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Test of a simple analytic model for fluids of hard linear molecules

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Pynn has proposed (1974, *J. chem. Phys.*, **60**, 4579) a simple, empirical generalization for fluids of hard linear molecules of the Percus-Yevick direct correlation function for hard spheres. We make a detailed numerical study of this analytic model for hard dumbbells, including comparisons with the true Percus-Yevick results, and find that it is surprisingly effective.

1. INTRODUCTION

Although the integral equations of liquid state theory can always be solved numerically, such solutions in practice are often quite difficult or time-consuming to obtain. For this reason, the analytic solution of a seemingly very special case, the Percus-Yevick (PY) equation [1] for hard spheres, by Wertheim [2] and Thiele [3] two decades ago, has had far-reaching effects in the modern theory of fluids. In particular, it has made possible the ongoing development of perturbation theory for simple fluids [4, 5], which ultimately rests, in nearly all cases, on this solution or its empirical improvements [6]. In addition, it has served as a paradigm for the solution of a host of hard sphere (HS) embellishments: HS mixtures [7]; sticky HS [8]; charged HS [9]; HS with Yukawa tail [10]; and dipolar HS [11].

The last of these, by Wertheim, and its generalization by Blum [12], involves an orientation-dependent intermolecular potential and so describes a molecular, rather than simple, fluid. The dominant repulsive forces, however, are still treated as isotropic (i.e., hard spheres). There is as yet no analytic solution of the Percus-Yevick equation (or other model) for a hard anisotropic core such as dumbbells or ellipsoids, with the consequence, among others, that molecular perturbation theories almost invariably must fall back on isotropic reference systems [4, 5]. It is the purpose of this note to call attention to a simple analytic model of hard linear molecules which, while in no sense exact, may quite effectively play much the same role for molecular fluids that the Wertheim-Thiele solution has played for simple fluids.

Proposed originally by Pynn [13] and apparently not studied since, the model is an *ad hoc* generalization of the PY hard sphere solution. Specifically, for the direct correlation function

$$C(12) = C(\mathbf{r}_{12}, \omega_1, \omega_2) \quad (1)$$

of a fluid of hard molecules we write

$$C(12) = a + b \left[\frac{r_{12}}{\sigma(12)} \right] + c \left[\frac{r_{12}}{\sigma(12)} \right]^3, \quad r_{12} < \sigma(12),$$

$$= 0, \quad r_{12} > \sigma(12), \quad (2)$$

with

$$a = -(1 + 2\eta)^2/(1 - \eta)^4, \quad (3a)$$

$$b = 6\eta(1 + \frac{1}{2}\eta)^2/(1 - \eta)^4, \quad (3b)$$

$$c = \frac{1}{2}\eta a \quad (3c)$$

and

$$\eta = \frac{1}{6}\pi\rho\sigma_0^3. \quad (4)$$

In equation (2), $\sigma(12)$ is the centre-to-centre separation between a pair of hard molecules at contact for the particular orientation (ω_1, ω_2) , i.e. an orientation-dependent 'hard sphere diameter'. By further analogy, one could choose σ_0 in equation (4) so that η is the molecular packing fraction, but the only real constraint here is that it reduce to a hard sphere diameter in the appropriate limit.

One deficiency of equation (2) is immediately apparent: in the limit of vanishing intermolecular separation r_{12} it yields a constant, a , with no orientation dependence at all, contrary to the known behaviour of $C(12)$ for, say, hard dumbbells [14]. Equation (2) may thus be expected to be qualitatively incorrect for small values of r_{12} . This need not be a serious flaw, however, for typically one wants $C(12)$ as an integrand where it will first be multiplied by a power of r_{12} [15, 16], a step which would in any case wash out most of the short-range structure of a more correct $C(12)$.

Ultimately, the only way to judge the utility of an empirical *ansatz* such as equation (2) is by direct computation and comparison. Pynn's original application [13] was for ellipsoids of revolution, but the analysis presented was not adequate to establish the relative merits of his proposed model. In the next section, we present a more extensive set of calculations using equation (2) for the hard dumbbell potential and compare the results with those obtained directly from the Percus-Yevick equation itself. The conclusion in brief is that equation (2) is surprisingly effective.

2. NUMERICAL RESULTS

The project here is to use equation (2) to obtain the complete structure and thermodynamics of a hard dumbbell fluid, much as the Wertheim-Thiele $C(r)$ completely describes the hard sphere fluid. The analysis needed to carry this out is just that described in [15] for the solution of integral equations with molecular potentials, with the difference that Step 1 in the summarized procedure there is replaced by the direct evaluation of the spherical harmonic coefficients

$$C_{l_1 l_2 m}(r_{12}) = \langle C(12) | l_1 l_2 m \rangle \quad (5)$$

using equation (2). (The notation is that of [15].) Following through with the additional steps (2) through (10) [15] produces the coefficients $S_{l_1 l_2 m}(r)$ of the

'series' function, from which $S(12)$ is reconstructed to finally yield

$$g_{l_1 l_2 m}(r_{12}) = \langle [1 + S(12)] \exp [-\beta \phi(12)] | l_1 l_2 m \rangle \quad (6)$$

in PY approximation, where $\phi(12)$ is the hard dumbbell potential.

The numerical analysis is evidently no simpler than that of solving the PY equation itself; in effect, it amounts to one iteration of such a solution. The advantage of equation (2), of course, is just that: *one* iteration may suffice where *many* might otherwise be called for.

As noted earlier, the parameter η for equations (3) may plausibly be chosen to be the molecular packing fraction. This requires

$$\sigma_0 = d \equiv (\sigma^3 + \frac{3}{2}\sigma^2 l - \frac{1}{2}l^3)^{1/3} \quad (7)$$

in equation (4), where l is the distance between sphere centres of the molecule and σ the sphere diameter. It was found empirically that the median diameter [17] produces somewhat better thermodynamic values. The effect on the various structural functions is mixed, but weighted towards (7) as giving somewhat better matching. The point is not critical for present purposes and we have arbitrarily chosen to present the results obtained using the median diameter [17] for σ_0 .

To check these results, we have iteratively solved the PY equation for the same states, again using the procedure described in [15] with the appropriate change in Step 1. (The modelled solution described above provides a good initial guess for the iteration process.) Five harmonic coefficients $S_{l_1 l_2 m}(r)$ were generated for all the cases, a number found to be adequate in previous studies [14].

Figures 1 and 2 show the first four spherical harmonic coefficients $C_{l_1 l_2 m}(r)$ obtained *directly* from equation (2) and from the PY equation for molecules of elongation $l = 0.4\sigma$ at the density $\rho d^3 = 0.8$. (Note the difference in scale of these two graphs.) The short-range deficiency of the modelled $C(12)$ is here manifest, particularly in figure 2 for the nonspherical harmonic coefficients. It is interesting to divide the range r according to the properties of the potential $\phi(12)$ in evaluating these figures. For centre-to-centre separations r less than

$$r_0 = (\sigma^2 - \frac{1}{2}l^2)^{1/2} \quad (8)$$

all orientations of the molecules produce core overlap, while for separations r greater than

$$r_1 = \sigma + l \quad (9)$$

the potential is zero for all orientations. Figures 1 and 2 suggest that for values of r greater than roughly $r_1 - r_0$ the functional form of equation (2) may indeed be correct, even if the coefficients there are not numerically accurate, while for smaller r values a different functional form is needed. One is reminded here of the hard sphere mixtures solution [7], a comparison that is particularly compelling in view of the analogy between orientations of a nonspherical molecule and different components of a mixture [18].

Going now through the steps of [15], one generates from $C(12)$ the coefficients of $S(12)$ shown in figures 3 and 4. The interesting feature here is that the short-range deficiencies of the modelled $C(12)$ have not propagated themselves: the modelled coefficients $S_{l_1 l_2 m}(r)$ are qualitatively correct over their entire range

Figure 1. Spherically symmetric part of $C(12)$ for hard dumbbells of elongation $l = 0.4\sigma$ at the density $\rho d^3 = 0.8$.

Figure 2. Spherical harmonic coefficients of $C(12)$ for hard dumbbells of elongation $l = 0.4\sigma$ at the density $\rho d^3 = 0.8$.

Figure 3. Spherically symmetric part of $S(12)$ for hard dumbbells of elongation $l = 0.4\sigma$ at the density $\rho d^3 = 0.8$.

and quantitatively in fairly good agreement with the computed PY forms. Finally, figure 5 shows that the modelled coefficients of the pair distribution function $g(12)$ obtained using equation (6) are in remarkably good agreement with the correct PY results. (It will be noted that having obtained qualitatively correct forms for $S(12)$ and $g(12)$, one may now patch up the original shortcomings of equation (2) by using

$$C(12) = g(12) - 1 - S(12), \quad (10)$$

if indeed the coefficients $C_{l_1 l_2 m}(r)$ are the primary objects of interest.)

Thermodynamic quantities are obtained in the usual way [14]. In the table, we show the computed pressure and compressibility for three elongations l at

Reduced pressures and compressibilities for the hard dumbbell fluid as obtained from the modelled solution (MOD), the Percus-Yevick equation (PY) and Monte Carlo simulation (MC).

		l/σ								
		0.2			0.4			0.6		
		MOD	PY	MC	MOD	PY	MC	MOD	PY	MC
0.4	$\beta p/\rho$	2.51	2.51	2.59	2.59	2.59	2.64	2.73	2.72	2.78
	$\rho\chi/\beta$	0.190	0.191	0.192	0.181	0.181	0.183	0.166	0.167	0.170
0.8	$\beta p/\rho$	7.16	7.13	8.02	7.58	7.52	8.42	8.38	8.20	9.23
	$\rho\chi/\beta$	0.0324	0.0328	0.0354	0.0291	0.0302	0.0334	0.0242	0.0262	0.0300

Figure 4. Spherical harmonic coefficients of $S(12)$ for hard dumbbells of elongation $l = 0.4\sigma$ at the density $\rho d^3 = 0.8$.

each of two densities. One sees again that equation (2) is surprisingly successful in mimicking the PY equation. For additional perspective, the correct values from computer simulations of hard dumbbell fluids [19] are also included in the table.

It seems fair to conclude from this study that, in the absence of a more rigorously based formula, Pynn's simple model can play a useful role in the theory of molecular fluids. This should be particularly so in variational perturbation theories, where one basically needs merely a correct functional form for quantities like $S(12)$.

Figure 5. Spherical harmonic coefficients of $g(12)$ for hard dumbbells of elongation $l = 0.4\sigma$ at the density $\rho d^3 = 0.8$.

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