Molecular Physics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tmph20

Percus-Yevick solutions for the planar dumbell fluid
D.A. Ward $^a$ & F. Lado $^b$

$^a$ Physics Department, Florida Southern College, Lakeland, Florida, 33802, U.S.A.
$^b$ Physics Department, North Carolina State University, Raleigh, North Carolina, 27695-8202, U.S.A.

Available online: 22 Aug 2006

To cite this article: D.A. Ward & F. Lado (1988): Percus-Yevick solutions for the planar dumbell fluid, Molecular Physics, 64:6, 1185-1193
To link to this article: http://dx.doi.org/10.1080/00268978800100793

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.
Percus–Yevick solutions for the planar dumbell fluid

by D. A. WARD
Physics Department, Florida Southern College,
Lakeland, Florida 33802, U.S.A.

and F. LADO
Physics Department, North Carolina State University,
Raleigh, North Carolina 27695-8202, U.S.A.

(Received 8 February 1988; accepted 21 March 1988)

The Percus–Yevick integral equation has been numerically solved for a fluid of hard planar dumbells 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 dumbell fluid also under a PY closure.

The hard planar dumbell 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 dumbell 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 dumbell 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

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

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,

$$g(12) = \{1 + S(12)\} \exp \{-\beta \Phi(12)\}.$$
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 dumbell is a linear, non-polar molecule, $S(12)$ may be expanded as

$$S(12) = S(r; \theta_1, \theta_2)$$

$$= \sum_{m, j} S(r; m, j) \cos (2m\theta_1 + 2j\theta_2),$$

where $r$ denotes the intermolecular distance and $\theta_1$ and $\theta_2$ 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 dumbell molecule, which yield [1]

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

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

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

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 $\theta_1$ and $\theta_2$, 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]

$$\frac{\rho \frac{\partial \rho}{\partial P}}{\rho} = \left[ 1 - 2\pi \rho \int_0^\infty c(r; 0, 0)rdr \right]^{-1},$$
The planar dumbell fluid

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

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

The hard planar dumbell 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

\[
\begin{align*}
    r_{aa'} & = (A - B_1 - B_2 + C)^{1/2}, \\
    r_{ab'} & = (A - B_1 + B_2 - C)^{1/2}, \\
    r_{ba'} & = (A + B_1 - B_2 - C)^{1/2}, \\
    r_{bb'} & = (A + B_1 + B_2 + C)^{1/2},
\end{align*}
\]

where

\[
\begin{align*}
    A & = r^2 + \frac{1}{2}l^2, \\
    B_i & = rl \cos \theta_i, \\
    C & = \frac{1}{2}l^2 \cos (\theta_1 - \theta_2),
\end{align*}
\]

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,

\[
\Phi(12) = \infty, \quad \text{if any } r_{jj'} < \sigma \\
= 0, \quad \text{otherwise.}
\]

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 \( \sigma \), and \( r \) solved for at contact. This yields the following values for \( r \) at contact,

\[
\begin{align*}
    r_x & = \frac{1}{2}(b_1 + b_2) + \frac{1}{2}[4\sigma^2 - (a_1 + a_2)^2]^{1/2}, \\
    r_\beta & = \frac{1}{2}(b_1 + b_2) - \frac{1}{2}[4\sigma^2 - (a_1 + a_2)^2]^{1/2}, \\
    r_\gamma & = \frac{1}{2}(b_1 - b_2) + \frac{1}{2}[4\sigma^2 - (a_1 - a_2)^2]^{1/2}, \\
    r_\delta & = \frac{1}{2}(b_1 - b_2) - \frac{1}{2}[4\sigma^2 - (a_1 - a_2)^2]^{1/2},
\end{align*}
\]

where

\[
\begin{align*}
    a_i & = l \sin \theta_i, \\
    b_i & = l \cos \theta_i,
\end{align*}
\]

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

\[
r_0(\theta_1, \theta_2) = \max \{ r_x, r_\beta, r_\gamma, r_\delta \},
\]
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, \( d \), is used to scale both the interparticle separation, \( r \), and interatomic spacing, \( l \). The associated reduced variables are therefore

\[
\begin{align*}
  r^* &= r/\sigma, \\
  l^* &= l/\sigma.
\end{align*}
\]

(16) \hspace{2cm} (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 dumbell with dimensions \( \sigma \) and \( l \). Equating the disc and dumbell areas yields

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

(18)

with the reduced density being given by

\[
\rho^* = \rho d^2.
\]

(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 dumbell 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

\[
\frac{\beta p}{\rho} = \frac{1 + (\alpha - 1)y}{(1 - y)^2},
\]

(20)

where

\[
\begin{align*}
  \alpha &= \frac{(2l^* + \pi)^2}{4\pi l^* + \pi^2}, \\
  y &= \frac{1}{2} \rho^* (l^* + \frac{1}{2}\pi)a,
\end{align*}
\]

(21) \hspace{2cm} (22)

with

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

(23)

3. Results

The PY equation has been solved at five elongations \( l^* \) and 23 densities \( \rho^* \). 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 dumbell 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
The planar dumbell fluid

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

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

region

$$1 < r^* < 1 + l^*$$

(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 $\theta$. Exceptions to this will be noted in the discussion that follows.
Iterations were continued until the largest difference between successive iterates of the $S(r; m, j)$ satisfied

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

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 $p^* = 0.826$ and elongation $l^* = 0.3$. In these figures, the number of base points, $M$, is 75. For this state, 4 coefficients...
The planar dumbell fluid

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 \( \theta_1 = \theta_2 = 1/2 \pi \) and \( \theta_1 = \theta_2 = 0 \). The other is the T-shaped configuration \( \theta_1 = 1/2 \pi, \theta_2 = 0 \). 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, \( \sigma \) and \( l \) [7].

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

![Figure 6](image-url)
Pressure and compressibility values for the hard planar dumbell fluid, along with the number of coefficients, $N_c$, used to describe the fluid.

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

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 $l^*$.

This work was supported by the National Science Foundation under Grant CHE-84-02144.
References