

# Results of Percus-Yevick approximation for a binary mixture of hard spheres with nonadditive diameters; $R_{11} = R_{22} = 0, R_{12} > 0^*$

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We investigate the properties of binary mixtures of hard sphere fluids with nonadditive diameters:

Calling  $R_{ij}$  the distance of closest approach between particles of species  $i$  and  $j$  we assume

$R_{12} = \frac{1}{2}(R_{11} + R_{22}) + \alpha$  with  $\alpha \neq 0$ . We find the exact solution of the Percus-Yevick integral

equation for this system in both one and three dimensions when  $R_{11} = R_{22} = 0, \alpha > 0$

(Widom-Rowlinson model). The solution of the PY equation for the Widom-Rowlinson model

exhibits a phase transition (corresponding to a separation of the components) in three but not in one

dimension. This is in agreement with the true behavior of this system. The critical indices in three

dimensions are classical.

## I. INTRODUCTION

In the absence of any exact results for the radial distribution function of dense gases and liquids, our understanding and interpretation of experiments in fluids relies heavily on the use of various approximate integral equations for these functions.

One of the more successful of these integral equations, the Percus-Yevick (PY) equation,<sup>1</sup> has a relatively simple closed form solution for a system of hard spheres. The solution for a single-component hard sphere fluid with interparticle potential,

$$\begin{aligned} v(r) &= \infty, & r < R \\ &= 0, & r > R, \end{aligned} \quad (1.1)$$

was obtained by Wertheim<sup>2</sup> and Thiele.<sup>3</sup> Lebowitz<sup>4</sup> generalized Wertheim's method to get the solution of the PY equation for mixtures of hard spheres with potential between a particle of species  $i$  and  $j$ ,

$$\begin{aligned} v_{ij}(r) &= \infty, & r < R_{ij} \\ &= 0, & r > R_{ij}, \end{aligned} \quad (1.2)$$

when the diameters are additive

$$R_{ij} = \frac{1}{2}(R_{ii} + R_{jj}). \quad (1.3)$$

These solutions have been used<sup>5</sup> extensively in connection with x-ray and neutron scattering data from simple fluids and from liquid metals. In the latter experiments it was noted that the assumption of additive diameters may be grossly invalid for some liquid-metal mixtures. Similar remarks apply also to other fluid mixtures.

The PY equation for mixtures of hard spheres with potential (1.2) but without the assumption of additive diameters was considered by Lebowitz and Zomick.<sup>6</sup> They considered in particular the case,

$$R_{12} = \frac{1}{2}(R_{11} + R_{22}) + \alpha, \quad (1.4)$$

where  $\alpha$  satisfies the following inequalities:

$$0 \leq \alpha \leq \frac{1}{2}(R_{22} - R_{11}), \quad R_{22} \geq R_{11}. \quad (1.5)$$

They obtained an exact solution in one dimension and a partial solution in three dimensions.

Recently Widom and Rowlinson<sup>7</sup> proposed a model for studying liquid-vapor phase transitions 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  $\alpha$  between particles of different species, i. e.,

$$\begin{aligned} R_{ij} &= \alpha, & (i \neq j) \\ &= 0, & (i = j). \end{aligned} \quad (1.6)$$

This model, and some generalization of it, was proven<sup>8</sup> 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, and some rigorous inequalities which can be derived in various ways,<sup>9</sup> has so far been obtained either from simple mean field theory or from low density expansions (via Padé approximations) and from some machine computations on related systems. In this paper we find the exact solution of the PY equation for this system in one and three dimensions.

In one dimension, the solution is unique up to a certain density and becomes nonunique after that. The "physical" solution can however be shown, using the continuity of the pressure, to be just the continuation of the low density solution. We compare the values of pressures with the exact result. For values of density less than 1,<sup>10</sup> in units in which  $2\alpha = 1$ , the agreement is very good. The direct correlation function is the Bessel function of zeroth order.

In three dimensions, but not in one, the solution does not extend beyond a certain density, that is, the PY integral equation does not yield a solution at a density higher than this one. Before reaching this maximum density we find, in three dimensions, a density at which the "susceptibility" diverges with "classical" critical indices. Correlation functions and their Fourier transforms are drawn for a few densities. These results are compared with some rigorous inequalities<sup>9</sup> on the correlation functions of this system.

A. Formulation of problem

In a uniform binary mixture with densities  $\rho_1$  and  $\rho_2$ , the direct correlation functions  $C_{ij}(r)$  are defined in terms of the radial distribution functions,  $g_{ij}(r)$ , by the Ornstein-Zernike equations,<sup>11</sup>

$$g_{ij}(r) - 1 = C_{ij}(r) + \sum_{l=1}^2 \rho_l \int [g_{il}(|\mathbf{r}'|) - 1] \times C_{lj}(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}'. \tag{1.7}$$

The symmetry  $g_{ij}(r) = g_{ji}(r)$  also gives  $C_{ij}(r) = C_{ji}(r)$  and  $r = |\mathbf{r}|$ .

The PY approximation<sup>1</sup> for hard spheres consists of the assumption that  $C_{ij}(r)$  does not extend beyond the range of potential,

$$C_{ij}(r) = 0, \text{ for } r > R_{ij}. \tag{1.8}$$

When this is combined with the exact relation  $g_{ij}(r) = 0$ , for  $r < R_{ij}$  we have a closed set of equations for  $C_{ij}(r)$  and  $g_{ij}(r)$  the solution of which constitutes our problem.

B. Thermodynamics

Given the solution of the PY equation for  $C_{ij}(r)$  and  $g_{ij}(r)$ , there are different ways of obtaining thermodynamic quantities from these correlation functions. These ways would all be equivalent if we had the exact functions. They are generally not equivalent for the PY solution (e.g., in the PY solution for the binary additive mixture of hard spheres solved by Lebowitz,<sup>4</sup> the compressibility pressure is slightly above and the virial pressure is slightly below the pressure obtained by machine computation.<sup>12</sup>)

Thus we may “get” a thermodynamics from the virial theorem which relates the pressure to the “contact” value of the distribution function. This pressure from the virial theorem, so-called virial pressure  $P^v$ , can be written for a two-component hard sphere system in the form,

$$\beta P^v = \sum_i \rho_i + \sum_{i,j} \rho_i \rho_j c g_{ij}(R_{ij}), \tag{1.9}$$

where

$$g_{ij}(R_{ij}) = \lim_{r \rightarrow R_{ij}^+} g_{ij}(r) = - \lim_{r \rightarrow R_{ij}^-} C_{ij}(r), \tag{1.10}$$

$\beta = (kT)^{-1}$  (we shall set  $\beta = 1$  from now on), and  $c$  is  $R_{ij}$  or  $\frac{2}{3}\pi R_{ij}^3$  in one and three dimensions, respectively.

Another way of obtaining thermodynamics from the correlation function is to use the “compressibility relations,”<sup>4</sup>

$$\rho_i \frac{\partial \mu_i^c(\rho_1, \rho_2)}{\partial \rho_j} = \delta_{ij} - \rho_i \int C_{ij}(r) d\mathbf{r} \tag{1.11}$$

$$1 - \sum_i \rho_i \int C_{ij}(r) d\mathbf{r} = \sum_i \rho_i \frac{\partial \mu_i^c}{\partial \rho_j} = \frac{\partial p^c(\rho_1, \rho_2)}{\partial \rho_j}, \tag{1.12}$$

where  $\mu_i^c$  and  $P^c$  are, respectively, the chemical potential of the  $i$ th species and the pressure, as obtained from the compressibility relations.

II. ONE DIMENSION

We consider the one-dimensional case first since it is simpler yet similar<sup>13</sup> to the three-dimensional case. This case also permits comparison with the exact solution. Instead of manipulating  $C_{ij}(r)$  and  $g_{ij}(r)$  (which are discontinuous at  $r = R_{ij}$ ), we introduce a new continuous function  $\sigma_{ij}(r)$ ,

$$\begin{aligned} \sigma_{ij}(r) &= -(\rho_i \rho_j)^{1/2} C_{ij}(r), \quad r \leq R_{ij} \\ &= (\rho_i \rho_j)^{1/2} g_{ij}(r), \quad r \geq R_{ij}. \end{aligned} \tag{2.1}$$

Combining (2.1) with (1.7) and (1.8) yields

$$\sigma_{ij}(r) = A_{ij} - \sum_{l=1}^2 \int dy \sigma_{il}(y) \sigma_{lj}(r - y), \tag{2.2}$$

where the integration over  $y$  is restricted to the region

$$|y| \geq R_{il}, \quad |r - y| \leq R_{lj},$$

and

$$\begin{aligned} A_{ij} &= (\rho_i \rho_j)^{1/2} \left[ 1 - \sum_{l=1}^2 \rho_l \int C_{il}(r) dr \right] \\ &= (\rho_i / \rho_j)^{1/2} A_{jj}. \end{aligned} \tag{2.3}$$

We look for the solutions of Eq. (2.2) such that  $\int |g_{ij}(r) - 1| dr < \infty$ . This asserts, essentially, that the system is in a single phase and leads to a boundedness property on the Laplace transform of  $\sigma_{ij}(r)$  which we shall use later. Writing out (2.2) more explicitly yields

$$\begin{aligned} \sigma_{ij}(r) &= A_{ij} - \sum_l \left\{ \int_{\min[-R_{il}, r - R_{lj}]}^{-R_{il}} \sigma_{il}(y) \sigma_{lj}(r - y) dy \right. \\ &\quad \left. + \int_{\max[R_{il}, r - R_{lj}]}^{\max[R_{il}, r + R_{lj}]} \sigma_{il}(y) \sigma_{lj}(r - y) dy \right\}. \end{aligned} \tag{2.4}$$

Since the right side of (2.4) is of a convolution type, we look for a solution in terms of the Laplace transforms.

Using (2.3), the Laplace transform of  $\sigma_{ij}(r)$ ,

$$\sigma_{ij}(s) = \int_0^\infty e^{-sr} \sigma_{ij}(r) dr, \tag{2.5}$$

can be written in the form,

$$\begin{aligned} \sigma_{ij}(s) &= s^{-1} A_{ij} - \sum_{l=1}^2 G_{il}(s) [F_{lj}(s) + F_{lj}(-s)] \\ &\quad - [U_{ij}(s) - U_{ij}(-s)] = F_{ij}(s) + G_{ij}(s), \end{aligned} \tag{2.6}$$

where

$$\begin{aligned} F_{lj}(s) &\equiv \int_0^{R_{lj}} e^{-sr} \sigma_{lj}(r) dr, \\ G_{il}(s) &\equiv \int_{R_{il}}^\infty e^{-sr} \sigma_{il}(r) dr, \end{aligned} \tag{2.7}$$

$$\begin{aligned} U_{ij}(s) &\equiv (1 - \delta_{ij}) \int_0^{R_{ij} - R_{ii}} e^{-sr} dr \\ &\quad \times \int_{r - R_{ij}}^{R_{ii}} \sigma_{ii}(y) \sigma_{ij}(r - y) dy, \end{aligned} \tag{2.8}$$

for  $R_{11} \leq R_{22} \leq R_{12}$  the case we shall be concerned with here.  $\delta_{ij}$  is the Kronecker’s delta function. Equation (2.8) can be rewritten in a  $2 \times 2$  matrix form,

$$\sigma(s) = s^{-1} \mathbf{A} - \mathbf{G}(s) \mathbf{F}^*(s) - \mathbf{U}^*(s) \tag{2.9}$$

or

$$\mathbf{G}(s) = \mathbf{H}(s) \mathbf{K}^{-1}(s), \tag{2.10}$$

where we have defined for any function  $f(s)$ ,

$$f^*(s) \equiv f(s) + f(-s), \quad (2.11)$$

$$f^*(s) \equiv f(s) - f(-s), \quad (2.12)$$

and

$$\mathbf{H}(s) = \mathbf{A} - s \mathbf{F}(s) - s \mathbf{U}^*(s), \quad (2.13)$$

$$\mathbf{K}(s) = s \mathbf{I} + s \mathbf{F}^*(s), \quad (2.14)$$

$$\mathbf{I} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \quad (2.15)$$

To exploit the condition  $\int |g_{ij}(r) - 1| dr < \infty$  we now define the matrices  $\mathbf{L}(s)$  and  $\mathbf{B}(s)$  by the relations,

$$\begin{aligned} \mathbf{L}(s) &\equiv \mathbf{G}(s) \mathbf{H}^T(-s) \\ &= \mathbf{H}(s) \mathbf{K}^{-1}(s) \mathbf{H}^T(-s) = -\mathbf{L}^T(-s), \end{aligned} \quad (2.16)$$

and

$$\mathbf{B}(s) \equiv \mathbf{L}(s) - s^{-1} \mathbf{A}', \quad (2.17)$$

where an element of  $\mathbf{A}'$  is  $A'_{ij}$ ,

$$A'_{ij} \equiv \sum_{i=1}^2 \sqrt{\rho_i \rho_i} A_{ji} = \sqrt{\rho_i \rho_j} a, \quad (2.18)$$

$$a \equiv (A_{11} + A_{22}), \quad (2.19)$$

with  $A_{ij}$  defined in (2.3). The diagonal components of  $\mathbf{B}(s)$  are

$$\begin{aligned} B_{ii}(s) &= G_{ii}(s) [A_{ii} + s F_{ii}(-s)] \\ &\quad + G_{ij}(s) [A_{ij} + s F_{ij}(-s) - s U_{ij}^*(s)] \\ &\quad - A'_{ii} s^{-1}, \quad i=1, 2, \quad j \neq i. \end{aligned} \quad (2.20)$$

The limit of  $B_{ii}(s)$  as  $s \rightarrow 0$  is finite due to (2.18). When  $Rls \rightarrow \infty$ ,  $G_{ij}(s) \sim s^{-1} \exp(-s R_{ij})$ ,  $F_{ij}(-s) \sim s^{-1} \exp(s R_{ij})$ , and  $U_{ij}^*(s) \sim s^{-1} \exp(R_{ij} - R_{ii})$ . Therefore we see that the  $B_{ii}(s)$ 's are analytic and bounded on all the rays in the right hand side of the complex  $s$  plane. We can say the same about the left hand side of the complex  $s$  plane since  $\mathbf{L}(-s) = -\mathbf{L}^T(s)$ . Thus by the Liouville theorem,<sup>14</sup> the  $B_{ii}(s)$ 's are constants. By looking at the value of  $B_{ii}(s)$  as  $s \rightarrow \infty$ , we conclude that  $B_{ii}(s)$  vanishes everywhere or

$$L_{ii}(s) = s^{-1} A'_{ii}. \quad (2.21)$$

We can therefore write  $\sigma_{ii}(s)$  more explicitly

$$\begin{aligned} \sigma_{ii}(s) &= s^{-1} A_{ii} - s^{-2} A'_{ii} + G_{ij}(s) [s^{-1} A_{ij} - F_{ij}(s) - U_{ij}^*(s)] \\ &\quad + G_{ii}(s) [s^{-1} A_{ii} - F_{ii}(s)], \quad i \neq j. \end{aligned} \quad (2.22)$$

Taking the inverse Laplace transform of (2.22) yields finally for  $R_{11} \leq R_{22} \leq R_{12}$ ,

$$\sigma_{ii}(r) = A_{ii} - A'_{ii} r, \quad r \leq R_{ii}, \quad (2.23)$$

since the last two terms in (2.22) die out for large value of  $Rls$  as, or faster than, the order of  $\exp(-s R_{ii})$ . We note here that the form of  $\sigma_{ii}(r)$  in (2.23) is the same for all binary mixtures<sup>6</sup> with  $\alpha \geq 0$  in (1.4).

The off-diagonal components of  $\mathbf{B}(s)$  do not give any simple relationship which give rise to various complexities for different values of  $R_{ij}$ 's. We therefore restrict ourselves now to the case  $R_{ij} = 0$ .

The PY approximation for this system, which has  $R_{ij} = 0$  and

$$\begin{aligned} R_{ij} &= \alpha, \quad \text{for } i \neq j \\ &= 0, \quad i = j \end{aligned} \quad (2.24)$$

sets  $C_{ii}(r) = 0$ . Using (2.4) or (2.23) gives

$$\sigma_{ii}(0) = A_{ii}. \quad (2.25)$$

We also find  $U_{ij}(s)$  and  $L_{ii}(s)$  from (2.8) and (2.21)

$$U_{ij}(s) = (1 - \delta_{ij}) \int_0^\alpha e^{-sr} dr \int_{r-\alpha}^0 \sigma_{jj}(y) \sigma_{12}(r-y) dy, \quad (2.26)$$

$$L_{ii}(s) = s^{-1} A_{ii}. \quad (2.27)$$

Writing out (2.4) for this system yields

$$\sigma_{ii}(r) = A_{ii} - \int_{\max[\alpha, r-\alpha]}^{r+\alpha} \sigma_{12}(y) \sigma_{12}(r-y) dy, \quad i=1, 2, \quad (2.28)$$

$$\sigma_{ij}(r) = A_{ij} - \int_{r-\alpha}^{r+\alpha} \sigma_{ii}(y) \sigma_{12}(r-y) dy, \quad i \neq j, \quad (2.29)$$

and

$$\sigma_{11}(r) - \sigma_{22}(r) = A_{11} - A_{22} = \rho_1 - \rho_2. \quad (2.30)$$

Equation (2.30) gives

$$\begin{aligned} \sigma_{22}(s) - \sigma_{11}(s) &= (\rho_2 - \rho_1)/s \\ &= G_{22}(s) - G_{11}(s). \end{aligned} \quad (2.31)$$

Equation (2.26) also yields with the help of (2.31),

$$\begin{aligned} U_{21}^*(s) - U_{12}^*(s) &= [(A_{21} - A_{12})/s] - [(\rho_2 - \rho_1)/s] \\ &\quad \times F_{12}^+(s). \end{aligned} \quad (2.32)$$

$L_{12}(s)$  and  $L_{21}(s)$  are explicitly

$$\begin{aligned} L_{ij}(s) &= G_{ij}(s) A_{ii} + G_{jj}(s) [A_{ij} + s F_{ij}(-s) - s U_{ij}^*(s)], \\ &\quad \times j \neq i. \end{aligned} \quad (2.33)$$

The difference between  $L_{21}(s)$  and  $L_{12}(s)$ , using Eqs. (2.31) and (2.32), is

$$L_{21}(s) - L_{12}(s) = (\rho_2 - \rho_1) F_{12}^+(s). \quad (2.34)$$

Now that the relation between the  $L_{ij}(s)$ 's and  $F_{ij}^+(s)$ 's has been obtained in (2.34), a relation for  $F_{ij}^+(s)$ 's and  $H_{ij}(s)$ 's is desired since they have the same behavior for large  $Rls$ . For this purpose, we derive from the definition of  $\mathbf{L}(s)$  in (2.16),

$$\mathbf{H}(-s) \mathbf{H}(s) = \mathbf{L}^T(s) \mathbf{K}(s). \quad (2.35)$$

Among the four matrix elements of the above equation, only two are linearly independent due to the symmetry of the system between 1 and 2 species. These are

$$H_{11}(-s) H_{11}(s) + H_{12}(-s) H_{21}(s) = s L_{11}(s) + s L_{21}(s) F_{12}^+(s), \quad (2.36)$$

$$H_{11}(-s) H_{12}(s) + H_{12}(-s) H_{22}(s) = L_{11}(s) K_{12}(s) + s L_{21}(s). \quad (2.37)$$

We can rewrite (2.36) and (2.37) using (2.34) in the form,

$$\begin{aligned} A_{11}^2 + \frac{1}{2} (H_{12}^+ - H_{12}^*) \left[ \frac{1}{2} H_{12}^+ + \frac{1}{2} H_{12}^* + (\rho_2 - \rho_1) F_{12}^+ \right] \\ = A_{11}' + \frac{1}{2} s F_{12}^+ [L_{21}^*(s) + (\rho_2 - \rho_1) F_{12}^+(s)], \end{aligned} \quad (2.38)$$

$$\begin{aligned} A_{11} H_{12}^+ + \frac{1}{2} (\rho_2 - \rho_1) (H_{12}^+ - H_{12}^*) = A_{11}' F_{12}^+ + \frac{1}{2} s \\ \times [L_{21}^* + (\rho_2 - \rho_1) F_{12}^+]. \end{aligned} \quad (2.39)$$

By eliminating  $L_{21}^*(s)$  from (2.38) and (2.39), we obtain

a functional relationship of the form,

$$\left(\frac{1}{2} H_{12}^+ - A_{11} F_{12}^+\right)^2 - (s^2 - 4\mu^2) \left(\frac{1}{2} F_{12}^+\right)^2 = A_{11}' - A_{11}^2, \quad (2.40)$$

or simply

$$\Psi^2(s) - E(s)\Phi^2(s) = \mu^2, \quad (2.41)$$

where we have defined

$$\Psi(s) \equiv \frac{1}{2} H_{12}^+ - A_{11} F_{12}^+(s), \quad (2.42)$$

$$\Phi(s) \equiv \frac{1}{2} F_{12}^+(s), \quad (2.43)$$

$$\mu^2 \equiv A_{11}' - A_{11}^2 = \sigma_{12}^2(\alpha), \quad (2.44)$$

$$E(s) \equiv s^2 - 4\mu^2. \quad (2.45)$$

The relation  $\mu^2 = \sigma_{12}^2(\alpha)$  can be seen by looking at the asymptotic behavior of  $sL_{11}(s)$  as  $Rs \rightarrow \infty$  in (2.20),

$$sL_{11}(s) = sG_{11}(s)A_{11} + sG_{12}(s)H_{12}(-s) \xrightarrow{s \rightarrow \infty} A_{11}' + \sigma_{12}^2(s) \quad (2.46)$$

along with (2.21).

The functional equation (2.41) is of the same form as in the work of Lebowitz and Zomick. The functions  $\Psi(s)$  and  $\Phi(s)$  are entire even functions of the complex variable  $s$  with the asymptotic behavior  $s^{-1} \exp[-\alpha |R|s|]$ , for large  $s$ . The solution to this functional relation is<sup>15</sup>

$$\Psi(s) = \mu \cosh \alpha \sqrt{E(s)}, \quad (2.47)$$

$$\Phi(s) = \mu \sinh[\alpha \sqrt{E(s)}] / \sqrt{E(s)}, \quad (2.48)$$

with  $\mu = \sigma_{12}(\alpha) = (\rho_1 \rho_2)^{1/2} g_{12}(\alpha)$  positive.

The quantity  $\mu$  in (2.41) enters as a parameter in the solution. It can be determined as follows. From (2.48)

$$\Phi(0) = \frac{1}{2} \sin 2\mu\alpha, \quad (2.49)$$

while from (2.19) and (2.30),

$$\mu^2 = A_{11}' - A_{11}^2 = \rho_1 \rho_2 - \frac{1}{4}(\alpha - \rho_1 - \rho_2)^2 = \rho_1 \rho_2 [1 - 4\Phi^2(0)], \quad (2.50)$$

since

$$A_{11} = \frac{1}{2}(\alpha - \rho_2 - \rho_1) = \rho_1 [1 + (\rho_2/\rho_1)^{1/2} 2\Phi(0)]. \quad (2.51)$$

This yields the equation for  $\mu$ ,

$$\mu = (\rho_1 \rho_2)^{1/2} \cos 2\mu\alpha \quad (2.52)$$

or simply

$$q = \eta \cos q, \quad (2.53)$$

with  $q \equiv \eta g_{12}(\alpha)$  and  $\eta$  the reduced density;  $\eta \equiv 2\alpha \sqrt{\rho_1 \rho_2}$ .

For  $\eta \geq \eta_0 \approx 2.97$ , the solution of (2.53) for  $\mu$  is not unique. The requirement that the pressure be a continuous function of the density will be satisfied only if we choose the solution along the first branch of  $\cos q$  where  $q \leq \frac{1}{2}\pi$ , that is, along the branch where it is the continuation of the low density solution. This will be seen from the expressions for the pressure, which we shall compute below. We remark here that the equation for  $\sigma_{12}(\alpha)$  obtained from (2.52), is of the same form as in the Lebowitz-Zomick case and the cases,<sup>16</sup>  $0 < R_{11} = R_{22} < R_{12}$ .

## A. Equation of state

The virial pressure is obtained from (1.9) and (2.44) namely

$$P^v = \rho + 2\alpha \sqrt{\rho_1 \rho_2} \mu, \quad (2.54)$$

where  $\rho$  is the total density,  $\rho_1 + \rho_2$ , and  $\mu$  is defined in (2.44).

From the compressibility relation, that is,

$$\partial P^c / \partial \rho_1 = 1 - \rho_2 \int C_{12}(r) dr = 1 + (\rho_2/\rho_1)^{1/2} \sin(2\mu\alpha), \quad (2.55)$$

we obtain, since  $\mu$  depends only on  $(\rho_1 \rho_2)^{1/2}$ ,

$$P^c = \rho + \alpha^{-1} \int_0^\eta \sin(2\alpha\mu) d\eta, \quad \eta = 2\alpha \sqrt{\rho_1 \rho_2}. \quad (2.56)$$

We can compare the pressure (2.54) and (2.56) with the exact pressure<sup>6</sup> which, for  $\rho_1 = \rho_2 = \frac{1}{2}\rho$ , is determined by the equation

$$P/\rho = 1 + \alpha P / [1 + \exp(\alpha P)]. \quad (2.57)$$

The different pressures are plotted in Fig. 2. From this we see that for  $\rho \leq 1$  (in units in which  $2\alpha = 1$ ), the agreement is very good, while for  $\rho \rightarrow \infty$  they converge to different values;

$$P^v/\rho \rightarrow 1 + \frac{1}{4}\pi, \quad P^c/\rho \rightarrow 2, \quad \text{and} \quad P^{ex}/\rho \rightarrow 1. \quad (2.58)$$

## B. $\sigma_{ij}(r)$ and their Fourier transforms

Equation (2.43) provides the Fourier transform of  $C_{12}(r)$  since

$$\begin{aligned} \frac{1}{2} F_{12}^+(s) &\equiv \int_0^\alpha \sigma_{12}(r) \frac{1}{2} (e^{-sr} + e^{s\tau}) dr \\ &= \frac{1}{2} \int_{-\alpha}^\alpha \sigma_{12}(r) e^{-sr} dr, \end{aligned} \quad (2.59)$$

and therefore with the help of (2.59), (2.43), and (2.48),

$$\begin{aligned} \tilde{C}_{12}(k) &\equiv \int_{-\alpha}^\alpha C_{12}(r) e^{-ikr} dr \\ &\equiv 2\mu (\rho_1 \rho_2)^{-1/2} \sin[\alpha(k^2 + 4\mu^2)^{1/2}] / (k^2 + 4\mu^2)^{1/2}. \end{aligned} \quad (2.60)$$

The inverse Fourier transform of  $\tilde{C}_{12}(k)$  yields  $C_{12}(r)$ ,

$$C_{12}(r) = -\mu (\rho_1 \rho_2)^{1/2} J_0[2\mu(\alpha^2 - r^2)^{1/2}] \quad \text{for } 0 < r < \alpha \\ = 0, \quad \text{for } r > \alpha, \quad (2.61)$$

where  $J_0$  is the Bessel function of zeroth order. It is seen from (2.61) that  $C_{12}(r) < 0$  for all  $|r| < \alpha$ .

The Fourier transforms of the correlation functions  $[g_{ij}(r) - 1]$  is denoted by  $\tilde{H}_{ij}(k)$ . Using (1.7), we find

$$\tilde{H}_{ij}(k) = \tilde{C}_{ij}(k) + \sum_l \rho_l \tilde{H}_{il}(k) \tilde{C}_{lj}(k), \quad (2.62)$$

hence

$$\tilde{H}_{11}(k) = (\rho_1 \rho_2)^{1/2} \tilde{C}_{12}^2(k) [1 - \rho_1 \rho_2 \tilde{C}_{12}^2(k)]^{-1}, \quad (2.63)$$

$$\tilde{H}_{12}(k) = \tilde{C}_{12}(k) [1 - \rho_1 \rho_2 \tilde{C}_{12}^2(k)]^{-1}. \quad (2.64)$$

The  $H_{ij}(k)$  were found numerically and are plotted in Figs. 3-5. The numerical calculation of the inverse Fourier transform of  $\tilde{H}_{12}(k)$  in (2.64) converges very slowly because of the slow decay of  $\tilde{C}_{12}(k)$  as  $k \rightarrow \infty$ . We note however that

$$\tilde{H}_{12}(k) - \tilde{C}_{12}(k) = \rho_1 \rho_2 \tilde{C}_{12}^3(k) [1 - \rho_1 \rho_2 \tilde{C}_{12}^2(k)]^{-1} \quad (2.65)$$

for which the inverse Fourier transformation is very rapidly convergent. Equation (2.65) yields not only the

radial distribution function but also automatically checks the accuracy in the region  $r < \alpha$  through the comparison with  $C_{12}(r)$  in (2.61).

### III. THREE-DIMENSIONAL SOLUTION

The analysis in three dimensions follows very closely the one dimensional case. Letting

$$\begin{aligned}\sigma_{ij}(r) &= -2\pi(\rho_i \rho_j)^{1/2} r C_{ij}(r), \quad \text{for } r < R_{ij} \\ &= 2\pi(\rho_i \rho_j)^{1/2} r g_{ij}(r), \quad \text{for } r > R_{ij},\end{aligned}\quad (3.1)$$

and the Laplace transforms  $\sigma_{ij}(s)$ ,  $F_{ij}(s)$ ,  $F'_{ij}(s)$ , and  $G_{ij}(s)$  are then defined in terms of this  $\sigma_{ij}(r)$  as in one dimension. We find that

$$s^2 \sigma(s) = \mathbf{A} + s \mathbf{G}(s) \mathbf{F}^*(s) - s \mathbf{U}^*(s) \quad (3.2)$$

or

$$\mathbf{G}(s) = \mathbf{H}(s) \cdot \mathbf{K}^{-1}(s), \quad (3.3)$$

where we now have

$$\mathbf{H}(s) = \mathbf{A} - s^2 \mathbf{F}(s) - s \mathbf{U}^*(s), \quad (3.4)$$

$$\mathbf{K}(s) = s^2 \mathbf{I} - s \mathbf{F}^*(s), \quad (3.5)$$

$$U_{ij}(s) = \int_0^\infty s^{-\alpha} P_{ij}(r) dr, \quad (3.6)$$

$$P_{ij}(r) \equiv \sum_i \left\{ \begin{array}{l} \max[R_{ij}, r + R_{ii}] \\ r + R_{ii} \end{array} \right\} \sigma_{ii}(r-z) \sigma_{ij}(z) dz. \quad (3.7)$$

We see from (3.7) that  $P_{ii}(r) = 0$  and that  $P_{ij}(r)$  vanishes for  $r \geq R_{ij} - R_{ii}$ , when  $R_{11} \leq R_{22} \leq R_{12}$ .

The requirement that  $g_{ij}(r) \rightarrow 1$  as  $r \rightarrow \infty$  in such a way that

$$\int r |g_{ij}(r) - 1| dr < \infty \quad (3.8)$$

implies that  $G_{ij}(s) - 2\pi\sqrt{\rho_i \rho_j}/s^2$  can have no singularity in the closed right-half complex  $s$  plane. To make use of this condition effectively we introduce the matrices  $\mathbf{L}(s)$  and  $\mathbf{B}(s)$  in the same manner as in the one-dimensional case,

$$\begin{aligned}\mathbf{L}(s) &\equiv \mathbf{G}(s) \mathbf{H}^T(-s) \\ &= \mathbf{H}(s) \mathbf{K}^{-1}(s) \mathbf{H}^T(-s) = \mathbf{L}^T(-s)\end{aligned}\quad (3.9)$$

$$\mathbf{B}(s) \equiv \mathbf{L}(s) - s^{-2} \mathbf{A}', \quad (3.10)$$

where

$$A'_{ij} \equiv \sum_{i=1}^2 2\pi\sqrt{\rho_i \rho_i} A_{ii} = 2\pi\sqrt{\rho_i \rho_i} a, \quad (3.11)$$

$$a \equiv A_{11} + A_{22}, \quad A_{ij} = 2\pi(\rho_1 \rho_2)^{1/2} \left[ 1 - \sum \rho_l \int C_{ij}(r) dr \right].$$

The diagonal components of  $\mathbf{B}(s)$  are

$$\begin{aligned}B_{ii}(s) &= G_{ii}(s) [A_{ii} - s^2 F_{ii}(-s)] + G_{ij}(s) [A_{ij} - s^2 F_{ij}(-s) \\ &\quad - s U_{ij}^*(s)] - s^{-2} A'_{ii}, \quad i=1, 2, \quad i \neq j.\end{aligned}\quad (3.13)$$

$B_{ii}(s)$  will again be seen finite as  $s \rightarrow 0$  due to (3.9). Also when  $Rls \rightarrow \infty$ ,  $G_{ij}(s) \sim s^{-1} \exp(-sR_{ij})$ ,  $F_{ij}(-s) \sim s^{-1} \exp(sR_{ij})$ , and  $U_{ij}^*(s) \sim s^{-1} \exp[s(R_{ij} - R_{ii})]$  for the system with  $R_{11} \leq R_{22} \leq R_{12}$ . Therefore the  $B_{ii}(s)$ 's are entire and bounded on all the rays in the right hand side of the complex  $s$  plane. Since  $\mathbf{L}(s) = \mathbf{L}^T(-s)$ ,  $\mathbf{B}(s) = \mathbf{B}(-s)$ , we can by using Liouville's theorem set  $B_{ii}(s)$

equal to a constant,  $2B_i$ . We then find that

$$L_{ii}(s) - s^{-2} A_{ii} = 2B_i. \quad (3.14)$$

We can now write  $\sigma_{ii}(s)$  more explicitly,

$$\begin{aligned}s \sigma_{ii}(s) &= s^{-1} A_{ii} + s^{-4} A_{ii} + s^{-2} 2B_i + G_{ii}(s) [F_{ii}(s) \\ &\quad - s^{-2} A_{ii}] + G_{ij}(s) [F_{ij}(s) - s^{-2} A_{ij} + s^{-1} U_{ij}^*(s)], \\ &\quad j \neq i.\end{aligned}\quad (3.15)$$

This yields, after taking the inverse Laplace transform,

$$\sigma_{ii}(r) = A_{ii} r + B_{ii} r^2 + A'_{ii} r^4 / 24 \quad \text{for } r \leq R_{ii}, \quad (3.16)$$

since the last two terms of (3.15) die out for large value of  $Rls$  as, or faster than, the order of  $\exp(-sR_{ii})$ .

To find  $\sigma_{ij}(r)$ ,  $i \neq j$ , needs different methods according to the system and gives rise to great complexities. We therefore again restrict ourselves to the case  $R_{ii} = 0$ .

#### A. Solution for Widom-Rowlinson model in three dimensions

For this system,  $R_{ii} = 0$ ,  $C_{ii}(r) = 0$  for  $r > 0$ . Hence using (3.16) yields

$$\sigma_{ii}^{(1)}(0) = A_{ii}, \quad (3.17)$$

$$L_{ii}(s) = 2B_i + A'_{ii} s^{-2}, \quad (3.18)$$

$$\begin{aligned}\sigma_{22}(s) - \sigma_{11}(s) &= G_{22}(s) - G_{11}(s) \\ &= 2\pi(\rho_2 - \rho_1) / s^2,\end{aligned}\quad (3.19)$$

and

$$U_{21}^*(s) - U_{12}^*(s) = s^{-1} (A_{21} - A_{12}) + 2\pi(\rho_2 - \rho_1) F_{12}^* s^{-2}. \quad (3.20)$$

The off-diagonal elements of  $\mathbf{L}(s)$  in (3.9) yield the following relations:

$$L_{21}(s) = G_{21}(s) A_{11} + G_{22}(s) [A_{12} - s^2 F_{12}(-s) - s U_{12}^*(s)], \quad (3.21)$$

$$L_{12}(s) = G_{12}(s) A_{22} + G_{11}(s) [A_{21} - s^2 F_{12}(-s) - s U_{21}^*(s)]. \quad (3.22)$$

Their difference is

$$L_{12}(s) - L_{21}(s) = 2\pi(\rho_1 - \rho_2) F_{12}^*(s), \quad (3.23)$$

which has the  $s^{-1} \exp(\alpha |Rls|)$  behavior for large  $Rls$  in common with  $U_{12}^*(s)$  and  $H_{12}(s)$ .

From the relation,

$$\mathbf{H}(-s) \mathbf{H}(s) = \mathbf{L}^T(s) \mathbf{K}(s), \quad (3.24)$$

we get two linearly independent equations,

$$H_{11}(-s) H_{11}(s) + H_{12}(-s) H_{21}(s) = s^2 L_{11}(s) - s F_{12}^*(s) L_{21}(s), \quad (3.25)$$

$$\begin{aligned}H_{11}(-s) H_{12}(s) + H_{12}(-s) H_{22}(s) &= -s F_{12}^*(s) L_{11}(s) \\ &\quad + s^2 L_{21}(s).\end{aligned}\quad (3.26)$$

The other two elements of (3.24) are the same as (3.25) and (3.26) after some manipulation with the help of (3.23). Equations (3.25) and (3.26) can be written as

$$\begin{aligned}A_{11}^2 + \frac{1}{2} (H_{11}^* + s^2 F_{12}^*) \left[ \frac{1}{2} H_{12}^*(s) - \frac{1}{2} s^2 F_{12}^* - s^{-1} F_{12}^* 2\pi(\rho_2 - \rho_1) \right] \\ = (A'_{11} - B_{11} s^2) - s F_{12}^*(s) L_{21}(s),\end{aligned}\quad (3.27)$$

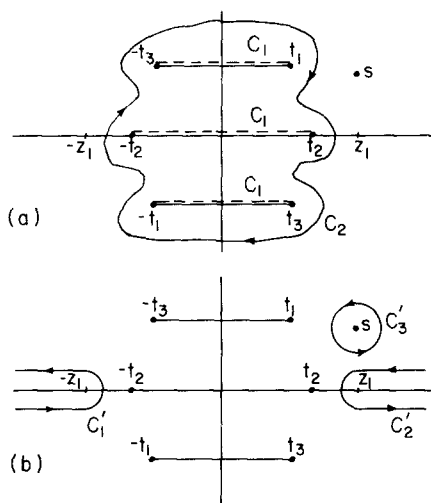


FIG. 1. Three integrations along three closed contours surrounding the three cuts  $C_1$  have the same effect as a single integration along a path  $C_2$  which encircles three branch cuts,  $C_1$ . This is equivalent to integrations along the paths  $C'_1$ ,  $C'_2$  and  $C'_3$ .  $\pm t_1, \pm t_2$  are the zeros of the sixth-order polynomial  $E(t)$ .  $\pm z_1$  are the zeros of  $h(z)$ .

$$A_{11}H_{12}^* + \pi(\rho_2 - \rho_1)(H_{12} + s^2 F_{12}^*) = -(A'_{11}s^{-2} - B_{11})s F_{12} + s^2 L_{21}(s). \quad (3.28)$$

Equations (3.27) and (3.28) may be combined into one relation by eliminating  $L_{21}(s)$ . We find

$$\left\{ \frac{1}{2} H_{12}^*(s) + s^{-1} A_{11} F_{12}^*(s) \right\}^2 - [s^6 - 4(A'_{11} - A_{11}^2 + B_{11}s^2)]$$

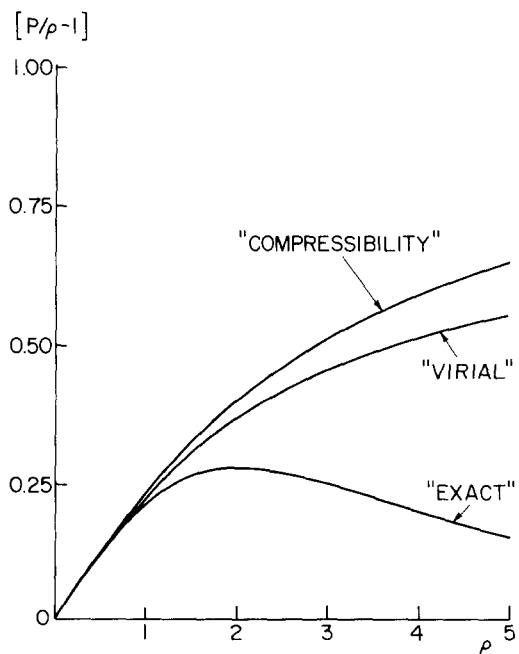


FIG. 2. Comparison of the PY pressures with the exact pressure in one-dimensional Widom-Rowlinson model. Three lines correspond to the pressures from the compressibility relation, the virial theorem, and the exact relation obtained by Zomick and Lebowitz, respectively.  $\rho$  is the total density  $\rho_1 + \rho_2$ , where  $\rho_1 = \rho_2$  in this graph. They converge to different limits shown in (2.58), while they are in good agreement for  $\rho < 1$ .

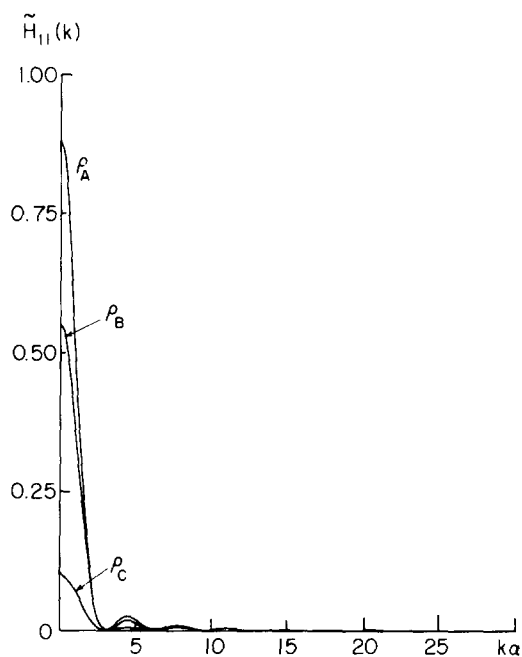


FIG. 3. One-dimensional Fourier transform of  $g_{11}(r) - 1$  of the Widom-Rowlinson model.  $\rho_A = 1.086$ ,  $\rho_B = 0.605$ , and  $\rho_C = 0.101$

$$\times \{F_{12}^*(s)/2s\}^2 = A'_{11} - A_{11}^2 + B_{11}s^2. \quad (3.29)$$

This leads to the equation,

$$\Psi^2(s) - E(s)\Phi^2(s) = h(s), \quad (3.30)$$

where we have defined

$$\Psi(s) \equiv \frac{1}{2} H_{12}^*(s) + A_{11} F_{12}^*(s)/s \quad (3.31)$$

$$\Phi(s) \equiv F_{12}^*(s)/2s, \quad (3.32)$$

$$E(s) \equiv s^6 - 4h(s), \quad (3.33)$$

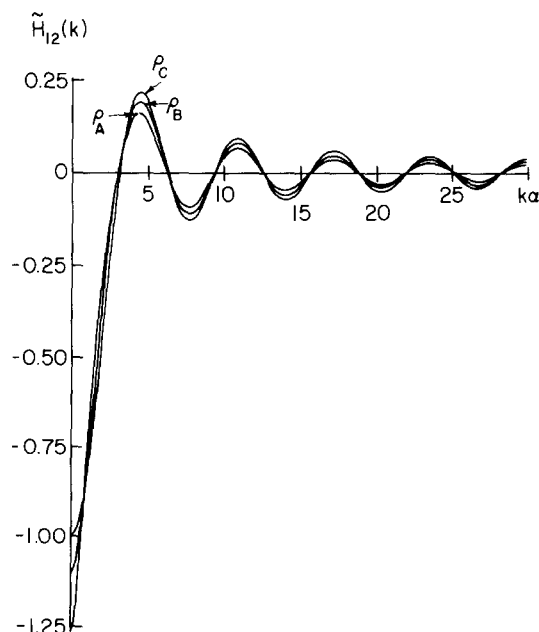


FIG. 4. One-dimensional Fourier transform of  $g_{12}(r) - 1$  for the Widom-Rowlinson model.  $\rho_A = 1.086$ ,  $\rho_B = 0.605$ , and  $\rho_C = 0.101$ .

$$h(s) \equiv 2B_{11}s^2 + \mu^2, \quad (3.34)$$

$$\mu^2 \equiv A'_{11} - A_{11}^2. \quad (3.35)$$

We also see that from (3.9) and (3.18)

$$\begin{aligned} L_{11}(s) &= G_{11}A_{11} + G_{12}[A_{12} - s^2F_{12}(-s) - sU_{12}^*] \\ &= s^{-2}A'_{11} + 2B_{11} \xrightarrow{s \rightarrow \infty} -\sigma_{12}^2(\alpha) \end{aligned} \quad (3.36)$$

or

$$2B_{11} = -\sigma_{12}^2(\alpha), \quad (3.37)$$

$$h(s) \equiv 2B_{11}(s^2 - z_1^2), \quad (3.38)$$

and

$$z_1 \equiv \mu/\sigma_{12}(\alpha). \quad (3.39)$$

$\Psi(s)$  and  $\Phi(s)$  are both even, and entire functions and have the  $s^{-1} \exp[\alpha |R|s|]$  behavior for large  $|R|s|$ , as can be seen from the way that they are defined.

## B. Solution of the functional equation

A functional equation of the type (3.30) was solved formally by Penrose and Lebowitz<sup>15</sup> for the PY equation of the system considered by Lebowitz and Zomick,<sup>6</sup> i. e.,  $R_{11} \leq R_{12}$ ,  $0 < \alpha < \frac{1}{2}(R_{22} - R_{11})$ . The PY equation for that system has not yet been solved explicitly, though, because of its complexity. Our system,  $R_{11} = R_{22} = 0$ , has however a relatively simpler structure. Let us define  $f(s)$  by the relation,

$$f(s) \equiv \Psi(s) + \sqrt{E(s)} \Phi(s), \quad (3.40)$$

with  $\sqrt{E(s)}$  defined to be an odd function of  $s$  since  $E(s)$  is even. We can then rewrite the functional equation (3.30) in the form,

$$f(s)f(-s) = h(s). \quad (3.41)$$

Penrose and Lebowitz<sup>15</sup> have shown that if  $E(s)$  and  $h(s)$  share no common zero, then a functional equation of the type (3.30) can be reduced to a Hilbert problem on the arc, the solution of which was found by Muskhelishvili.<sup>17</sup>

To manipulate this recipe, we observe that  $E(s)$  and  $h(s)$  do not share any common zeros since  $E(s) = s^6 - 4h(s)$  and  $h(0) \neq 0$ . Then the final solution yields

$$f(s) = \pm \sqrt{2|B_{11}|} (s + z_1) \exp[I(s)], \quad (3.42)$$

with the condition

$$\alpha = (2\pi i)^{-1} \int_{C_1} dt t \ln J(t) / \sqrt{E(t)}. \quad (3.43)$$

Here

$$I(s) = (2\pi i)^{-1} \sqrt{E(s)} \int_{C_1} dt \ln J(t) / [\sqrt{E(t)} (t - s)] \quad (3.44)$$

and

$$J(t) \equiv (t - z_1) / (t + z_1). \quad (3.45)$$

$C_1$  is the path along the cuts parallel to the real axis as shown in Fig. 1; branches of  $\ln J(t)$  are chosen so that  $\ln J(t)$  is an odd function; and  $\sqrt{E(t)}$  means  $\sqrt{E(t)}$  along the dotted positive cuts  $C_1$  shown in Fig. 1. The integration on the right hand side of (3.44) equals one-half of the integral around the closed contour surrounding the three branch cuts,  $C_2$ . By the Cauchy theorem we can

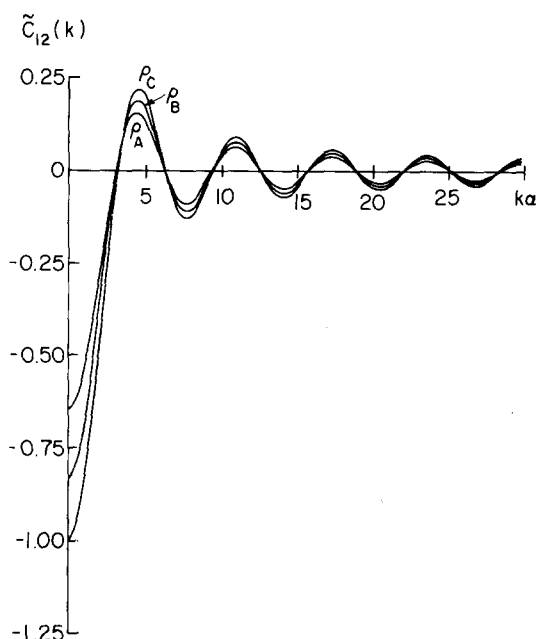


FIG. 5. One-dimensional Fourier transform of  $C_{12}(r) - 1$  for the Widom-Rowlinson model.  $\rho_A = 1.086$ ,  $\rho_B = 0.605$ , and  $\rho_C = 0.101$ .

change the integration path into  $C'_1 + C'_2 + C'_3$  where  $C'_1$  is a contour around the logarithmic branch of  $J(t)$  on the real axis and  $C'_3$  is a contour around the single pole in the integrand at  $t = s$ . Thus

$$\begin{aligned} I(s) &= \frac{1}{2} (2\pi i)^{-1} \sqrt{E(s)} \int_{C_2} dt \ln J(t) / [\sqrt{E(t)} (t - s)] \\ &= \frac{1}{2} (2\pi i)^{-1} \sqrt{E(s)} \int_{C'_1 + C'_2 + C'_3} dt \ln J(t) / [\sqrt{E(t)} (t - s)] \\ &= \frac{1}{2} \sqrt{E(s)} \left\{ \int_{-z_1}^{-\infty} dt / [\sqrt{E(t)} (t - s)] + \int_{z_1}^{\infty} dt / [\sqrt{E(t)} (t - s)] \right. \\ &\quad \left. - \ln J(s) / \sqrt{E(s)} \right\}. \end{aligned} \quad (3.46)$$

The function  $\ln J(s) / \sqrt{E(s)}$  has discontinuities  $2\pi i / \sqrt{E(s)}$  across the cuts  $(z_1, \infty)$  and  $(-\infty, -z_1)$ . These are cancelled by the discontinuities in the integral which can be found from the Plemelj formulas given by Muskhelishvili.<sup>17</sup> The sign of  $f(s)$  in (3.42) can be shown to be negative either from the behavior of the functional relationship near  $s = 0$  or from the behavior of  $G_{12}(s)$  as  $s \rightarrow \infty$ . Using (3.46)  $I(s)$  has the form,

$$I(s) = iI_1(s) + \frac{1}{2} \ln J(s), \quad (3.47)$$

so that on the imaginary axis,  $s = ik$ ,

$$\Phi(ik) = -\sigma_{12} (k^2 + z_1^2)^{1/2} [k^6 + 4\sigma_{12}^2 (k^2 + z_1^2)]^{-1/2} \sin I_1(ik), \quad (3.48)$$

$$\Psi(ik) = -\sigma_{12} (k^2 + z_1^2)^{1/2} \cos I_1(ik), \quad (3.49)$$

where we have written  $\sigma_{12}$  for  $\sigma_{12}(\alpha)$  and

$$\begin{aligned} I_1(ik) &= [k^6 + 4\sigma_{12}^2 (k^2 + z_1^2)]^{1/2} \\ &\quad \times \int_{z_1}^{\infty} dt t [t^6 + 4\sigma_{12}^2 (t^2 - z_1^2)]^{-1/2} (t^2 + k^2)^{-1}. \end{aligned} \quad (3.50)$$

To obtain an expression for  $\sigma_{12}$  and the other parameters entering the solution, we note that

$$\Phi(ik) = [F_{12}^*(s) / 2s]_{s=ik} = -\int_0^\alpha dr \sigma_{12}(r) \sin kr / k$$

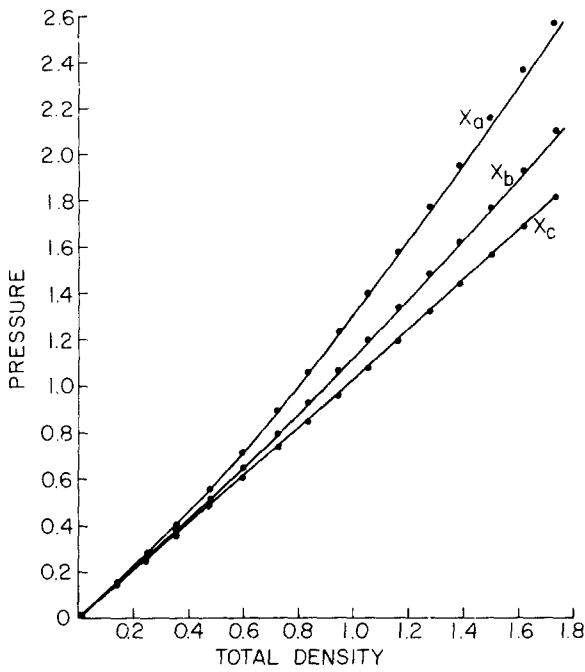


FIG. 6. Three-dimensional pressures vs the total density at fixed compositions for Widom-Rowlinson model. Points correspond to the compressibility pressures and lines to the virial pressures. They are drawn for three values of composition ratios,  $x_i = \rho_i/\rho$ , that is,  $x_a = 0.5$ ,  $x_b = 0.2$ , and  $x_c = 0.05$ .

$$\begin{aligned}
 &= \frac{1}{2}(\rho_1 \rho_2)^{1/2} [4\pi \int_0^\infty dr C_{12}(r) \sin kr/k] \\
 &= \frac{1}{2}(\rho_1 \rho_2)^{1/2} \tilde{C}_{12}(k), \tag{3.51}
 \end{aligned}$$

where  $\tilde{C}_{12}(k)$  is the Fourier transform of  $C_{12}(r)$ , and  $\tilde{C}_{12}(0) = \int C_{12}(\vec{r}) d\vec{r}$ . (3.52)

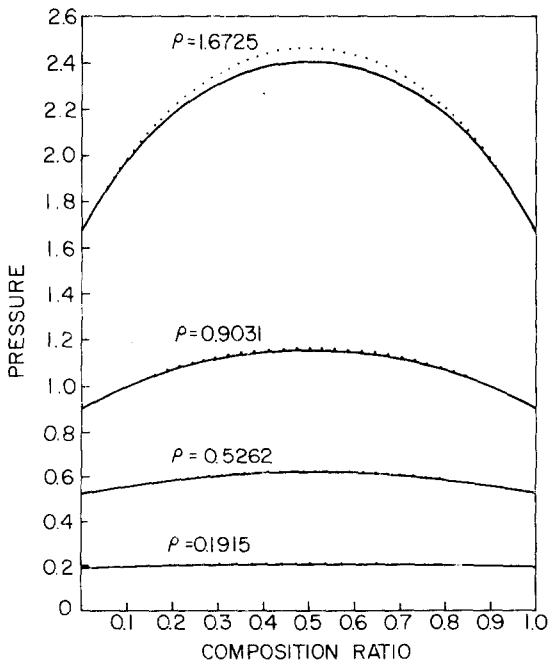


FIG. 7. Three-dimensional pressures vs composition at fixed densities for Widom-Rowlinson model. The compressibility and virial pressures are shown with points and lines, respectively, for four densities where  $2\pi\alpha^3$  is set equal to unity.

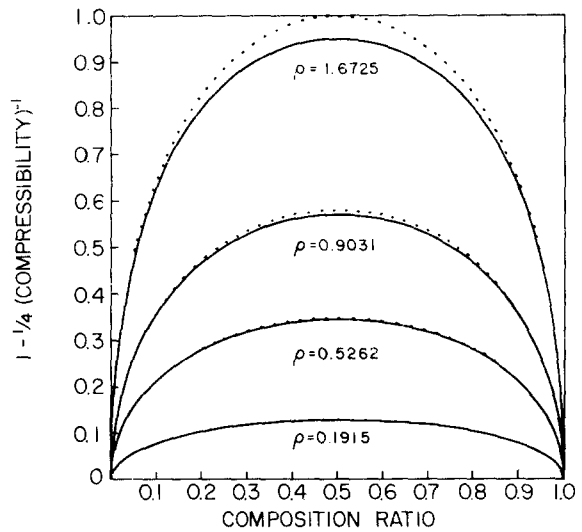


FIG. 8.  $[1 - 0.25\chi^{-1}]$  vs composition at fixed densities in three dimensional Widom-Rowlinson model. The susceptibility,  $\chi$ , diverges at the density,  $\rho \approx 1.673$  for the compressibility relation and at  $\rho \approx 1.78$  for the virial expression.

Also from (3.48), (3.43), and (3.50), respectively,

$$\Phi(0) \equiv \Phi_0 = -\frac{1}{2} \sin[I_1(0)], \tag{3.53}$$

$$\alpha = \int_{z_1}^\infty dt t/\sqrt{E(t)}, \tag{3.54}$$

$$I_1(0) = 2\mu \int_{z_1}^\infty dt t/[\sqrt{E(t)} t^2]. \tag{3.55}$$

By changing the variable  $t$  to  $z$  inside the integral,

$$t^2 = z[\eta(1 - 4\Phi_0^2)^{1/2}]^{2/3}/\alpha^2, \tag{3.56}$$

we get for (3.55) and (3.54),

$$I_1(0) = (\alpha^3 I_1/2\eta)(1 - 4\Phi_0^2)^{-1/2} \tag{3.57}$$

and

$$\alpha = (\alpha/2)[\eta(1 - 4\Phi_0^2)^{1/2}]^{-1/3} I_2, \tag{3.58}$$

where

$$I_1 \equiv \int_{z_0}^\infty (dz/z)(z^3 + 4z/z_0 - 4)^{-1/2}, \tag{3.59}$$

$$I_2 \equiv \int_{z_0}^\infty \frac{dz}{(z^3 + 4z/z_0 - 4)^{1/2}}, \tag{3.60}$$

$$\Phi_0 = -\frac{1}{2} \sin I_1, \tag{3.61}$$

and

$$\eta = (I_2/2)^3 / \cos I_1. \tag{3.62}$$

The contact value is obtained in terms of the parameter  $z_0$ ,

$$|C_{12}(\alpha)| = g_{12}(\alpha) = (2\cos I_1)/(\sqrt{z_0} I_2). \tag{3.63}$$

### C. Equation of state

The virial pressure is given by

$$\begin{aligned}
 P^v &= \rho + \left(\frac{4}{3}\right)\pi\alpha^3 \rho_1 \rho_2 g_{12}(\alpha) \\
 &= \rho + \left(\frac{4}{3}\right)\pi\alpha^3 \rho_1 \rho_2 2(\cos I_1)/(\sqrt{z_0} I_2), \tag{3.64}
 \end{aligned}$$

while the compressibility relation assumes the form



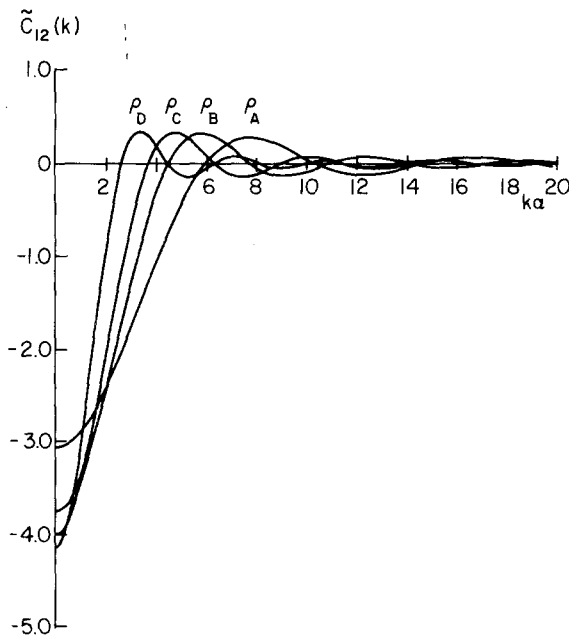


FIG. 9. Three-dimensional Fourier transform of the direct correlation function between distinct species for the Widom-Rowlinson model.  $\rho_A=1.6725$ ,  $\rho_B=0.9031$ ,  $\rho_C=0.5262$ , and  $\rho_D=0.1915$  where  $2\pi\alpha^3$  is set equal to unity.

$$\begin{aligned} \partial P^c / \partial \rho_1 &= 1 - \rho_2 \int C_{12}(r) dr \\ &= 1 - 2(\rho_2/\rho_1)^{1/2} \Phi_0. \end{aligned} \quad (3.65)$$

These pressures are drawn in Figs. 6 and 7 as functions of total density and composition, respectively. We note that both  $P^v - \rho$  and  $P^c - \rho$  are in the PY approximation functions of  $\eta = 2\pi\alpha^3 \sqrt{\rho_1 \rho_2}$  alone.

The low-density expansion for the pressure is obtained by expanding  $I_1$  and  $I_2$  in the parameter  $z_0^{-1/2}$ , then eliminating  $z_0$  in favor of  $\eta$  using (3.62). Let us first expand  $I_1$  and  $I_2$ ,

$$I_1 = \sum_{n=0}^{\infty} 2(-1)^n \frac{4^n \{1 \times 3 \times 5 \cdots (2n-1)\} (z_0^{-3/2})^{2n-1}}{(4n+3)(4n+5) \cdots \{4n+(2n+3)\}}, \quad (3.66)$$

$$I_2 = \sum_{n=0}^{\infty} 2(-1)^n \frac{4^n \{1 \times 3 \times 5 \cdots (2n-1)\} (z_0^{-3/2})^{2n+1}}{(4n+3)(4n+5) \cdots \{4n(2n+3)\}}. \quad (3.67)$$

These expansions will converge for  $z_0^3 > \frac{16}{27}$ . Then using (3.59)–(3.63) the coefficients are found for the density expansion of  $\tilde{C}_{12}(k)$  at  $k=0$  and  $|C_{12}(\alpha)|$ ,

$$\sqrt{\rho_1 \rho_2} \tilde{C}_{12}(0) = \left(\frac{2}{3}\right) \eta (1 - D_1 \eta^2 + D_2 \eta^4 - D_3 \eta^6 + \cdots), \quad (3.68)$$

$$|C_{12}(\alpha)| = 1 - C_1 \eta^2 + C_2 \eta^4 - \cdots. \quad (3.69)$$

This yields the following virial expansions for the pressure:

$$\begin{aligned} P^v &= \rho_1 + \rho_2 + \eta^2 \{1 - 0.24285\eta^2 + 0.08714\eta^4 - 0.03908\eta^6 \\ &\quad + 0.01969\eta^8 - 0.01145\eta^{10} + 0.00785\eta^{12} - \cdots\}, \end{aligned} \quad (3.70)$$

$$\begin{aligned} P^c &= \rho_1 + \rho_2 + \eta^2 \{1 - 0.16190\eta^2 + 0.04665\eta^4 - 0.01721\eta^6 \\ &\quad + 0.00732\eta^8 - 0.00386\eta^{10} + 0.00216\eta^{12} - \cdots\}, \end{aligned} \quad (3.71)$$

where the first six coefficients in the expansion of  $P^c$  agree exactly with those obtained by Melnyk, Rowlinson, and Sawford<sup>18</sup> for the PY equation.

The fact that the direct correlation function  $C_{12}$  in the PY approximation is a function only of  $\eta$  (and not  $\rho_1$  and  $\rho_2$  separately) is a consequence of the fact that only certain types<sup>19</sup> of Mayer diagrams are summed in this approximation and that the Mayer functions for this system are

$$\begin{aligned} f_{ii}(r) &= 0, \quad i=1, 2, \quad f_{12}(r) \\ &= f_{21}(r) = \begin{cases} -1, & r < \alpha \\ 0, & r > \alpha. \end{cases} \end{aligned} \quad (3.72)$$

#### D. Phase transition at high densities

As mentioned in the Introduction we know from a rigorous analysis of the Widom-Rowlinson model that it exhibits a phase transition in two or higher dimensions corresponding to a separation into two phases one rich in species one and one rich in species two. Melnyk, Rowlinson, and Sawford<sup>18</sup> have investigated this phase transition in the Percus-Yevick approximation by means of a Padé analysis based on the first seven terms (with first five exact coefficients in the virial expansion [corresponding to the compressibility pressure (3.71)]). They found such a transition with a critical density,  $\rho_c = \frac{2}{3}\eta_c$ ,  $\eta_c = 1.674 \pm 0.003$ . They also concluded that the critical indices of this transition are, in the PY approximation, classical. Our exact solution confirms their results.

The critical total density  $\rho_c$  is determined here as the density at which the susceptibility  $\chi(\rho)$  diverges, where

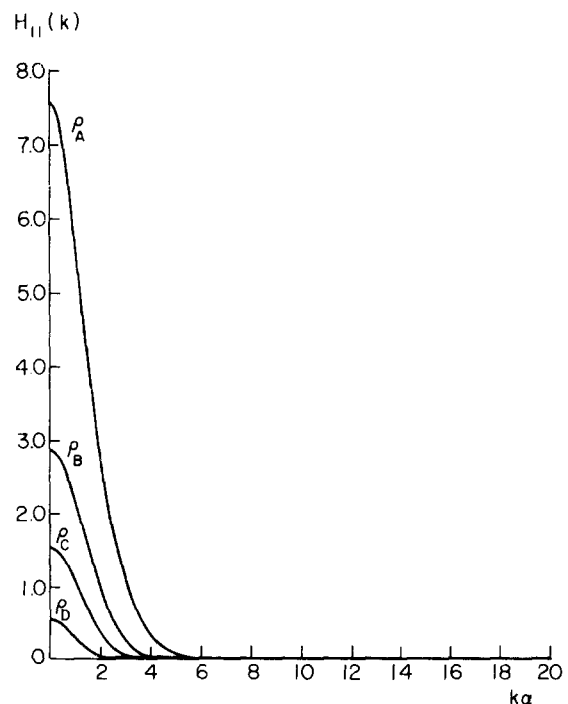


FIG. 10. Three-dimensional Fourier transform of  $g_{11}(r) - 1$  for the Widom-Rowlinson model  $\rho_A=1.6725$ ,  $\rho_B=0.9031$ ,  $\rho_C=0.5262$ , and  $\rho_D=0.1915$  where  $2\pi\alpha^3$  is set equal to unity.

$$\chi^{-1}(\rho, x) = \partial^2 f(\rho, x) / \partial x^2. \tag{3.73}$$

Here  $\rho = \rho_1 + \rho_2$ ,  $x = \rho_1 / \rho$  is the fraction of species 1 and  $f(\rho, x)$  is the Helmholtz free energy per unit volume (where  $\beta = 1$ ). As we have noted earlier in the PY approximation the pressure, and thus also the free energy, is the sum of ideal mixture term and a term which depends only on  $\eta = 2\pi\alpha^3 \rho \sqrt{x(1-x)}$ ,

$$f = \sum_{i=1,2} x_i \ln x_i + \ln \rho + [\eta / (\pi \rho \alpha^3)] \times \int_0^\eta [P^\Delta(\eta') / \eta'^2] d\eta', \quad \eta' = 2\pi\alpha^3 \sqrt{\rho_1 \rho_2}, \tag{3.74}$$

where  $P^\Delta = P - \rho$ . We find, by numerical computation, the critical densities corresponding to the compressibility and virial pressures to be (Fig. 8)

$$\eta_c \approx 1.6736, \quad \eta_c \approx 1.7876, \tag{3.75}$$

respectively. The critical indices are classical.

We note here also that the set of equations (3.59)–(3.63), which determines the solution of the Percus–Yevick equation, have no solution for  $\eta \geq \eta_{\max} \sim 3, 0$ , i. e., beyond a certain maximum density. This is similar to the results found by Waisman<sup>20</sup> for the solution of the mean spherical model equations for a binary system of hard spheres with equal diameters and a Yukawa-type repulsion between unequal species.

**E.  $\sigma_{ij}$  and their Fourier transforms**

Equations (3.48) and (3.51) provide the Fourier transforms of the direct correlation function and radial distribution functions,

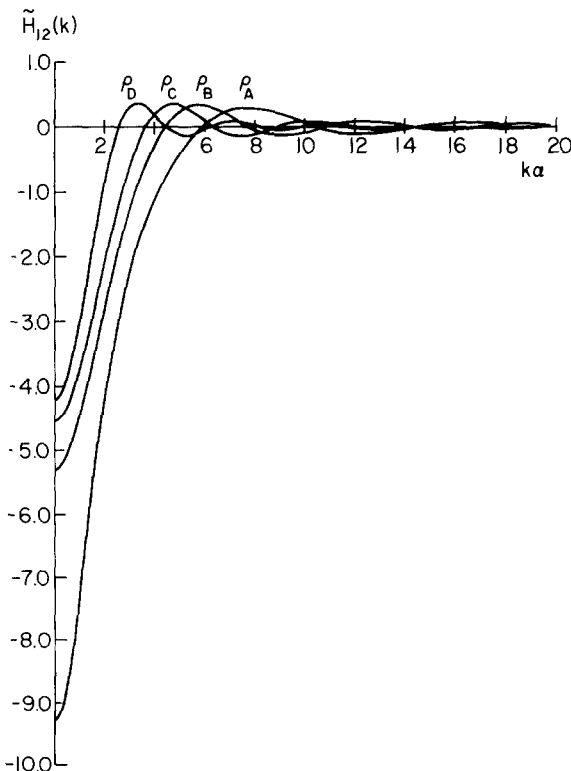


FIG. 11. Three-dimensional Fourier transform of  $g_{12}(r) - 1$  for the Widom–Rowlinson model  $\rho_A = 1.6725$ ,  $\rho_B = 0.9031$ ,  $\rho_C = 0.5262$ , and  $\rho_D = 0.1915$  where  $2\pi\alpha^3$  is set equal to unity.

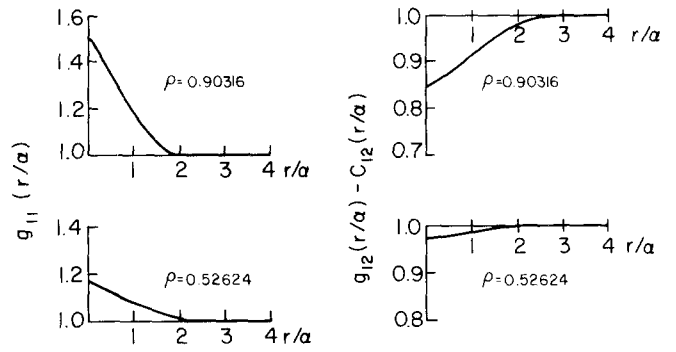


FIG. 12. Three-dimensional radial distribution and direct correlation functions in the Widom–Rowlinson model.

$$\begin{aligned} \tilde{C}_{12}(k) &= 2(\rho_1 \rho_2)^{-1/2} \Phi(ik) \\ &= 2(\rho_1 \rho_2)^{-1/2} \sigma_{12}(\alpha) [k^2 + z_1^2]^{1/2} \times (-1) \\ &\quad \times [k^6 + 4\sigma_{12}^2(k^2 + z_1^2)]^{-1/2} \sin I_1(ik) \\ &= -2(\rho_1 \rho_2)^{-1/2} (1 + Y)^{1/2} (z_0^3 Y^3 + 4Y + 4)^{-1/2} \sin \\ &\quad \times \left\{ \frac{1}{2} (z_0^3 Y^3 + 4Y + 4)^{1/2} \int_1^\infty dz / [4z(z_0^3 z^3 + 4z - 4)^{1/2}] \right\}, \end{aligned} \tag{3.76}$$

where

$$Y = 4k^2 / I_2^2. \tag{3.77}$$

The Fourier transforms of the correlation functions  $g_{ij}(r) - 1$ ,  $\tilde{H}_{ij}(k)$ , follow directly from  $\tilde{C}_{12}(k)$  via the original defining equation (1.7),

$$\tilde{H}_{11}(k) = (\rho_1 \rho_2)^{1/2} \tilde{C}_{12}^2(k) [1 - \rho_1 \rho_2 \tilde{C}_{12}^2(k)]^{-1}, \tag{3.78}$$

$$\tilde{H}_{12}(k) = \tilde{C}_{12}(k) [1 - \rho_1 \rho_2 \tilde{C}_{12}^2(k)]^{-1}. \tag{3.79}$$

The  $g_{ij}(r)$ ,  $C_{ij}(r)$ , and their Fourier transforms are found with the help of machine computation and are shown in Figs. 9–12.

It is seen from the graphs that the PY  $g_{ii}(r)$  is larger than 1 and  $g_{12}(r)$  is less than 1 for “almost all” values of  $r$ . The exact radial distribution functions satisfy<sup>9</sup> the inequalities  $g_{ii}(r) \geq 1$  and  $g_{12}(r) \leq 1$  for all  $r$ .

**IV. CONCLUSION**

Using the methods employed in this paper, it is also possible to obtain an exact solution of the Percus–Yevick equation for the more general binary mixture system<sup>16</sup> in which  $R_{11} = R_{22} = R > 0$ ,  $R_{12} = R + \alpha$ ,  $\alpha > 0$ . The solution for this system in one dimension yields the “same form” for the thermodynamics as those obtained here for the Widom–Rowlinson model and by Lebowitz and Zomick<sup>6</sup> for the system  $R_{11} < R_{22}$ ,  $0 < \alpha \leq \frac{1}{2}(R_{22} - R_{11})$ . In three dimensions it has not yet been possible to obtain a complete solution because of the complexity of the equation relating the various coefficients.

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