g}(z_j) \tag{32}$$

$$= d_j + \frac{12\eta}{z_j} \left[\frac{\gamma - 1}{z_j^2} - \sum_{i=1}^M \frac{\Delta_i \lambda_i^2}{z_j^2 - \lambda_i^2} \right] \tag{33}$$

The form of c_j comes from noting that for $x > 1$ the form of $q(t)$ in the last integral in Eq. (30) is simply given by Eq. (9). Equation (31) corresponds exactly with Eq. (21) of Høye and Blum,⁽¹³⁾ although the derivation given here appears to be more straightforward. Multiplying both sides of Eq. (31) by e^{-sx} and integrating from 1 to infinity, we find that

$$\begin{aligned}
 & \int_1^\infty xg(x)e^{-sx} dx \\
 & = \left\{ \frac{1}{s^2} \left[\frac{Q_2}{\gamma} (1 + s) + \frac{Q_1}{\gamma} s \right] + \sum_{j=1}^N \frac{\beta_j c_j z_j}{s + z_j} \right\} e^{-s} + 12\eta \tilde{q}(s) \tilde{g}(s)
 \end{aligned} \tag{34}$$

where $\tilde{q}(s)$ is the Laplace transform of $q(r)$. From Eq. (2) we then find that

$$\tilde{g}(s) = F(s)/[1 - 12\eta \tilde{q}(s)] \tag{35a}$$

where

$$\begin{aligned}
 F(s) = & - \left(\sum_{i=1}^M \Delta_i \lambda_i^2 \right) \frac{1}{s^2} + \sum_{i=1}^M \frac{\Delta_i \lambda_i^2}{\lambda_i^2 - s^2} \\
 & + \left\{ \frac{1}{s^2} \left[\left(\frac{Q_2}{\gamma} + \sum_{i=1}^M \Delta_i \lambda_i^2 \right) (1 + s) + \frac{Q_1}{\gamma} s \right] \right. \\
 & \left. + \sum_{i=1}^M \Delta_i \lambda_i \frac{\lambda_i \cosh \lambda_i + s \sinh \lambda_i}{\lambda_i^2 - s^2} + \sum_{j=1}^N \frac{\beta_j c_j z_j}{s + z_j} \right\} e^{-s}
 \end{aligned} \tag{35b}$$

Combining Eqs. (26), (33), and (35) yields the remaining N equations which determine the parameters generated in the solution.

3. DISCUSSION

The analysis presented in Section 2 represents a complete resolution of the problem given by Eqs. (1), (2), and (4). A method must now be found for determining the parameters a_i , λ_i ($i = 1, \dots, M$) and K_j , z_j ($j = 1, \dots, N$) in such a way that the conditions of Eqs. (2) and (4) are relevant to some real, soft-core fluid. With this in mind we examine two extreme cases:

3.1. $M = N = 1$

When the number of parameters used to describe $h(x)$ and $c(x)$ is small, it would seem to be desirable to use thermodynamic criteria in calibrating the model. For $M = N = 1$, we must find four conditions to specify α , λ , K , and z . It should be noted that in this case the parameter β [Eq. (10)] is found to be the solution of a quartic whose coefficients are related to the corresponding quartic in the hard-core Yukawa fluid.⁽⁹⁾ In fact, a very interesting feature of the solution presented in Section 2 is that the assumed forms of $h(x)$ [Eq. (2)] and $c(x)$ [Eq. (4)] do not interfere functionally in the resulting form of $q(x)$ [Eqs. (9) and (23)]. In view of this we find that for $M = N = 1$ the parameters Q_1 , Q_2 , Q_{11} , Q_{12} , β , and d are found quite easily. There are then a number of ways in which to prescribe α , λ , K , and z . One method which we are currently investigating numerically is to assume Eqs. (2) and (4) are functional representations of $h(x)$ and $c(x)$ over the domains stated for a system of particles interacting with realistic potential $\phi(r)$. Given the availability of a reasonable equation of state for a fluid with potential $\phi(r)$, three conditions may be found from the imposition of thermodynamic consistency between the three routes to the pressure and the known equation of state. The final fourth condition would be that $h(x)$ be continuous at $x = 1$. Under these conditions we expect that the resulting correlation functions will be closely related to those of a real fluid.

The case $M = N = 1$ can also be used in the model sense to investigate the effect on the critical region, correlation functions, and structure factor of the inclusion of a soft core, by arbitrarily setting λ and z , setting α by continuity of $h(x)$ at $x = 1$, and identifying K as a measure of inverse temperature. This would be assuming a mean spherical approximation-like condition for a soft-core Yukawa fluid.

3.2. Large M, N

When the number of parameters used to describe $h(x)$ and $c(x)$ is large, it would not be possible to specify the required number of conditions by

purely thermodynamic and continuity considerations. In this case the parametrized forms of $h(x)$ and $c(x)$ [Eqs. (2) and (4)] may be used to formulate a method of investigating the inverse problem in statistical mechanics.⁽¹⁴⁾ The model structure factor $S_M(k)$ is given by

$$S_M(k) = S_M(k, \alpha, \lambda, \mathbf{K}, \mathbf{z}) = 1 - \rho \hat{c}(k) = \hat{Q}(k) \hat{Q}(-k) \quad (36)$$

In formulating the inverse problem, we may regard the parameters α , λ , \mathbf{K} , and \mathbf{z} as adjustable constants in a least squares fit to an experimental structure factor $S_E(k)$. By using one of the well-known approximations, such as Percus–Yevick or hypernetted chain, we can use the correlation functions $h(x)$ and $c(x)$ to extract the interaction potential $\phi_A(r)$, where the subscript A refers to the fact that the potential is obtained from an integral equation approximation.

Previous work on relaxation of the hard-core condition from a correlation function viewpoint⁽¹⁵⁾ has shown appreciable improvement in the radial distribution function by lowering the first peak and dampening oscillations at large distances. It is hoped to be able to obtain the same degree of improvement using the analytically solvable model proposed in this paper.

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