SOLUTION OF THE PERCUS-YEVICK EQUATION FOR
THE WIDOM-ROWLINSON MODEL

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The Percus-Yevick equation for the Widom-Rowlinson model is solved exactly in one and three dimensions. In
one dimension the direct correlation function is obtained explicitly. In three dimensions only the thermodynamic
properties have been obtained so far implicitly in terms of elliptic integrals, and there is a maximum density be-
Yond which the P.Y. equation has no solution and that before that density is 'critical density' at which the ho-
menous state becomes unstable.

Widom and Rowlinson [1] have studied the proper-
ties of a model fluid which is isomorphic to a two
component system in which there are no interactions
between particles of the same species and a hard core of
diameter $R$ between particles of different species.
This model, and some generalizations of it, were prov-
en [2, 3] to undergo phase transitions (in two and
higher dimensions) corresponding to a separation of
the components when the density is sufficiently high.
These results follow from very general arguments and
do not give any other information about this system.
Such information, apart from its inherent symmetry
so nicely exploited by Widom and Rowlinson, has so
far been obtained either from simple mean field theory
or from low density expansions [4, 5] (via Padé approxi-
imations) and from some machine computations on re-
lated systems [6]. (Some rigorous inequalities on the
correlation functions of this system have also been ob-
tained recently [7].) In this note we give the results of
the Percus-Yevick (P.Y.) approximation for this sys-
tem which can be thought of as a mixture of hard
spheres with (extremely) non-additive diameters, a type
of system we have studied earlier [8, 9]. On the basis
of experience with the P.Y. equation with additive di-
ameters we may expect the results of this approxima-
tion to be quite accurate at low and moderate densities.

The P.Y. equations for the radial distribution func-
tion $g_{ij}(r)$, $i,j=1,2$, in this system are [8]

$$[g_{ij}(r) - 1] = C_{ij}(r)$$

$$+ \sum_{k=1}^{2} \rho_j \int [g_{ij}(r') - 1] C_{ik}(r-r') \, dr',$$

$$C_{11}(r) = C_{22}(r) = 0;$$

$$C_{12}(r) = C_{21}(r) = 0 \quad \text{for } r > R;$$

$$g_{12}(r) = g_{21}(r) = 0 \quad \text{for } r < R.$$  (3)

The $C_{ij}(r)$, defined by eq. (1), are the direct correla-
tions of Ornstein and Zernike, $\rho_j$ is the density of
species $i$, assumed spatially uniform, and the P.Y.
approximation consist in setting $C_{ij}(r) = 0$, for all val-
ues of $r$ at which the interaction between a particle of
species $i$ and one of species $j$ vanishes, as expressed in
eq. (2). We look for a solution of (1--3) such that
$g_{ij}(r) \rightarrow 1$ as $r \rightarrow \infty$ making $\int_0^\infty r |g_{ij}(r) - 1| \, dr < \infty$.

Given the solution of the P.Y. equation for $C_{ij}$ and
$g_{ij}$ there are different ways of obtaining thermodynamic
quantities from these correlation functions. These
ways would all be equivalent if we had the exact func-
tions. They are generally not equivalent for the P.Y.
solution. Thus we may 'get' a thermodynamics from
the virial theorem which relates the pressure to the
'contact' value of the distribution function. For the
model considered here this has the form

$$\beta p^*(\rho_1, \rho_2) = p_1 + p_2 + \frac{\beta}{2} \rho_1 \rho_2 g_{12}(R)$$

(4)

where $\beta = (kT)^{-1}$ (we shall set $\beta = 1$ from now on) and

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\[ g_{12}(R) = \lim_{R^{-} \to R^{+}} g_{12}(r) = -\lim_{R^{-} \to R^{+}} C_{12}(r) \]  

(5)

the last equality being a consequence of (1) and (2).

Another way of obtaining thermodynamics from the \( C_{ij}(r) \) is to use the ‘compressibility’ relations

\[ \rho_j \frac{\partial \rho_j}{\partial \rho_i} = \delta_{ij} - \rho \int C_{ij}(r) \, dr, \quad i, j = (1, 2), \]  

(6)

\[ 1 - 2 \sum_{i=1}^{2} \rho_i \int C_{ij}(r) \, dr = \frac{2}{3} \sum_{i=1}^{2} \delta_{ij} \rho_i \frac{\partial p^i}{\partial \rho_j} - \delta_{ij} \frac{\partial p^i}{\partial \rho_j} \]  

(7)

where \( \rho^i \) and \( p^i \) are respectively the chemical potential of the \( i \)th species and the pressure, both obtained from the compressibility relations.

For the case of hard spheres with additive diameters it has been found that both the virial and compressibility relations give quite accurate agreement (2–3%) with machine computations up to fairly high densities.

Taking Laplace transforms of (1), using the methods developed in references [8] and [9] the solution of the P.Y. equation reduces to the solution of a single nonlinear functional equation in the complex s-plane (s is a Laplace transform variable). When applied to the Widom-Rowlinson model the results are as follows:

One dimension. Using units in which \( 2R = 1 \) we obtain the following expression for \( C_{12}(r) \),

\[ C_{12}(r) = \rho_0 \left[ 1 - (1 - 3r^2)^{1/2} \right] \eta, \]  

(8)

where \( \eta \) is the Beesol of zero argument, and \( \eta = \eta g_{12}(R) \) is the solution of the equation \( q = \eta \cos q \). This equation for \( q \) will have a unique solution for low densities, \( \eta < \eta_0 \approx 2.80 \). For \( \eta > \eta_0 \) there is more than one solution for \( q \). It is however always possible, and the physics of the situation (continuity of the pressure) dictates that we simply continue with the low density solution. The free energy obtained from this solution remains stable for all value of \( \eta \). We compared the values of pressures along the line of symmetry, i.e. \( \rho_1 = \rho_2 = \rho/2 \) obtained from the P.Y. equation with the exact result, \( p/\rho = 1 + (\rho/2)/[1 + \exp(\rho/2)] \) [8]. For values of \( \rho \ll 2 \), in units in which \( 2R = 1 \), the agreement is very good. However as \( \rho \to \infty \) the exact \( p/\rho \to 1 \) while the P.Y. equation gives \( p/\rho = 1 + \eta/4 \) and \( p^2/\rho = 2 \).

Three dimensions. In this case we have not yet obtained the complete solution for \( C_{12}(r) \) but the quantities \( g_{12}(R) \) and \( \int C_{12}(r) \, dr \) which are relevant for the thermodynamics are related to the densities \( \rho_1 \) and \( \rho_2 \) by the following relations: (using units in which \( \pi R^3 = 1 \).

\[ g_{12}(R) = 2 \cos \frac{I_1}{(1 - \rho \rho_2)} \]  

(9)

\[ \int C_{12}(r) \, dr = -\sin \frac{I_1}{(1 - \rho \rho_2)} \]  

(10)

where \( I_1 \) and \( I_2 \) are elliptic integrals depending on a parameter \( z_0 \).

\[ I_1 = \int_1^{z} \frac{dz}{(z_0^2 x^2 + 4 z - 4)^{1/2}}, \]  

(11)

\[ I_2 = \int_1^{z_0} \frac{dz}{(z_0^2 x^2 + 4 z - 4)^{1/2}}, \]  

(12)

and \( z_0 \) has to be obtained from the solution of the equation \( \eta \approx 1 (\rho_1 \rho_2) \)\( \eta_0 = 1 \)8 \cos \frac{I_1}{(1 - \rho \rho_2)} \) so that \( \eta \approx 0 \) when \( z_0 = \infty \). As \( z_0 \) decreases \( \eta \) at first increases monotonically reaching a maximum value \( \eta_{\max} \approx 3.0 \) at \( z_0 \approx 0.949 \) and then decreases to the value \( \eta_0 \approx 1.72 \) at \( z_0 = 0 \). For \( \eta > \eta_0 \) there is thus, as in one dimension, more than one solution of the P.Y. equation but again the reasonable thing seems to be to follow the low density branch as far as it will go. (The existence of a maximum density beyond which there are no solutions to the integral equations is very similar to that found by Wainman [10] in the solution of the MSS for a similar system.)

We find that before \( \eta \) reaches \( \eta_{\max} \), there is a critical value \( \eta_c \), such that for \( \eta > \eta_c \) the free energy obtained from the P.Y. equation on the assumption that the system is uniform is no longer thermodynamically stable. The value of \( \eta_c \) obtained from the compressibility and virial equations are respectively \( \eta_c = 1.676 \pm 0.005 \) and \( \eta_c = 1.7876 \pm 0.005 \). These values are remarkably close to the value \( \eta_c = 1.674 \pm 0.003 \) obtained by Melnyk, Rowlinson and Sawford [4] from a Padé approximation calculation based on the first ten virial coefficients obtained from the P.Y. compressibility pressure.

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References