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Percus-Yevick solutions for the planar dumbbell fluid

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The Percus-Yevick integral equation has been numerically solved for a fluid of hard planar dumbbells in two dimensions. Solutions have been obtained for a variety of densities and elongations. Comparison of the pressure results with Monte Carlo pressures reveals discrepancies of at most 8 per cent over the densities and elongations studied.

1. Introduction

A general procedure whereby any integral equation may be solved for the structure and thermodynamics of a classical, two-dimensional fluid was developed by Ward and Lado [1], who applied it to the hard ellipse fluid using the Percus-Yevick (PY) closure [2]. Here, we apply the procedure to study the hard planar dumbbell fluid also under a PY closure.

The hard planar dumbbell fluid has been previously studied, using both the reference interaction site model (RISM) and Monte Carlo (MC) simulation, by Talbot and Tildesley [3]. Comparison of pressure values obtained by the RISM and MC methods reveal that the RISM theory is not very useful for predicting thermodynamic properties. Talbot and Tildesley also found that applying the Scaled Particle Theory (SPT) [4] to a convex representation of the planar dumbbell seemed to be a reasonably accurate and easy-to-apply method for calculating the pressure.

In §2, we shall focus on some specifics needed in order to apply the iterative procedure described in [1] to obtain both the structure and thermodynamics of the hard planar dumbbell fluid in a PY closure. Following this in §3 we present a discussion of the results, including a comparison between the PY pressure values and those obtained by MC simulation and SPT.

2. Formulation of the problem

The PY closure for the direct correlation function $c(12)$ in terms of the series function, $S(12) = h(12) - c(12)$, is

$$c(12) = \{1 + S(12)\} \{\exp [-\beta\Phi(12)] - 1\}, \quad (1)$$

where $\Phi(12)$ denotes the intermolecular pair potential and $h(12) = g(12) - 1$. The pair correlation function $g(12)$ is, under the PY closure,

$$g(12) = \{1 + S(12)\} \exp [-\beta\Phi(12)]. \quad (2)$$

Figure 1. The coordinate system for two hard planar dumbbells.

It is preferable to work in terms of the series function as it is more slowly-varying and is thus more suitable for numerical manipulation. Since the hard planar dumbbell is a linear, non-polar molecule, $S(12)$ may be expanded as [1]

$$S(12) = S(r; \theta_1, \theta_2) = \sum_{m, j=-\infty}^{\infty} \sum_{j=-\infty}^{\infty} S(r; m, j) \cos(2m\theta_1 + 2j\theta_2), \quad (3)$$

where r denotes the intermolecular distance and θ_1 and θ_2 denote the molecular orientations (see figure 1). The iterative algorithm of [1] yields the series function coefficients $S(r; m, j)$. All other quantities may be found from these coefficients.

The largest number of *distinct* coefficients used in this work is 9, with the majority of cases solved with 4 coefficients. This is due to the fact that no more than 9 coefficients were ever needed to consistently yield thermodynamic values to 3 significant figures. By this we mean that the addition of more coefficients results in essentially no change in the computed thermodynamics. The total number of different cases studied in this work is 23, with 4 coefficients used in but 2 cases. A representative sample of these coefficients will be given in § 3.

It should be mentioned here that knowledge of 4 distinct coefficients actually yields 9 coefficients, and 9 distinct coefficients yields 25 coefficients. This is due to the symmetries of the planar dumbbell molecule, which yield [1]

$$S(r; m, j) = S(r; j, m) = S(r; -m, -j). \quad (4)$$

Once the series function coefficients are found, the pressure may be found via [5]

$$\frac{\beta p}{\rho} = 1 + \frac{\rho}{2\pi} \int_0^\pi d\theta_1 \int_0^\pi d\theta_2 r_0^2(\theta_1, \theta_2) g[r_0(\theta_1, \theta_2); \theta_1, \theta_2], \quad (5)$$

which applies to a fluid of linear, infinitely-hard, and non-polar molecules in two dimensions. The hard-core distance, $r_0(\theta_1, \theta_2)$, is the distance of closest approach of two particles with orientations θ_1 and θ_2 , while $g[r_0(\theta_1, \theta_2); \theta_1, \theta_2]$ denotes the value of the pair correlation function at contact for a given orientation.

The compressibility may be found from [6]

$$\frac{\rho\chi}{\beta} = \left[1 - 2\pi\rho \int_0^\infty c(r; 0, 0) r dr \right]^{-1}, \quad (6)$$

where $c(r; 0, 0)$ is the circular part of the $c(12)$ expansion.

The hard planar dumbbell molecule consists of two fused hard discs. The hard disc diameter will be denoted by σ , and l denotes the interatomic separation. We will refer to l as the elongation.

The hard planar dumbbell potential is expressed in terms of the separations between the individual hard discs. Labelling the atoms of molecules 1 and 2 as a, b and a', b' respectively, yields

$$r_{aa'} = (A - B_1 - B_2 + C)^{1/2}, \quad (7a)$$

$$r_{ab'} = (A - B_1 + B_2 - C)^{1/2}, \quad (7b)$$

$$r_{ba'} = (A + B_1 - B_2 - C)^{1/2}, \quad (7c)$$

$$r_{bb'} = (A + B_1 + B_2 + C)^{1/2}, \quad (7d)$$

where

$$A = r^2 + \frac{1}{2}l^2, \quad (8)$$

$$B_i = rl \cos \theta_i, \quad (9)$$

$$C = \frac{1}{2}l^2 \cos(\theta_1 - \theta_2), \quad (10)$$

with r being the separation between molecular centres and the $r_{jj'}$, the distance between sites j and j' (see figure 1).

The potential energy is infinite for any overlap configuration and zero otherwise,

$$\begin{aligned} \Phi(12) &= \infty, & \text{if any } r_{jj'} < \sigma \\ &= 0, & \text{otherwise.} \end{aligned} \quad (11)$$

For all $r < \sigma$ there is overlap for all orientations, while for $r > \sigma + l$, the potential is zero.

The $r_{jj'}$ in (7a-d) may each be set equal to σ , and r solved for at contact. This yields the following values for r at contact,

$$r_\alpha = \frac{1}{2}(b_1 + b_2) + \frac{1}{2}[4\sigma^2 - (a_1 + a_2)^2]^{1/2}, \quad (12a)$$

$$r_\beta = \frac{1}{2}(b_1 + b_2) - \frac{1}{2}[4\sigma^2 - (a_1 + a_2)^2]^{1/2}, \quad (12b)$$

$$r_\gamma = \frac{1}{2}(b_1 - b_2) + \frac{1}{2}[4\sigma^2 - (a_1 - a_2)^2]^{1/2}, \quad (12c)$$

$$r_\delta = \frac{1}{2}(b_1 - b_2) - \frac{1}{2}[4\sigma^2 - (a_1 - a_2)^2]^{1/2}, \quad (12d)$$

where

$$a_i = l \sin \theta_i, \quad (13)$$

$$b_i = l \cos \theta_i, \quad (14)$$

with $i = 1, 2$. Thus, for a given orientation, there are four distances between molecular centres for which the two discs will be tangent. Only the largest value will be physically allowed, as the smaller values will allow overlap. The value of r at contact, $r_0(\theta_1, \theta_2)$, will then be

$$r_0(\theta_1, \theta_2) = \max \{r_\alpha, r_\beta, r_\gamma, r_\delta\}, \quad (15)$$

where 'max' means that the largest value of the set is to be used. This value will be specifically needed when the pressure is computed from (5).

The diameter, σ , is used to scale both the interparticle separation, r , and interatomic spacing, l . The associated reduced variables are therefore

$$r^* = r/\sigma, \quad (16)$$

$$l^* = l/\sigma. \quad (17)$$

The length, d , that is chosen to characterize the molecular packing is the diameter of a disc whose area equals that of a planar dumbbell with dimensions σ and l . Equating the disc and dumbbell areas yields

$$d^2 = 2\sigma^2 \left[1 - \frac{\arccos l^*}{\pi} + \frac{l^*(1 - l^{*2})}{\pi} \right], \quad (18)$$

with the reduced density being given by

$$\rho^* = \rho d^2. \quad (19)$$

All pressures obtained will be compared to pressures calculated by SPT [4]. Strictly speaking, SPT applies to convex particles, but Talbot and Tildesley [3] found that an excellent representation of the equation of state for the hard planar dumbbell fluid could be obtained by using the hard planar spherocylinder geometry in the two-dimensional SPT results [4]. The resulting approximation for the pressure is then

$$\frac{\beta p}{\rho} = \frac{1 + (\alpha - 1)y}{(1 - y)^2}, \quad (20)$$

where

$$\alpha = \frac{(2l^* + \pi)^2}{4\pi l^* + \pi^2}, \quad (21)$$

$$y = \frac{1}{2}\rho^*(l^* + \frac{1}{4}\pi)a, \quad (22)$$

with

$$\frac{\pi}{a} = 1 - [\arccos l^* - l^*(1 - l^{*2})^{1/2}]. \quad (23)$$

3. Results

The PY equation has been solved at five elongations l^* and 23 densities ρ^* . The densities chosen were those simulated by Talbot and Tildesley [3]. For each elongation and density, values of the pressure (5) and compressibility (6) were obtained, as well as the series function and pair correlation function coefficients. The orientational coefficients discussed in [1] remained zero to three decimal places, thus indicating a lack of an orientational ordering in the hard planar dumbbell fluid.

The grids and quadratures used are those discussed in [1], with the only exception being the number of base points, M , used in producing the $g(r; m, j)$ for plotting purposes. The numerical evaluation of the $g(12)$ coefficients is quite sensitive to the value of M in the region where the anisotropy of $\Phi(12)$ plays a role. This is the

Figure 2. $S(r; 0, 0)$ for hard planar dumbbells of density $\rho^* = 0.826$ and elongation $l^* = 0.3$.

Figure 3. $S(12)$ coefficients for hard planar dumbbells of density $\rho^* = 0.826$ and elongation $l^* = 0.3$.

region

$$1 < r^* < 1 + l^*, \quad (24)$$

where the $g(r; m, j)$ exhibit a great deal of structure.

In general, 2048 grid points were used in r and k , with $M = 60$ for the gaussian quadratures used in integrations over θ . Exceptions to this will be noted in the discussion that follows.

Figure 4. $g(12)$ coefficients for hard planar dumbbells of density $\rho^* = 0.826$ and elongation $l^* = 0.3$.

Iterations were continued until the largest difference between successive iterates of the $S(r; m, j)$ satisfied

$$r_i |S_{in}(r_i; m, j) - S_{out}(r_i; m, j)| < 10^{-3}, \quad (25)$$

for each r_i , m , and j set.

A representative sample of the function involved in the calculation is presented in figures 2 through 5, for the state with density $\rho^* = 0.826$ and elongation $l^* = 0.3$. In these figures, the number of base points, M , is 75. For this state, 4 coefficients

Figure 5. Cross-sections through $g(12)$ for two parallel and one T -shaped configuration for hard planar dumbbells of density $\rho^* = 0.826$ and elongation $l^* = 0.3$.

were found to be sufficient to obtain thermodynamics to three significant figures. Indeed, as we have mentioned, no more than 9 coefficients were ever needed to obtain a good representation of fluid structure and thermodynamics in the cases studied here.

Figures 2 and 3 show the first four series function coefficients. Note the large disparity in scale between the circular part of $S(12)$, $S(r; 0, 0)$, and the remaining three coefficients. It is also seen that the $S(r; m, j)$ equal zero at the origin whenever $m + j \neq 0$, which was discussed in [1].

The $g(12)$ coefficients of figure 4 show a great deal of structure in the anisotropic region, equation (24). The circular part of the expansion, $g(r; 0, 0)$, exhibits a very pronounced oscillatory structure beyond the anisotropic region. All the $g(12)$ coefficients show some oscillatory behaviour for $r/\sigma > 1.0$, with a kink present where the potential 'switches off' at $1 + l^* = 1.3$. All of the $g(12)$ coefficients take on their largest values within the anisotropic region and then oscillate with diminishing amplitude beyond the discontinuity.

Figure 5 presents cross-sections for $g(12)$ for three configurations. Two are the parallel configurations $\theta_1 = \theta_2 = \frac{1}{2}\pi$ and $\theta_1 = \theta_2 = 0$. The other is the T-shaped configuration $\theta_1 = \frac{1}{2}\pi$, $\theta_2 = 0$. In these cross-sections we note that the peaks of $g(12)$ are somewhat broader than what one would normally expect for the simple liquid. Further, note the presence of a slight bump, or shoulder, in the secondary peaks. These added features are due to interference between the two lengths that scale the system, σ and l [7].

In figure 6, we present the equation of state of the hard planar dumbbell fluid of

Figure 6. The equation of state of the hard planar dumbbell fluid with elongation $l^* = 0.3$.

Pressure and compressibility values for the hard planar dumbbell fluid, along with the number of coefficients, N_c , used to describe the fluid.

l^*	ρ^*	PY	$\frac{\beta P}{\rho}$ MC	SPT	$\rho\chi/\beta$	N_c
0.1	0.113	1.20		1.20	0.694	4
	0.225	1.48		1.48	0.468	4
	0.338	1.86		1.86	0.306	4
	0.451	2.40		2.40	0.191	4
	0.564	3.20		3.23	0.114	4
0.3	0.138	1.26		1.26	0.663	4
	0.275	1.64		1.64	0.385	4
	0.413	2.22	2.22	2.22	0.222	4
	0.550	3.14	3.16	3.16	0.118	4
	0.668	4.71	4.94	4.85	0.0566	4
	0.826	7.75	8.41	8.36	0.0229	4
0.5	0.161	1.33		1.33	0.576	4
	0.322	1.84		1.84	0.312	4
	0.483	2.70	2.71	2.71	0.156	4
	0.644	4.25	4.35	4.37	0.0685	4
	0.805	7.45	8.09	8.14	0.0246	9
0.7	0.181	1.40		1.40	0.521	4
	0.362	2.08		2.09	0.251	4
	0.543	3.32	3.39	3.41	0.107	4
	0.724	5.90	6.35	6.45	0.0379	4
1.0	0.200	1.52		1.53	0.449	4
	0.400	2.50	2.52	2.57	0.180	4
	0.600	4.58	4.57	5.08	0.0605	9

elongation $l^* = 0.3$. The most notable feature of this particular figure is the accuracy of the SPT equation of state, which was first pointed out by Talbot and Tildesley [3].

All the thermodynamic data computed in this work are given in the table, along with the MC values for the pressure [3], and the SPT pressure values. The last two columns of the table contain the compressibility and the number of coefficients, N_c , needed to describe the fluid here. Unfortunately, there are no simulation results currently available for the compressibility.

Examining the table, we first note that no more than 9 coefficients were ever needed to consistently obtain thermodynamic values to three significant figures. For the most part, only 4 coefficients were used, save for a high density or very elongated molecule.

At low densities, all three values of the pressure agree quite well, differing by but 1–2 per cent. Overall, the SPT yields superior values for the pressure, though it begins to break down as the elongation becomes large. This is most evident for the elongation $l^* = 1.0$, where the SPT pressure begins to grow too rapidly, while the PY pressure values lag behind the MC values with a smaller error. Thus, the PY results seem to possess more consistent reliability at all l^* .

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