

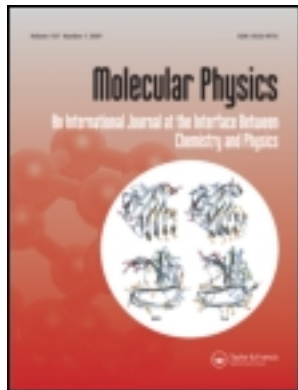
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A fast method of solving the hypernetted-chain equation for molecular Lennard-Jones fluids

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A fast method of solving the hypernetted-chain equation for molecular Lennard-Jones fluids

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A fast and stable procedure for solving hypernetted-chain type integral equations for molecular Lennard-Jones fluids is presented. The method is a hybrid algorithm based on the combination of multidimensional angular integration of the closure relation and a linearization technique devised by Fries and Patey (1985, *Molec. Phys.*, **55**, 751). The combination of the two techniques leads to a remarkable reduction in the CPU time required to evaluate the closure relation in these systems, which is usually the most time-consuming task. As an application of the method, phase coexistence curves have been calculated for two-centre Lennard-Jones fluids with and without point dipoles.

1. Introduction

Integral equations, and in particular the hypernetted-chain (HNC) approximation, have been used widely to determine the structure and thermodynamic properties of fluids and fluid mixtures [1]. For fluids of non-spherical particles, however, the use of HNC theory and related integral equations has been hindered somewhat by the angular dependence of the intermolecular potential. In principle, this difficulty could be eliminated by turning to approximations of the HNC relation such as the linearized [2–4] and quadratic [4, 5] hypernetted-chain equations (LHNC and QHNC, respectively). Both approximations are obtained by expanding the HNC closure and retaining only leading terms. The resulting set of equations can then be treated easily by expanding the angular functions in rotational invariants [7], whereby both the Ornstein–Zernike relation and the closure relation decouple as simple r -dependent functions. The accuracy of these theories, unfortunately, is very limited.

In the early 1980s, Lado [6] developed a general technique to solve the full nonlinear HNC equation and related approximations (such as the RHNC) for fluids

with angle-dependent interactions. His method is essentially based on the excellent convergence of the spherical harmonic expansion of the indirect correlation function used to build the molecular pair correlation function, which in turn is projected onto spherical harmonics by means of multidimensional angular integration. This is a very general but time consuming procedure, particularly the multidimensional integration that must be performed repeatedly along discretized intermolecular separations [8–10].

Fries and Patey [11] independently proposed a procedure to solve the HNC and RHNC equations for fluids of spherically shaped multipolar particles based on an elegant linearization of the closure relation. Their method was subsequently applied to the Stockmayer fluid by Lee *et al.* [12]. In their work, Fries and Patey showed that it is possible to rearrange the HNC closure such that, when expanded in rotational invariants (or spherical harmonics), the relation between all the coefficients involved in the closure is essentially linear. The crucial advantage of this approach is that multidimensional integration is bypassed. A principal drawback is that the interaction potential must be expressed in terms of its spherical harmonic expansion. This makes the method particularly useful for fluids composed of multipolar spherical particles, whose rotational invariant expansion is known and finite.

It is then a natural step to try to apply Fries and Patey's method to those systems for which, so far, only the multidimensional integration algorithms have been used, for instance, models in which molecular shape cannot be neglected. The simplest of these is the two-centre Lennard-Jones fluid. One would thus achieve a faster algorithm, provided, of course, that the required expansion of the site–site potential was known. Such an expansion indeed exists [13], and has been applied successfully in the context of perturbation theories [14].

Nevertheless, the poor convergence of the expansion of site–site Lennard-Jones potentials at short distances poses an insurmountable difficulty. The alternative we propose here in order to circumvent this obstacle is a careful combination of the two methods, i.e. Lado's multidimensional integration at overlapping distances, and linearization of the closure for larger intermolecular separations. The resulting procedure is both rapid and stable, requiring much less computer time per closure relation evaluation than the standard procedure. In addition, the multidimensional integrations that are still performed have been speeded up significantly with a new fast-transform technique.

These improvements make, for instance, the computation of the coexistence curve of a molecular fluid from the integral equation solution feasible, a task that was hitherto considered too demanding. We have calculated the phase diagrams of a two-centre Lennard-Jones fluid using two models with different bond lengths, as well as a third and more general case with an embedded dipole. Despite poor agreement of the HNC approximation with simulation results [15], these calculations are interesting in themselves; they are, to our knowledge, the first application of an integral equation approach to the determination of coexistence curves in molecular fluids.

In section 2 of this paper we briefly describe the standard procedure for solving the HNC equation for angle-dependent potentials. In section 3 we present the main features of the computational procedure proposed in this work and report a comparison showing the improvement gained by implementing the hybrid procedure to evaluate the closure. Finally, phase coexistence results are presented in section 4.

2. Theory

2.1. HNC molecular approximation: general approach

For linear molecular fluids the Ornstein–Zernike (OZ) equation reads

$$\gamma(12) = \frac{\rho}{4\pi} \int c(13)[c(32) + \gamma(32)] d\mathbf{3} \quad (1)$$

with $\gamma(12) = g(12) - 1 - c(12)$, where $c(12)$ and $\gamma(12)$ are, respectively, the direct and indirect correlation functions and, as usual, $g(12)$ is the pair distribution function. In HNC theory, the OZ equation is coupled with the closure

$$c(12) = \exp[-\beta u(12) + \gamma(12)] - \gamma(12) - 1, \quad (2)$$

where $u(12)$ is the interaction potential between molecules 1 and 2. All correlation functions can be expanded in spherical harmonics in the axial reference frame,

$$\gamma(12) = 4\pi \sum_{m=0}^{\infty} \sum_{l_1, l_2=m}^{\infty} \gamma_{l_1 l_2 m}(r_{12}) Y_{l_1 m}(\theta_1, \phi_1) Y_{l_2 m}(\theta_2, \phi_2). \quad (3)$$

Following Lado [6], we can solve equations (1) and (2) in the following steps:

- (1) Sum the spherical harmonic expansion of $\gamma(12)$ rewritten in terms of the associated Legendre functions \mathcal{P}_m (normalized to 2) and Chebyshev polynomials T_m ,

$$\begin{aligned} \gamma(12) &= \gamma(r_{12}, x_1, x_2, y) \\ &= \sum_{m=0}^{\infty} \sum_{l_1, l_2=m}^{\infty} \gamma_{l_1 l_2 m}(r_{12}) \mathcal{P}_{l_1 m}(x_1) \mathcal{P}_{l_2 m}(x_2) \alpha_m (-1)^m T_m(y), \end{aligned} \quad (4)$$

with $x_1 = \cos \theta_1$, $x_2 = \cos \theta_2$, $y = \cos \phi_{12}$, and

$$\alpha_m = \begin{cases} 1, & m = 0 \\ 2, & m > 0. \end{cases} \quad (5)$$

- (2) Evaluate the pair distribution function

$$g(r_{12}, x_1, x_2, y) = \exp[-\beta u(r_{12}, x_1, x_2, y) + \gamma(r_{12}, x_1, x_2, y)]. \quad (6)$$

- (3) Evaluate the spherical harmonic coefficients $c_{l_1 l_2 m}(r_{12})$ of the direct correlation function via

$$c_{l_1 l_2 m}(r_{12}) = g_{l_1 l_2 m}(r_{12}) - \delta_{l_1 l_2 m, 000} - \gamma_{l_1 l_2 m}(r_{12}), \quad (7)$$

where the $g_{l_1 l_2 m}(r_{12})$ are calculated via

$$\begin{aligned} g_{l_1 l_2 m}(r_{12}) &= \frac{1}{4\pi} \int_{-1}^1 \int_{-1}^1 \int_{-1}^1 g(r_{12}, x_1, x_2, y) \\ &\quad \times \mathcal{P}_{l_1 m}(x_1) \mathcal{P}_{l_2 m}(x_2) (-1)^m T_m(y) dx_1 dx_2 \frac{dy}{(1-y^2)^{1/2}}. \end{aligned} \quad (8)$$

This multidimensional integral can be evaluated easily by Gauss–Legendre and Gauss–Chebyshev quadrature. It is the most time-consuming part of the

procedure, although a notable improvement over earlier versions of this calculation has been achieved with a fast-transform algorithm described in Appendix A.

- (4) Fourier transform the direct correlation function and solve the OZ equation to produce the new estimate of $\gamma(12)$.

2.2. Linearization of the hypernetted chain closure

HNC closure (2) can be rewritten in the form

$$c(12) = h(12) - \log [g(12)] - \beta u(12). \quad (9)$$

Fries and Patey [11] found that it is possible to manipulate the HNC closure to obtain an expression that, once expanded in rotational invariants, includes only linear combinations of coefficients. By differentiation of the expression above with respect to the radial coordinate one gets

$$\frac{\partial c(12)}{\partial r_{12}} = \frac{\partial h(12)}{\partial r_{12}} - \frac{1}{g(12)} \frac{\partial g(12)}{\partial r_{12}} - \beta \frac{\partial u(12)}{\partial r_{12}}. \quad (10)$$

With the definition

$$x(12) = -\log g(12) = -\gamma(12) + \beta u(12), \quad (11)$$

equation (10) reads

$$\frac{\partial c(12)}{\partial r_{12}} = -h(12) \frac{\partial x(12)}{\partial r_{12}} - \beta \frac{\partial u(12)}{\partial r_{12}}. \quad (12)$$

Since all the pair functions vanish at $r_{12} = \infty$, equation (12) can be integrated to yield

$$c(12) = -\beta u(12) + \int_{r_{12}}^{\infty} h(1, 2) \frac{\partial x(12)}{\partial r'_{12}} dr'_{12}. \quad (13)$$

If we now expand the functions occurring in the integrand and apply the 'product rule' of the spherical harmonics [13], we arrive at the linear closure

$$c_{l_1 l_2 m}(r_{12}) = -\beta u_{l_1 l_2 m}(r_{12}) + \int_{r_{12}}^{\infty} A_{l_1 l_2 m}(r'_{12}) dr'_{12}, \quad (14)$$

where the $A_{l_1 l_2 m}(r_{12})$ are linear combinations of the spherical harmonic components of the functions $h(12)$ and $\partial x(12)/\partial r_{12}$, as shown in Appendix B. Equation (14) avoids the computationally expensive multidimensional integration of equation (8).

3. A hybrid computational procedure

One might think that a straightforward use of the linearization technique to molecular systems would be simple enough, if a spherical harmonic expansion for the potential is to hand. However, the numerical differentiation and integration needed to evaluate equation (14) make this method extremely inaccurate for overlapping distances, i.e. when the expansion coefficients of the potential $u_{l_1 l_2 m}(r_{12})$ and their derivatives reach huge values and the convergence of the expansion is poor.

The difficulties increase as the elongation or bond length L increases [13]. This indicates that Fries and Patey's linearization will fail in the region where the anisotropy of the system is strongest. In a two-centre Lennard-Jones fluid (2CLJ), this region ranges from the minimum overlap distance (for which $g(12) \approx 0$ for all orientations) to $\sigma + L$ (σ being the Lennard-Jones (LJ) range parameter).

All this suggests that a hybrid method, based on a combination of the procedure outlined in section 2 applied for distances less than $\sigma + L$, and the linearization technique sketched in the previous section used for the rest of the r_{12} range might be a more efficient alternative. In fact, the linearization of the closure can be applied for distances somewhat smaller than $\sigma + L$. We therefore define a delimiting radius r_l that will separate the regions where each method is more efficient. We will typically choose r_l as a compromise between computing time (the smaller r_l , the faster the algorithm) and accuracy (for $r_l < \sigma + L$, especially when L is large, the linearization is less accurate). Finally, an analytical expansion for the 2CLJ potential [13, 14] which will provide the spherical harmonic components $u_{l_1 l_2 m}(r_{12})$ required in equation (14) is to be desired. Explicit expressions for calculating these coefficients are given in Appendix C.

The proposed method can be summarized as follows.

- (1) For a given bond length $L^* = L/\sigma$ and an upper limit M in the spherical harmonic expansions ($l_1, l_2, m \leq M$), we compute the spherical harmonic coefficients of the 2CLJ potential $u_{l_1 l_2 m}(r_{12})$ for distances down to r_l , as well as their derivatives, using in this calculation equations (C1), (C2) and (C3). Since we deal here with polar 2CLJ fluids, we also evaluate the required coefficients of the dipole potential [13],

$$u_{110}(r) = \frac{2}{3} \frac{\mu^{*2}}{T^* r^3} \quad (15)$$

$$u_{111}(r) = \frac{1}{2} u_{110}(r), \quad (16)$$

with $T^* = kT/\epsilon$ and $\mu^* = \mu(\epsilon\sigma^3)^{1/2}$, where ϵ and σ are the parameters defining the LJ potential.

- (2) We start from initial estimates for $\gamma(12)$ and $c(12)$ from a previous computation or use their low-density limit values, i.e., $\gamma(12) = 0$ and $c(12) = \exp(-\beta u(12))$.
- (3) Equations (7) and (8) are used to compute a new estimate of $c_{l_1 l_2 m}(r_{12})$ for $r < r_l$ and closure (14) for $r > r_l$, bearing in mind that $h_{l_1 l_2 m}(r_{12}) = c_{l_1 l_2 m}(r_{12}) + \gamma_{l_1 l_2 m}(r_{12})$. We now have a new $c(12)$ function for the whole range of distances.
- (4) The $c_{l_1 l_2 m}(r_{12})$ coefficients calculated in the previous step are employed to compute a new set of $\gamma_{l_1 l_2 m}(r_{12})$ functions via the OZ equation using the standard Fourier transform techniques [6].
- (5) With the new $c(12)$ and $\gamma(12)$, we return to 3 and repeat the cycle until convergence is achieved. An iterative-mixing technique can be used to enhance convergence and stability [16].

As a further improvement of the iterative process, we have implemented for all coefficients the acceleration strategy proposed by Ng [17]. This method implies working with the Fourier transform of $\gamma(12)$ as a third iteration variable.

For the numerical integration and differentiation required in equation (14), a five-point formula was employed to compute the derivatives of the functions $\gamma_{l_1 l_2 m}(r_{12})$

CPU time per iteration determined for a DEC station 5000/33; t_0 stands for CPU time when just the angular integration of the closure is used. Details are given in the text.

	$L^* = 0.3292$			$L^* = 0.6$			$L^* = 0.7$		
	r_l	Time/s	t/t_0	r_l	Time/s	t/t_0	r_l	Time/s	t/t_0
Standard method	1.3292	43	1.00	1.6	56	1.00	1.7	65	1.00
Hybrid method	1.3292	15	0.35	1.6	18	0.32	1.7	24	0.37
	1.2	11	0.26	1.5	16	0.29	1.6	18	0.28
	1.1	9	0.21	1.4	14	0.25	1.5	16	0.25

while the integration of the coefficients $A_{i_1 i_2 m}(r_{12})$ was performed using the trapezoidal rule.

In the table we show a comparison of CPU time per iteration as a function of r_l for the hybrid procedure versus the standard procedure. In both cases 30 points were used per angular variable in the Gauss quadratures required to evaluate the integral of equation (8) for $r \leq r_l$. For distances $r > \sigma + L$, this integral was evaluated with only 16 points per angular variable, since in this region the interaction is considerably less anisotropic. Under these conditions we see that the hybrid method is between three and five times faster, the efficiency being significantly dependent on the r_l value chosen. The application of Ng's acceleration technique produces an additional reduction of around 40% in the number of iterations needed to achieve convergence.

4. Phase coexistence for the two-centre Lennard-Jones fluid

As a test of the algorithm, we undertake the task of determining the coexistence curve in a relatively realistic model of molecular fluid, the 2CLJ system with and without embedded point dipoles. We are aware of the limitations of the HNC equation, the poor performance of which, as far as thermodynamics is concerned, is well known [10]. Further, this equation displays a no-solution line different in nature from a spinodal line [18, 19]. One cannot therefore expect the HNC coexistence predictions to match those of even simple perturbation theories [15], but our calculations will show nonetheless that the approach is feasible and not too demanding, leaving the way open to the implementation of more accurate integral equations with reference bridge functions like the restricted hypernetted chain [18] or imposed thermodynamic self-consistency conditions like the hybrid mean spherical approximation of Zerah and Hansen [20, 21]. Here we have determined the coexistence curves for two 2CLJ models of two different elongations ($L = 0.3292\sigma$ and $L = 0.6\sigma$) and have performed an additional calculation for a polar model with $\mu^* = 2$.

To obtain the HNC coexistence data, we carried out calculations along several isotherms on both the liquid and the gas side of the phase diagrams so as to apply the equilibrium conditions

$$\left. \begin{aligned} \beta\mu(\rho_l, T)/N &= \beta\mu(\rho_g, T)/N, \\ \beta P(\rho_l, T)\sigma^3 &= \beta P(\rho_g, T)\sigma^3, \end{aligned} \right\} \quad (17)$$

where μ and P are, respectively, the chemical potential and the pressure of the system. Since in the HNC approximation the free energy and the virial pressure are thermodynamically consistent [23], we have evaluated P as the ρ -derivative of the Helmholtz free energy of the system,

$$\frac{P}{\rho kT} = \rho \left(\frac{\partial A/NkT}{\partial \rho} \right)_T, \quad (18)$$

instead of using the virial pressure, which is computationally more expensive. The chemical potential may be calculated via

$$\beta\mu/N = \ln \rho + A^{\text{ex}}/NkT + P/\rho kT + f(T), \quad (19)$$

where $f(T)$ is a function of the temperature irrelevant in the isothermal construction of equation (17). To compute the free energy we have used the standard HNC expression for molecular fluids [6],

$$\begin{aligned} \frac{A}{NkT} = & \frac{1}{2} \rho (\beta/\rho \chi_i - 1) - \frac{1}{2\rho} \int \left\{ \rho^2 \sum_{l_1, l_2, m} \tilde{h}_{l_1, l_2, m}(k) \left(\frac{1}{2} \tilde{h}_{l_1, l_2, m}(k) - \tilde{y}_{l_1, l_2, m}(k) \right) \right. \\ & \left. + \sum_m \log \text{Det} [I + (-1)^m \rho \tilde{H}_m(k)] - (-1)^m \rho \text{Tr} \tilde{H}_m(k) \right\} \frac{dk}{(2\pi)^3}, \quad (20) \end{aligned}$$

where \tilde{H}_m is a matrix whose elements are $[\tilde{H}_m]_{l_1, l_2} = \tilde{h}_{l_1, l_2, m}$ for $l_1, l_2 \geq m$ and χ_i is the isothermal compressibility.

In all computations, we have used 1024 grid points with a grid size $\Delta r = 0.01\sigma$ and an upper limit $M = 4$ for l_1, l_2, m . The integration of equation (8) was evaluated by Gauss–Legendre and Gauss–Chebyshev quadrature using 30 points per angle and the fast-transform method described in Appendix A. The significant parameter r_l was fixed at 1.2σ for $L^* = 0.3292$, 1.45σ for $L^* = 0.6$, and 1.6σ at the liquid densities for the polar case ($L^* = 0.6$ and $\mu^* = 2.0$). In figure 1 we show pressure and chemical potential for the polar fluid along several isotherms. In figures 2–4 we show the coexistence curves determined from the HNC equation together with Gibbs ensemble simulation results from [15]. In figure 4 the completed no-solution line of the HNC is plotted.

From the figures we see that the HNC approach, as expected, is rather poor, in particular for liquid densities, and describes the phase behaviour of the fluid only qualitatively. Moreover, the no-solution line of equation unfortunately hides a considerable portion of the coexistence curve in the vicinity of the critical point [24]. Nonetheless, the calculations presented here are relatively undemanding so far as computer resources are concerned and demonstrate that integral equations may be a viable alternative for this sort of calculation in molecular fluids.

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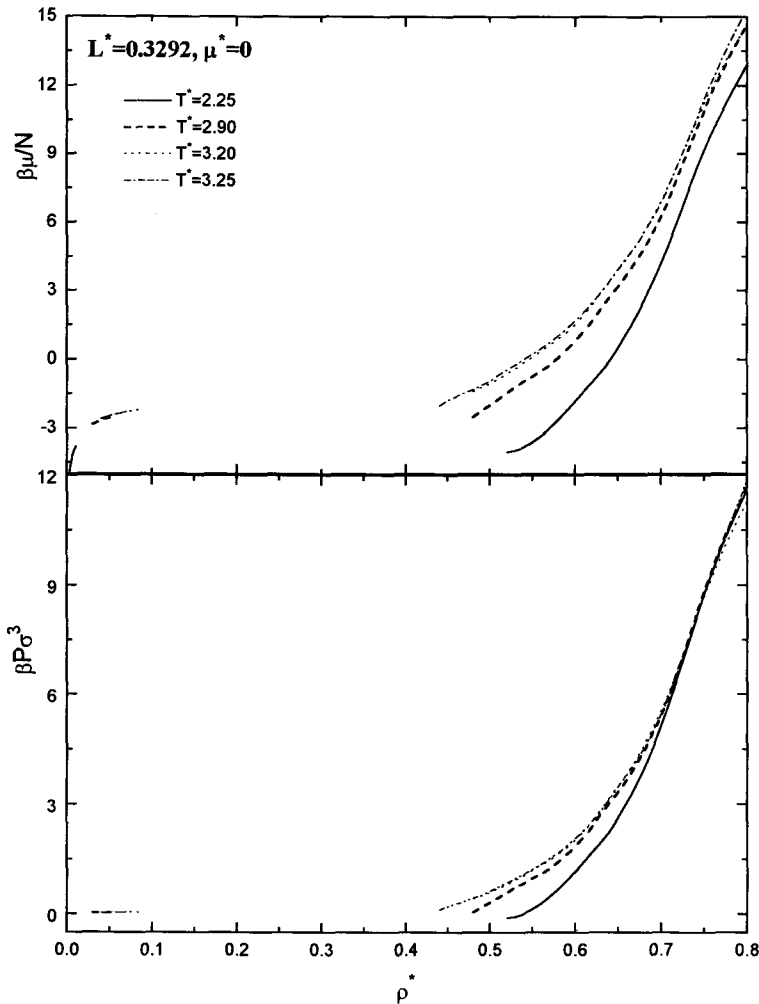


Figure 1. Chemical potential and pressure versus density obtained with the HNC equation at four temperatures for a polar 2CLJ fluid with bond length $L^* = 0.6$ and dipole moment $\mu^* = 2.0$.

Appendix A

Fast transform method for spherical harmonic expansions and their inverse

The most time-consuming part of the calculation occurs for the spherical harmonic expansion of equation (4), and the inverse operation of equation (8). For the numerical versions of these equations we will write k_1, k_2, j for x_1, x_2, y taken at discrete intervals numbered $1-n$ and suppress the dependence on r_{12} . The spherical harmonic expansion then requires the evaluation of

$$f(k_1, k_2, j) = \sum_{m=0}^M \sum_{l_1, l_2=m}^M f_{l_1 l_2 m} \mathcal{P}_{l_1 m}(k_1) \mathcal{P}_{l_2 m}(k_2) \alpha_m (-1)^m T_m(j) \quad (\text{A } 1)$$

at n^3 points, for a total of $n^3(M+1)(M+2)(2M+3)/6$ operations, while the inverse,

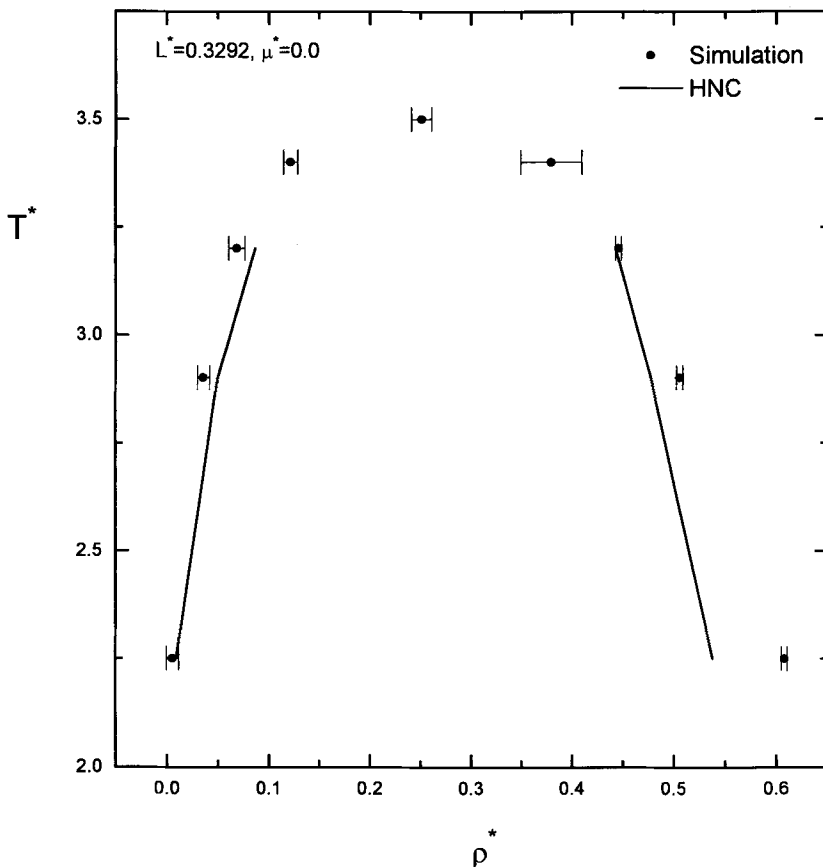


Figure 2. Phase coexistence data for the 2CLJ fluid with bond length $L^* = 0.3292$. Simulation data are taken from [15] and are shown as full circles. Solid lines represent HNC results.

$$f_{l_1 l_2 m} = \sum_{k_1, k_2, j=1}^n w_{k_1} w_{k_2} w_j f(k_1, k_2, j) \mathcal{P}_{l_1 m}(k_1) \mathcal{P}_{l_2 m}(k_2) (-1)^m T_m(j), \quad (\text{A } 2)$$

is evaluated for $(M + 1)(M + 2)(2M + 3)/6$ coefficients and thus results in the same number of total operations. (We are ignoring any savings that might be achieved by exploiting symmetries.) The w_i in equation (A 2) are Gaussian quadrature weights [6].

Both of these equations constitute separable, three-dimensional transforms that can be performed by a generalized fast-transform algorithm proposed by Orszag [25]. In brief, they are each replaced by three one-dimensional transforms. Thus, equation (A 1) is evaluated as the following sequence of three transforms:

$$f_1(k_1, l_2, m) = \sum_{l_1=m}^M f_{l_1 l_2 m} \mathcal{P}_{l_1 m}(k_1), \quad (\text{A } 3)$$

which requires $n(M + 1)(M + 2)(2M + 3)/6$ operations,

$$f_2(k_1, k_2, m) = \sum_{l_2=m}^M f_1(k_1, l_2, m) \mathcal{P}_{l_2 m}(k_2), \quad (\text{A } 4)$$

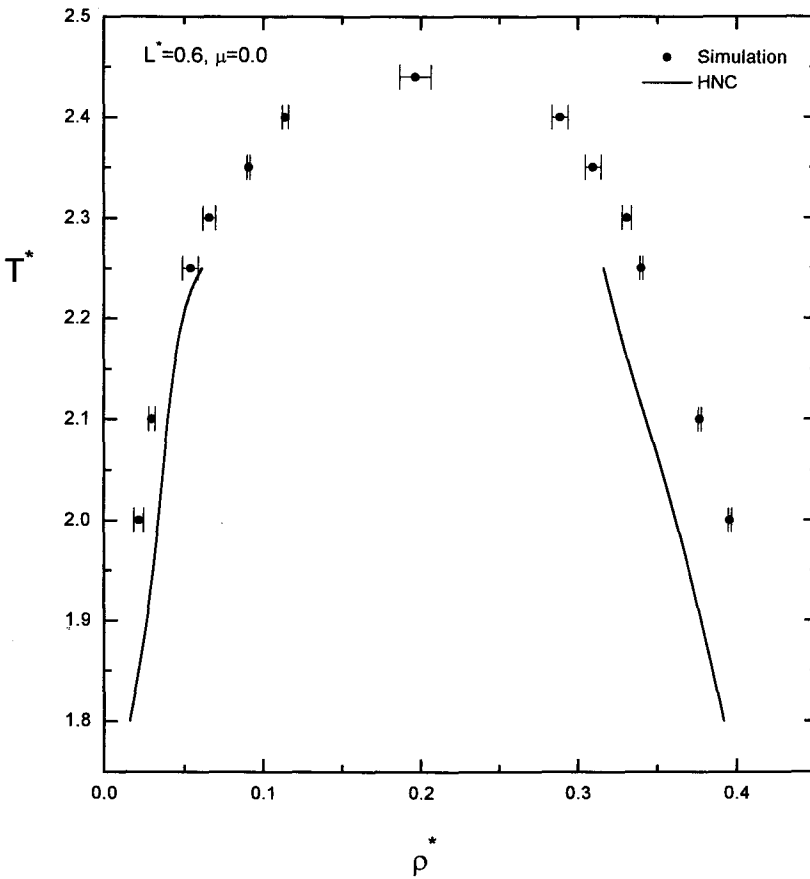


Figure 3. As figure 2 for $L^* = 0.6$.

which takes another $n^2(M+1)(M+2)/2$ operations, and finally

$$f(k_1, k_2, j) = \sum_{m=0}^M f_2(k_1, k_2, m) \alpha_m (-1)^m T_m(j), \quad (\text{A } 5)$$

with $n^3(M+1)$ operations. The sum of these counts is asymptotically smaller than the original count for equation (A 1), and the procedure thus constitutes a 'fast separable transform' [25].

The inverse transform (A 2) proceeds through a similar sequence of one-dimensional transforms in reverse order and requires the same number of operations.

For $n = 30$ and $M = 4$, for example, the fast-transform method reduces computing time for this step by a factor of about 10.

Appendix B

Analytical evaluation of $A_{L_1 L_2 M}$

The 'product rule' of spherical harmonics is

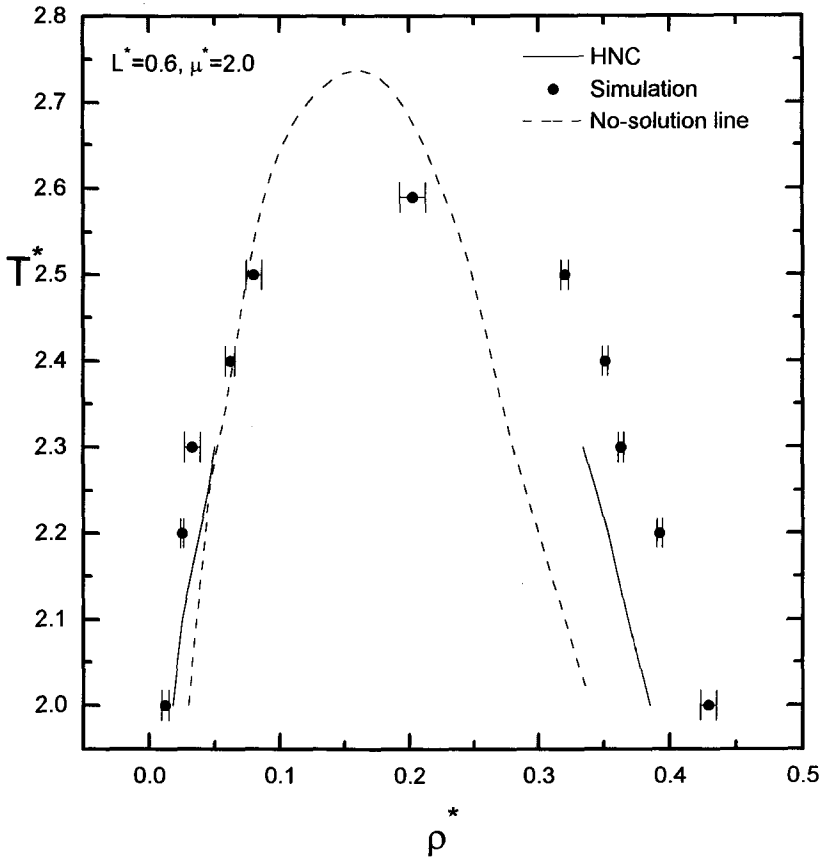


Figure 4. Phase coexistence data for the polar 2CLJ fluid with bond length $L^* = 0.6$ and dipole moment $\mu^* = 2.0$. The dashed line indicates the no-solution boundary of the HNC equation. Remaining symbols are as in figure 2.

$$Y_{lm}(\theta, \phi) Y_{l'm'}(\theta, \phi) = \sum_{LM} \left[\frac{(2l+1)(2l'+1)}{(4\pi)(2L+1)} \right]^{1/2} \times C(l'l'L; 000) C(l'l'L; mm'M) Y_{LM}(\theta, \phi), \quad (B 1)$$

where the $C(l'l'L; mm'M)$ are Clebsch–Gordan coefficients in the convention of Rose [22].

If we expand in spherical harmonics both functions occurring in the integrand of equation (13) as in (3), we obtain

$$\frac{\partial x(12)}{\partial r_{12}} h(12) = (4\pi)^2 \sum_{l_1 l_2 m} \sum_{l'_1 l'_2 m'} h_{l_1 l_2 m}(r_{12}) \frac{\partial x_{l_1 l_2 m'}}{\partial r_{12}} \times Y_{l_1 m}(\omega_1) Y_{l_2 m}(\omega_2) Y_{l'_1 m'}(\omega_1) Y_{l'_2 m'}(\omega_2). \quad (B 2)$$

By applying the product rule in equation (B 2) twice, this is transformed into

$$\frac{\partial x(12)}{\partial r_{12}} h(12) = 4\pi \sum_{L_1 L_2 M} A_{L_1 L_2 M}(r_{12}) Y_{L_1 M}(\theta_1, \phi_1) Y_{L_2 M}(\theta_2, \phi_2), \quad (B 3)$$

with the coefficients

$$\begin{aligned}
 A_{L_1 L_2 M}(r_{12}) &= [(2L_1 + 1)(2L_2 + 1)]^{-1/2} \sum_{l_1 l_2 m} \sum_{l'_1 l'_2 m'} [(2l_1 + 1)(2l_2 + 1)(2l'_1 + 1)(2l'_2 + 1)]^{1/2} \\
 &\times C(l_1 l'_1 L_1; 000) C(l_1 l'_1 L_1; mm' M) C(l_2 l'_2 L_2; 000) C(l_2 l'_2 L_2; mm' M) \\
 &\times h_{l_1 l_2 m}(r_{12}) \frac{\partial x_{l'_1 l'_2 m'}}{\partial r_{12}}. \quad (\text{B } 4)
 \end{aligned}$$

Appendix C

The spherical harmony expansion of the 2CLJ potential

For diatomic homonuclear molecules interacting via a two-centre Lennard-Jones potential, the spherical harmonic components of the site-site potential are given by [13, 14]

$$u_{l_1 l_2 m}(r_{12}) = (-1)^{l_2} \sum_{j=|l_1-l_2|}^{l_1+l_2} \frac{C(l_1 l_2 j; m \bar{m} 0) C(l_1 l_2 j; 000)}{[(2l_1 + 1)(2l_2 + 1)]^{1/2}} \sum_{\alpha\beta} u_{\alpha\beta}(l_1 l_2 j; r_\alpha r_\beta r_{12}), \quad (\text{C } 1)$$

with the parameter r_γ ($\gamma = \alpha, \beta$) being the distance of the γ interaction site from the molecular centre (for a homonuclear molecule $r_\alpha = r_\beta = L/2$) and

$$\begin{aligned}
 u_{\alpha\beta}(l_1 l_2 j; r_\alpha r_\beta r_{12}) &= 4 \sum_n \tau_n \frac{\binom{n}{2} \binom{n-1}{2}}{\binom{1}{2}_{l_1} \binom{1}{2}_{l_2}} \lambda \left(\frac{\sigma_\alpha r_\alpha}{r_{12}} \right)^{l_1} \left(\frac{\sigma_\beta r_\beta}{r_{12}} \right)^{l_2} \left(\frac{1}{r_{12}} \right)^n \\
 &\times F\left(A + \frac{n}{2}, \lambda + \frac{n-1}{2}, k + \frac{3}{2}, l + \frac{3}{2}; \left(\frac{\sigma_\alpha r_\alpha}{r_{12}} \right)^2, \left(\frac{\sigma_\beta r_\beta}{r_{12}} \right)^2\right), \quad (\text{C } 2)
 \end{aligned}$$

where $n = 12, 6$, $\tau_{12} = 1$, $\tau_6 = -1$, $A = (l_1 + l_2 + j)/2$, $\lambda = (l_1 + l_2 - j)/2$, σ_γ ($\gamma = \alpha, \beta$) equals +1 if the γ site is in the positive z axis (molecular axis) or -1 otherwise, and F is the Appell function [13],

$$F(\alpha, \beta, \gamma, \delta; x, y) = \sum_{u,v=0}^{\infty} \frac{(\alpha)_{u+v} (\beta)_{u+v} x^u y^v}{(\gamma)_u (\delta)_v u! v!}. \quad (\text{C } 3)$$

In equations (C2) and (C3), $(f)_s$ represents a shifted factorial,

$$(f)_s = f(f+1) \cdots (f+s-1), \quad (\text{C } 4)$$

with $(f)_0 = 1$, and $(1)_s = s!$.

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