ABSTRACT

SOLUTION OF THE PERCUS-YEVICK EQUATION

Saeyoung Ahn

We investigate the properties of binary mixtures of hard sphere fluids with non-additive 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). We also find the complete solution in one dimension and a partial solution in three dimensions for the case when $R_{11} = R_{22} \equiv R > 0$ and $0 < \alpha < R$.

The solution of the P.Y. equation for the Widom-Rowlinson model exhibits a 'classical' 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 solutions of the P.Y. equations are much more complicated than in the additive diameter case, $\alpha = 0$. Graphs of the thermodynamic quantities, direct correlation functions, and radial distribution functions are given for the Widom-Rowlinson model.

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by

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Submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy
in the Belfer Graduate School of Science
Yeshiva University
New York

September 1973

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ACKNOWLEDGEMENTS

I am grateful to my thesis advisor, Professor Joel L. Lebowitz, for my thesis in all aspects. I am also very much indebted to him for his clear suggestions, fruitful criticisms and many bright ideas during the whole range of my thesis. I also thank him for his patient readings and useful corrections of my thesis.

I want to thank Professor Oliver Penrose for his reading the part of the solution to the functional equation and for his useful criticism.

I also wish to thank the United States Air Force for their support under Grant #73-2430, during my research for this thesis, and Mrs. Anne Cooper for the beautiful typewriting.

I want to thank all the people who helped me in my graduate and undergraduate study, many teachers at Belfer Graduate School of Science of Yeshiva University and those at Seoul National University, especially Professor Chul Soo Kim.

I want to thank my parents and my wife, Kunsook, whose understanding and encouragement have been crucial throughout all my studies and dedicate my thesis to them.

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ABSTRACT

We investigate the properties of binary mixtures of hard sphere fluids with non-additive 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). We also find the complete solution in one dimension and a partial solution in three dimensions for the case when $R_{11} = R_{22} \equiv R > 0$ and $0 < \alpha < R$.

The solution of the P.Y. equation for the Widom-Rowlinson model exhibits a 'classical' 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.

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CHAPTER 1. INTRODUCTION

The thermodynamic properties of liquids and liquid mixtures in equilibrium can be obtained from a knowledge of their distribution functions as they are ordinarily defined in statistical mechanics[1]. These functions also give information about the microscopic structure of these systems. Unfortunately however it is generally even more difficult to obtain exact expressions for the radial distribution functions than it is to obtain the exact thermodynamic functions. The only methods we have for computing these functions exactly are the cluster expansions (in powers of the fugacity or density) and these are only useful at very low densities (rare gases).

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. These equations are usually non-linear and their solution therefore generally requires the use of a computer which reduces their usefulness[2] although they yield many results for comparison with molecular dynamics or Monte-Carlo calculations. One of the more successful of these integral equations, the Percus-Yevick (P.Y.) equation[3], has a relatively simple closed form solution for a system of hard spheres[4]. The solution for a single component hard sphere fluid with interparticle potential

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

was obtained by Wertheim[5] and Thiele[6]. Lebowitz[7] generalized Wertheim's method to get the solution of the P.Y. equation for mixtures of hard spheres with potential between particle of species i and j,

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

when the diameters are additive

$$R_{ij} = \tfrac{1}{2}\,(R_{ii} + R_{jj}) \tag{1.3}$$

These solutions have been used[8] 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.

Following this the P.Y. equation for mixtures of hard spheres with potential (1.2) but without the assumption of additive diameters was considered by Lebowitz and Zomick[9]. They considered in particular the case

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

where α satisfies the following inequalities

$$0 \leq \alpha \leq \tfrac{1}{2}(R_{22}-R_{11}),\ R_{22} \geq R_{11} \tag{1.5}$$

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

Recently Widom and Rowlinson[10] 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 α between particles of different species. This model, and some generalization of it, were proven[11] 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 (via Pade approximations) and from some machine computations on related systems. This system has the interparticle potential (1.2) with the distance of closest approach between species i and j,

$$R_{ij} = \begin{cases} \alpha, & (i \neq j) \\ 0, & (i = j), \end{cases} \tag{1.6}$$

In Chapter 3 of this paper we deal with this system in detail and find the exact solutions in one and three dimensions.[12] In one dimension, the solution is unique up to a certain density and becomes non-unique after that. The physical solution can, however, be found from the continuity of the pressure and is just the continuation of low density solution. The free energy obtained from this solution of the P.Y. equation remains stable for all values of the density . We compare the values of pressures with the exact result. For values of density less than 1, 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, a solution is obtained explicitly, by making use of the technique devised by Penrose and Lebowitz[13], in a parametric form. This solution gives a maximum density, that is, the integral equation does not yield a solution at a density higher than this one. Below this, we find a density at which the susceptibility diverges with 'classical' critical indices. The low density expansions are given for the pressures both as obtained from the compressibility relation and from the virial theorem. The radial distribution functions, correlation functions and their Fourier transforms are drawn in the graphs at the end. These results are compared with some rigorous inequalities[14] on the correlation functions of this system.

In Chapter 4 we consider the P.Y. equation for another case of hard sphere mixtures with potential (1.2) and R_{12} in (1.4),

but with different inequalities for R_{ii} and α, namely

$$R_{11} = R_{22} = R, \quad R \geq \alpha \geq 0 \tag{1.7}$$

In one dimension we get an exact solution, while in three dimensions we fail to obtain an explicit solution due to the great complexity of the remaining algebraic equations.[1] Solutions of this system reduces to two limiting cases, that is, to the case of one-component system as $\alpha \to 0$, and to the case of Widom-Rowlinson model as $R \to 0$. The latter case is obviously not to be derived from (1.7), and this suggests that there might be a general way of getting the solution for P.Y. equations of mixtures of hard spheres with potential (1.2) and the distance of closest approach (1.4) defined with the equality

$$R_{11} = R_{22} = R \tag{1.8}$$

regardless of the value of α(positive) and R.

CHAPTER 2. FORMULATION OF PROBLEMS

In this section we derive the P.Y. equation for a general binary mixture of hard spheres, in one and three dimensions, and discuss the general approach to its solution.

The earlier work done by Ornstein and Zernike[15] contributes to the definition of the direct correlation functions between particles of species i and j, $C_{ij}(r)$. These are defined in terms of the radial distribution functions, $g_{ij}(r)$. In a uniform binary mixture with densities ρ_1 and ρ_2,

$$g_{ij}(r) - 1 = C_{ij}(r) + \sum_{\ell=1}^{2} \rho_\ell \int [g_{i\ell}(|\bar{r}'|) - 1]\, C_{\ell j}(|\bar{r}-\bar{r}'|)\, d\bar{r}' \qquad (2.1)$$

where ρ_ℓ is the density of species ℓ, assumed spatially uniform.

The symmetry $g_{ij}(r) = g_{ji}(r)$ also gives

$$C_{ij}(r) = C_{ji}(r) \qquad (2.2)$$

The P.Y. approximation[16] is written in the form

$$g_{ij}(r)\, [e^{-v_{ij}(r)} - 1] = C_{ij}(r)\, e^{-v_{ij}(r)} \qquad (2.3)$$

and we see that with the potential $v_{ij}(r)$ defined in (1.2) the right hand side of (2.3) vanishes for $r < R_{ij}$ and the left hand side does for $r > R_{ij}$,

$$g_{ij}(r) = 0 \qquad \text{for } r < R_{ij}$$

$$C_{ij}(r) = 0 \qquad \text{for } r > R_{ij} \tag{2.4}$$

The 'contact values' $g_{ij}(R_{ij})$ are to be understood in the sense of limit,

$$g_{ij}(R_{ij}) = \lim_{r \to R_{ij}^{+}} g_{ij}(r)$$

$$= \lim_{r \to R_{ij}^{-}} C_{ij}(r) \tag{2.5}$$

(One dimension)

We consider the one-dimensional case first since it is simpler yet similar[17] 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 $\sigma_{ij}(r)$,

$$\sigma_{ij}(r) = \begin{cases} -(\rho_i \rho_j)^{\frac{1}{2}} C_{ij}(r) & r \leq R_{ij} \\ (\rho_i \rho_j)^{\frac{1}{2}} g_{ij}(r) & r \geq R_{ij} \end{cases} \tag{2.6}$$

Combining (2.6) with (2.1) and (2.4) yields,

$$\sigma_{ij}(r) = A_{ij} - \sum_{\ell=1}^{2} \int dy\, \sigma_{i\ell}(y)\, \sigma_{\ell j}(r-y) \qquad |y| \geq R_{i\ell},\ |r-y| < R_{\ell j} \tag{2.7}$$

where

$$\begin{aligned} A_{ij} &= (\rho_i \rho_j)^{\frac{1}{2}} \left[1 - \sum_{\ell=1}^{2} \rho_\ell \int C_{\ell j}(r)\, dr\right] \\ &= (\rho_i/\rho_j)^{\frac{1}{2}} A_{jj} \end{aligned} \tag{2.8}$$

for $r \geq 0$. We look for the solutions of eq. (2.7) such that

$$\int |g_{ij}(r) - 1|\, dr < \infty \tag{2.9}$$

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 (2.7) explicitly yields

$$\begin{aligned} \sigma_{ij}(r) = A_{ij} - \sum_{\ell} \Bigg\{ &\int_{\min[-R_{i\ell}, r-R_{\ell j}]}^{-R_{i\ell}} \sigma_{i\ell}(y)\, \sigma_{\ell j}(r-y)\, dy \\ &+ \int_{\max[R_{i\ell}, r-R_{\ell j}]}^{\max[R_{i\ell}, r+R_{\ell j}]} \sigma_{i\ell}(y)\, \sigma_{\ell j}(r-y)\, dy \Bigg\} \end{aligned} \tag{2.10}$$

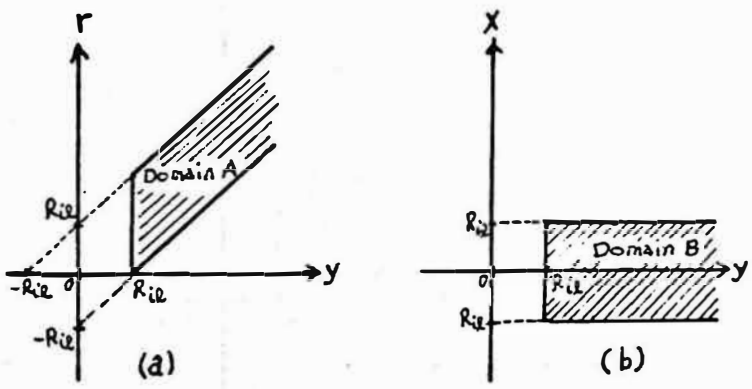
Since the right side of (2.10) is of a convolution type, we look for a solution in terms of the Laplace transforms.

Using (2.10) the Laplace transform of $\sigma_{ii}(r)$, which we shall denote by $\sigma_{ii}(s)$, can be written in the form

$$\sigma_{ii}(s) = \int_0^\infty e^{-sr} \sigma_{ii}(r)\, dr \tag{2.11}$$

$$= \frac{A_{ii}}{s} - \sum_{\ell=1}^{2} \int_0^\infty e^{-sr}\, dr \int_{\mathrm{Max}\,[R_{i\ell}, r-R_{i\ell}]}^{r+R_{i\ell}} \sigma_{i\ell}(y)\, \sigma_{\ell j}(r-y)\, dy$$

$$= \frac{A_{ii}}{s} - \sum_{\ell=1}^{2} \int_{-R_{i\ell}}^{R_{i\ell}} e^{-sx} \sigma_{\ell j}(s)\, dx \int_{R_{i\ell}}^{\infty} e^{-sy} \sigma_{i\ell}(y)\, dy$$



The domain A for the integration of the second equality in (2.4) is shown in (a), and changes to domain B in (b) after the variable r is switched to x where $x \equiv r-y$.

Fig. 1

Eq. (2.11) can be written as

$$\sigma_{ii}(s) = \frac{A_{ii}}{s} - \sum_{\ell=1}^{2} G_{i\ell}(s)\, \{F_{\ell i}(s) + F_{\ell i}(-s)\} \tag{2.12}$$

$$= F_{ii}(s) + G_{ii}(s)$$

where

$$F_{\ell j}(s) \equiv \int_0^{R_{\ell j}} e^{-sr}\, \sigma_{\ell j}(r)\, dr\ , \tag{2.13a}$$

and

$$G_{i\ell}(s) \equiv \int_{R_{i\ell}}^{\infty} e^{-sr}\, \sigma_{i\ell}(r)\, dr\ . \tag{2.13b}$$

The Laplace transform of $\sigma_{ij}(r)$, $i \neq j$, generates additional terms other than $G_{ij}(s)$ and $F_{ij}(s)$, as can be seen from the domain of double integration shown in Fig. 2. A similar discussion to (2.11) gives

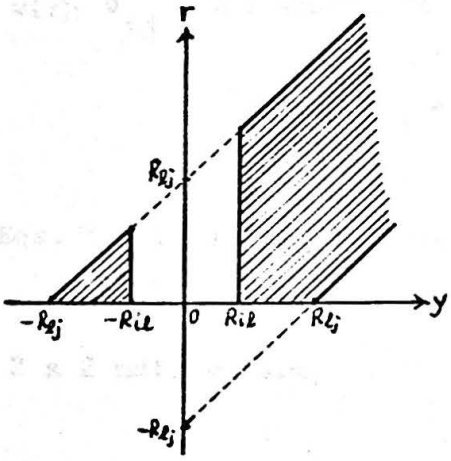


Fig. 2

$$\sigma_{ij}(s) = \frac{A_{ij}}{s} - \sum_{\ell=1}^{2} G_{i\ell}(s)\{F_{\ell j}(s)+F_{\ell j}(-s)\}$$

$$-\{U_{ij}(s)-U_{ij}(-s)\} \tag{2.14}$$

assuming $R_{11} \leq R_{22}$ without losing any generality,

where $U_{ij}(s)$ has one of three possible expressions according to values of R_{ij}'s,

$$U_{ij}(s) = \begin{cases} (1-\delta_{ij}) \int_0^{R_{ij}-R_{ii}} e^{-sr}\, dr \int_{r-R_{ij}}^{R_{ii}} \sigma_{ii}(y)\, \sigma_{ij}(r-y)\, dy, \\ \qquad \text{for } R_{11} \leq R_{22} \leq R_{12} & (2.15a) \\ (1-\delta_{ij}) \int_0^{R_{jj}-R_{ij}} e^{-sr}\, dr \int_{r-R_{jj}}^{R_{ij}} \sigma_{ij}(y)\sigma_{jj}(r-y)dy, \\ \qquad \text{for } R_{12} \leq R_{11} \leq R_{22} & (2.15b) \\ \sum_{\ell=1}^{2} \delta_{i1}\, \delta_{j2} \int_0^{R_{\ell j}-R_{i\ell}} e^{-sr}\, dr \int_{r-R_{\ell j}}^{R_{i\ell}} \sigma_{i\ell}(y)\, \sigma_{\ell j}(r-y)\, dy, \\ \qquad \text{for } R_{11} \leq R_{12} \leq R_{22} & (2.15c) \end{cases}$$

with δ_{ij} the Kronecker's delta function,

$$\delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j. \end{cases} \tag{2.16}$$

Eqs. (2.12) and (2.14) with (2.13) and (2.15) provide the whole set of Laplace transforms for $\sigma_{ij}(r)$'s and can be rewritten in a 2 x 2 matrix form,

$$\underline{\underline{\sigma}}(s) = \frac{1}{s}\underline{\underline{A}} - \underline{\underline{G}}(s)\, \overset{+}{\underline{\underline{F}}}(s) - \underline{\underline{U}}^{*}(s) \tag{2.17a}$$

or

$$\underline{\underline{G}}(s) = \underline{\underline{H}}(s)\, \underline{\underline{K}}^{-1}(s) \tag{2.17b}$$

where we have defined

$$\underline{\underline{F}}^{+}(s) \equiv \underline{\underline{F}}(s) + \underline{\underline{F}}(-s) \tag{2.18a}$$

$$\underline{\underline{U}}^{*}(s) \equiv \underline{\underline{U}}(s) - \underline{\underline{U}}(-s) \tag{2.18b}$$

$$\underline{\underline{\sigma}}(s) = \underline{\underline{G}}(s) + \underline{\underline{F}}(s) \tag{2.18c}$$

$$\underline{\underline{H}}(s) = \underline{\underline{A}} - s\underline{\underline{F}}(s) - s\underline{\underline{U}}^{*}(s) \tag{2.18d}$$

$$\underline{\underline{K}}(s) = s \quad \underline{\underline{I}} + s \quad \underline{\underline{F}}^{+}(s) \tag{2.18e}$$

$$\underline{\underline{I}} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{2.18f}$$

To exploit the condition (2.9) we now define the matrices $\underline{\underline{L}}(s)$ and $\underline{\underline{B}}(s)$ by the relations,

$$\begin{aligned} \underline{\underline{L}}(s) &\equiv \underline{\underline{G}}(s)\ \underline{\underline{H}}^{T}(-s) \\ &= \underline{\underline{H}}(s)\ \underline{\underline{K}}^{-1}(s)\ \underline{\underline{H}}^{T}(-s) = -L^{T}(-s) \end{aligned} \tag{2.19a}$$

and

$$\underline{\underline{B}}(s) \equiv \underline{\underline{L}}(s) - \frac{1}{s}\ \underline{\underline{A}}' \tag{2.19b}$$

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

$$A'_{ij} \equiv \sum_{\ell=1}^{2} \sqrt{\rho_i \rho_\ell}\, A_{j\ell} = \sqrt{\rho_i \rho_j}\, a \tag{2.20a}$$

$$a \equiv (A_{11} + A_{22}) \tag{2.20b}$$

with A_{ij} defined in (2.8). The diagonal components of $\underline{\underline{B}}(s)$ are

$$B_{11}(s) = G_{11}(s)\,[A_{11} + s\,F_{11}(-s)] + G_{12}(s)\,[A_{12} + sF_{12}(-s) - s\,U^*_{12}(s)] - \frac{A'_{11}}{s}, \tag{2.21a}$$

$$B_{22}(s) = G_{21}(s)\,[A_{22} + s\,F_{22}(-s)] + G_{21}(s)\,[A_{21} + sF_{21}(-s) - s\,U^*_{21}(s)] - \frac{A'_{22}}{s}. \tag{2.21b}$$

The limit of $B_{11}(s)$,

$$\begin{aligned} \lim_{s \to 0} B_{ii}(s) &= \lim_{s \to 0} \left\{ \sum_{\ell} G_{i\ell}(s)\, A_{i\ell} - \frac{A'_{ii}}{s} \right\} \\ &= \sum_{\ell} \lim_{s \to 0} \left\{ G_{i\ell}(s) - \frac{\sqrt{\rho_i \rho_\ell}}{s} \right\} A_{i\ell}, \end{aligned} \tag{2.22}$$

is finite due to (2.9). When $R_{\ell s} \to \infty$, $G_{ij}(s) \to \frac{1}{s} e^{-sR_{ij}}$, $F_{ij} \to \frac{1}{s} e^{sR_{ij}}$ and $U^*_{ij}(s) \to \frac{1}{s} e^{s(R_{ij} - R_{ii})}$ for the system with $R_{11} \leq R_{22} \leq R_{12}$. Therefore we see that the $B_{ii}(s)$'s are bounded

and entire 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 $\underline{\underline{L}}(-s) = -\underline{\underline{L}}^T(s)$, and by the Liouville's theorem,[18] the $B_{ii}(s)$'s are constants. By looking at the value of $B_{ii}(s)$ as $s \to \infty$, we conclude that $B_{ii}(s)$'s vanish all over the complex plane, that is,

$$L_{ii}(s) - \frac{A'_{ii}}{s} = 0 \tag{2.23}$$

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

$$\begin{aligned}\sigma_{ii}(s) = \frac{1}{s} A_{ii} - \frac{1}{s^2} A'_{ii} + G_{ij}(s) \left[\frac{1}{s} A_{ij} - F_{ij}(s) - U^*_{ij}(s)\right] \\ + G_{ii}(s) \left[\frac{1}{s} A_{ii} - F_{ii}(s)\right], \; i \neq j\end{aligned} \tag{2.24}$$

Taking the inverse Laplace transform of (2.24) yields finally for $R_{11} \leq R_{22} \leq R_{12}$,

$$\sigma_{ii}(r) = A_{ii} - A'_{ii}\, r, \qquad r \leq R_{ii}, \tag{2.25}$$

since the last two terms of (2.24) die out for large value of $R\ell s$ as, or faster than, order of $e^{-sR_{ii}}$.

The off-diagonal components of $\underline{\underline{B}}(s)$ do not give any simple

relationship which gives rise to various complexities for different values of R_{ij}'s. Therefore finding the form of $\sigma_{12}(r)$ constitutes the main problem in Chapter 3 and 4. The solution in three dimensions follows very closely the one dimensional case.

(Three dimensions)

Similar steps are taken in the three-dimensional case as in the one-dimensional case. Defining

$$\sigma_{ij}(r) = \begin{cases} -2\pi\,(\rho_i\rho_j)^{\frac{1}{2}}\, r\;\; C_{ij}(r) & \text{for } r < R_{ij} \\ 2\pi\,(\rho_i\rho_j)^{\frac{1}{2}}\, r\;\; g_{ij}(r) & \text{for } r > R_{ij} \end{cases} \tag{2.26}$$

we have from (2.1) and (2.4)

$$\sigma_{ij}(r) = A_{ij}r - \sum_{\ell=1}^{2} \int_{\substack{|r'| > R_{i\ell},\ |\bar{r}-\bar{r}'| < R_{\ell j}}} \frac{r}{r'2\pi|\bar{r}-\bar{r}'|} \cdot \sigma_{i\ell}(|\bar{r}|)\, \sigma_{\ell j}(|\bar{r}-\bar{r}'|)\, d\bar{r}' \tag{2.27}$$

Switching the volume element $d\bar{r}'$ ($\equiv r'^2 dr \sin\theta d\theta d\varphi$) to $dr'\, dx\, d\theta$ with r', r, x and θ shown in Fig. 3 and using the volume

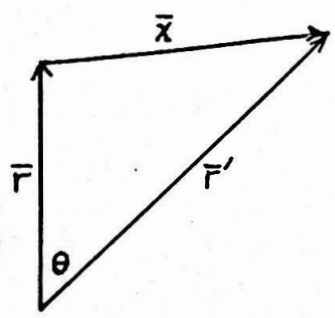


Fig. 3 $\vec{x} = \vec{r}' - \vec{r}$,
$|\bar{r}'| \equiv y$, $|\bar{r}| = r$ and $|\bar{x}| = x$

converting factor (Jacobian) of $-x/r\cdot r'$, in the integral, (2.27) becomes,

$$\sigma_{ij}(r) = r \cdot A_{ij} - \sum_{\ell=1}^{2} \int_{R_{i\ell}}^{\infty} \sigma_{i\ell}(y)\, dy \int_{\min[|\bar{r}-\bar{y}|,R_{\ell j}]}^{\min[r+y,R_{\ell j}]} \sigma_{\ell j}(x)\, dx \quad (2.28)$$

where

$$\frac{A_{ij}}{2\pi\sqrt{\rho_i \rho_j}} \equiv 1 - \Sigma\, \rho_\ell \int C_{\ell j}\,(|\bar{r}|)\, d\bar{r} \quad (2.29)$$

From the way of defining $\sigma_{ij}(r)$ in (2.26) we expect that the first derivative of $\sigma_{ij}(r)$ with respect to r, $\sigma_{ij}^{(1)}(r)$, will have some similarity to $\sigma_{ij}(r)$ defined in one dimension. $\sigma_{ij}^{(1)}(r)$ is obtained from (2.28) in the form

$$\sigma_{ij}^{(1)}(r) = A_{ij} - \sum_{\ell} \left\{ \int_{|r-z|\geq R_{i\ell},\, 0\geq z\geq -R_{\ell j}} \sigma_{i\ell}(r-z)\, \sigma_{\ell j}(z)dz - \right.$$

$$\left. \int_{|r-z|\geq R_{i\ell},\, 0\leq z\leq R_{\ell j}} \sigma_{i\ell}(r-z)\, \sigma_{\ell j}(z)dz \right\} - P_{ij}(r) \quad (2.30)$$

where

$$P_{ij}(r) \equiv \sum_{\ell} \int_{r+R_{i\ell}}^{\max[R_{\ell j}, r+R_{i\ell}]} \sigma_{i\ell}(r-z)\, \sigma_{\ell j}(z)\, dz \qquad (2.31)$$

The Laplace transform of (2.30) can be written in the form of 2 x 2 matrices

$$s^2\, \underline{\underline{\sigma}}(s) = \underline{\underline{A}} + s \cdot \underline{\underline{G}}(s)\, \underline{\underline{F}}^*(s) - s\, \underline{\underline{U}}^*(s) \qquad (2.32a)$$

or

$$\underline{\underline{G}}(s) = \underline{\underline{H}}(s) \cdot \underline{\underline{K}}^{-1}(s) \qquad (2.32b)$$

where we have defined

$$\underline{\underline{F}}^*(s) = \underline{\underline{F}}(s) - \underline{\underline{F}}(-s) \qquad (2.33a)$$

$$\underline{\underline{U}}^*(s) = \underline{\underline{U}}(s) - \underline{\underline{U}}(-s) \qquad (2.33b)$$

$$\underline{\underline{\sigma}}\,(s) = \underline{\underline{G}}(s) + \underline{\underline{F}}(s) \qquad (2.33c)$$

$$\underline{\underline{H}}\,(s) = \underline{\underline{A}} - s^2\, \underline{\underline{F}}(s) - s\underline{\underline{U}}^*(s) \qquad (2.33d)$$

$$\underline{\underline{K}}\,(s) = s^2\underline{\underline{I}} - s\underline{\underline{F}}^*(s) \qquad (2.33e)$$

$$\underline{\underline{I}} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} . \qquad (2.33f)$$

$$U_{ij}(s) = \int_0^{\infty} e^{-sr}\, P_{ij}(r)\, dr \qquad (2.33g)$$

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

$$\int r|g_{ij}(r) - 1|\, dr < \infty \tag{2.34}$$

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

$$\underline{\underline{L}}(s) \equiv \underline{\underline{G}}(s)\, \underline{\underline{H}}^T(-s) \tag{2.35a}$$

$$= \underline{\underline{H}}(s)\, \underline{\underline{K}}^{-1}(s)\, \underline{\underline{H}}^T(-s) = \underline{\underline{L}}^T(-s)$$

$$\underline{\underline{B}}(s) \equiv \underline{\underline{L}}(s) - \underline{\underline{A}}'/s^2 \tag{2.35b}$$

where

$$A'_{ij} \equiv \sum_{\ell=1}^{2} 2\pi\sqrt{\rho_i\rho_\ell}\, A_{i\ell} = 2\pi\sqrt{\rho_i\rho_j}\, a \tag{2.36a}$$

$$a \equiv A_{11} + A_{22} \tag{2.36b}$$

with A_{ij} defined in (2.29). The diagonal components of $\underline{\underline{B}}(s)$ are

$$B_{11}(s) = G_{11}(s)\,[A_{11} - s^2F_{11}(-s)] + G_{12}(s)[A_{12}-s^2F_{12}(-s) - sU^*_{12}(s)]$$

$$\frac{-A'_{11}}{s^2}\,, \tag{2.37a}$$

$$B_{22}(s) = G_{22}(s)\,[A_{22} - s^2F_{22}(-s)] + G_{21}(s)\,[A_{21}-s^2F_{21}(-s)-sU^*_{21}(s)]$$

$$\frac{-A'_{22}}{s^2}\,, \tag{2.37b}$$

and can be seen finite as $s \to 0$ due to (2.34), that is,

$$\lim_{s\to 0} B_{11}(s) = \lim_{s\to 0}\left\{\Sigma G_{i\ell}(s)\,A_{i\ell} - \frac{A'_{ii}}{s^2}\right\}$$

$$= \Sigma \lim_{s\to 0}\left\{G_{i\ell}(s) - \frac{2\pi\sqrt{\rho_i\rho_\ell}}{s}\right\}A_{i\ell} < \infty\,. \tag{2.38}$$

Also when $R_\ell s \to \infty$. $G_{ij}(s) \to \frac{1}{s}e^{-sR_{ij}}$, $F_{ij}(-s) \to \frac{1}{s}e^{sR_{ij}}$ and $U_{ij}(s) \to \frac{1}{s}e^{s(R_{ij}-R_{ii})}$ for the system with $R_{11} \leq R_{22} \leq R_{12}$, where the last bahavior for $U_{ij}(s)$ is obtained from (2.33g) and (2.31). Therefore the $B_{ii}(s)$'s are bounded and entire on all the rays in right hand side of the complex s-plane. Since $\underline{\underline{L}}(s) = \underline{\underline{L}}^T(-s)$, $\underline{\underline{B}}(s) = \underline{\underline{B}}(-s)$, so that we can set $B_{ii}(s)$ equal to a constant, $2B_i$, by using Liouville's theorem.[18] We then find that

$$L_{ii}(s) - \frac{A'_{ii}}{s^2} = 2B_i \text{ (constant)}. \tag{2.39}$$

Now we can write $\sigma_{ii}(s)$ explicitly :

$$s\,\sigma_{ii}(s) = \frac{A_{ii}}{s} + \frac{A'_{ii}}{s^4} + \frac{2B_{ii}}{s^2} + G_{ii}(s)\left[F_{ii}(s) - \frac{A_{ii}}{s^2}\right] + G_{ij}(s)\left[F_{ij}(s) - \frac{A_{ij}}{s^2} + \frac{1}{s}U^*_{ij}(s)\right] \tag{2.40}$$

This yields after taking the inverse Laplace transform

$$\sigma_{ii}(r) = A_{ii}\,r + B_{ii}\,r^2 + \frac{A'_{ii}}{24}\,r^4 \text{ for } r \leq R_{ii} \tag{2.41}$$

since the last two terms of (2.40)die out for large value of $R\ell s$ as, or faster than, the order of $e^{-sR_{ii}}$. To find $\sigma_{ij}(r), i\neq j$, needs different methods according to the system and gives rise to great complexities.

These direct correlation functions, $C_{ij}(r)$'s, allow us to get the thermodynamic properties of the system as will now be explained.

(Thermodynamics)

Given the solution of the P.Y. 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 P.Y. solution (e.g. in the P.Y. solution for the binary additive mixture of hard spheres solved by Lebowitz, the compressi-

bility pressure is slightly above and the virial pressure is slightly below the 'exact' one[19] in the low density region.)

Thus we may 'get' a thermodynamics from the virial theorem[20] 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

$$\beta P^v = \sum_i \rho_i + \sum_{i,j} \rho_i \rho_j c\, g_{ij}(R_{ij}) \tag{2.42}$$

where $\beta = 1/(kT)$ (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 functions is to use the 'compressibility relations'[7]

$$\rho_i \frac{\partial \mu_i^c(\rho_1,\rho_2)}{\partial \rho_j} = \delta_{ij} - \rho_i \int C_{ij}(r)\, d\bar{r} \tag{2.43a}$$

$$1 - \sum_i \rho_i \int C_{ij}(r)\, d\bar{r} = \sum_i \rho_i \frac{\partial \mu_i^c}{\partial \rho_j} = \frac{\partial P^c(\rho_1,\rho_2)}{\partial \rho_j} \tag{2.43b}$$

where μ_i^c and P^c are respectively the chemical potential of the ith species and the pressure, as obtained from the compressibility relations.

CHAPTER 3. SOLUTION OF P.Y. EQUATION FOR WIDOM-ROWLINSON MODEL

3-1. One dimensional solution

The P.Y. equation of this system with (1.5)

$$R_{ij} = \begin{cases} \alpha & \text{for } i \neq j \\ 0 & i = j, \end{cases}$$

yields $\sigma_{ii}(0)$ directly from (2.7) or (2.25) in the form

$$\sigma_{ii}(0) = A_{ii} \tag{3.1}$$

We also find $U_{ij}(s)$ and $L_{ii}(s)$ for this system from (2.15a) and (2.23)

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

$$L_{ii}(s) = \frac{A'_{ii}}{s}$$

Writing out (2.10) for this system yields

$$\sigma_{ii}(r) = A_{ii} - \int_{\max[\alpha, r-\alpha]}^{r+\alpha} \sigma_{12}(y)\, \sigma_{12}(r-y)\, dy \;, i = 1,2 \tag{3.2}$$

$$\sigma_{ij}(r) = A_{ij} - \int_{r-\alpha}^{r+\alpha} \sigma_{ii}(y)\, \sigma_{12}(r-y)\, dy \;, \; i \neq j \tag{3.3}$$

and

$$\begin{aligned} \sigma_{11}(r) - \sigma_{22}(r) &= A_{11} - A_{22} \\ &= \rho_1 - \rho_2 \end{aligned} \tag{3.4}$$

Eq. (3.4) gives

$$\sigma_{22}(s) - \sigma_{11}(s) = (\rho_2-\rho_1)/s$$
$$= G_{22}(s) - G_{11}(s) \quad . \tag{3.5}$$

Eq. (2.17a) also yields

$$U^*_{21}(s) - U^*_{12}(s) = \frac{A_{21}-A_{12}}{s} - \frac{\rho_2-\rho_1}{s} \cdot F^+_{12}(s) \tag{3.6}$$

where we are using the notation introduced in the last section; for any function f(s)

$$f^+(s) = f(s) + f(-s) \tag{3.7a}$$

$$f^*(s) = f(s) - f(-s) \tag{3.7b}$$

For the off-diagonal elements of $\underline{\underline{L}}(s)$ in (2.19a), we cannot find such a bounded and entire function as for the diagonal elements. $L_{12}(s)$ and $L_{21}(s)$ are explicitly

$$L_{21}(s) = G_{21}(s)\, A_{11} + G_{22}(s)[A_{12} + sF_{12}(-s) - sU^*_{12}(s)] \tag{3.8a}$$

$$L_{12}(s) = G_{12}(s)\, A_{22} + G_{11}(s)\, [A_{21} + sF_{21}(-s) - sU^*_{21}(s)] \tag{3.8b}$$

The difference between $L_{21}(s)$ and $L_{12}(s)$, however, yields using eqs. (3.5) and (3.6)

$$L_{21}(s) - L_{12}(s) = (\rho_2-\rho_1)\, F^+_{12}(s) \tag{3.9}$$

Now that the relations between the $L_{ij}(s)$'s and $F^{+}_{ij}(s)$'s have been obtained in (2.23) and (3.9) a relation for $F^{+}_{ij}(s)$'s and $H_{ij}(s)$'s is desired since they have the same behavior for large $R\ell s$. For this purpose, we derive from the definition of $\underline{\underline{L}}(s)$ in (2.19a)

$$\underline{\underline{H}}(-s)\ \underline{\underline{H}}(s) = \underline{\underline{L}}^{T}(s)\ \underline{\underline{K}}(s) \tag{3.10}$$

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

$$H_{11}(-s)\ H_{11}(s) + H_{12}(-s)\ H_{21}(s) = s\ \ L_{11} + sL_{21}\ F^{+}_{12} \tag{3.11a}$$

$$H_{11}(-s)\ H_{12}(s) + H_{12}(-s)\ H_{22}(s) = L_{11}(s)\ K_{12}(s) + L_{21}s \tag{3.11b}$$

We then can rewrite (3.11a) and (3.11b) using (3.7) in the form,

$$A_{11}^{2} + \tfrac{1}{2}(H_{12}^{+} - H_{12}^{*})\ [\tfrac{1}{2}\ H_{12}^{+} + \tfrac{1}{2}\ H_{12}^{*} + (\rho_2-\rho_1)\ F_{12}^{+}] \tag{3.12a}$$

$$= A'_{11} + \frac{s}{2}\ F_{12}^{+}\ [L_{21}^{*}(s) + (\rho_2-\rho_1)\ F_{12}^{+}(s)]$$

$$A_{11}H_{12}^{+} + \frac{\rho_2-\rho_1}{2}\ (H_{12}^{+} - H_{12}^{*}) = A'_{11}F_{12}^{+} + \frac{s}{2}\ [L_{21}^{*} + (\rho_2-\rho_1)F_{12}^{+}] \tag{3.12b}$$

By eliminating $L^*_{21}(s)$ from (3.12), we obtain a functional relationship of the form

$$\left(\tfrac{1}{2}H^+_{12} - A_{11}F^+_{12}\right)^2 - (s^2-4\mu^2)\left(\tfrac{1}{2}F^+_{12}\right)^2 = A'_{11} - A^2_{11} \qquad (3.13a)$$

or simply

$$\Psi^2(s) - E(s)\,\Phi^2(s) = \mu^2 \qquad (3.13b)$$

where we have defined

$$\Psi(s) \equiv \frac{H^+_{12}}{2} - A_{11}\,F^+_{12}(s) \qquad (3.14a)$$

$$\Phi(s) \equiv \frac{F^+_{12}(s)}{2} \qquad (3.14b)$$

$$\mu^2 \equiv A'_{11} - A^2_{11} \qquad (3.14c)$$

$$E(s) \equiv s^2 - 4\mu^2. \qquad (3.14d)$$

The right side of (3.14c) proves to be positive and equal to $\sigma^2_{12}(\alpha)$. This can be seen by looking at the asymptotic behavior of $sL_{11}(s)$ as $R\ell s \to \infty$ in (2.19a).

$$sL_{11}(s) = sG_{11}(s)\,A_{11} + sG_{12}(s)\,H_{12}(-s)$$

$$\xrightarrow{s \to \infty} A^2_{11} + \sigma^2_{12}(\alpha) \qquad (3.15)$$

along with (2.23)

The functional equation (3.13) 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 $s^{-1} \exp[-\alpha\ |R\ell s|]$, for large s. The solution to this functional relation is

$$\Psi(s) = \pm\mu \cosh \alpha \sqrt{E(s)} \tag{3.16}$$

$$\Phi(s) = \pm\mu \sinh[\alpha \sqrt{E(s)}]/\sqrt{E(s)} \tag{3.17}$$

The signatures of $\Psi(s)$ and $\Phi(s)$, i.e., the signs in (3.16) and (3.17) are to be taken positive with $\mu = \sigma_{12}(\alpha) > 0$. This follows from the behavior of $G_{12}(s)$ as $R\ell s \to \infty$ in (2.32b), that is,

$$G_{12}(s) = H_{11}(s)\ K_{12}^{-1} + H_{12}(s)\ K_{22}^{-1}(s)$$

$$= \frac{-A_{11}\ F_{12}^{+}}{s(1-F_{12}^{+2})} + \frac{H_{12}(s)}{s(1-F_{12}^{+2})} \qquad \text{(from Eq. (2.33e)}$$

$$\xrightarrow{s \to \infty} \frac{e^{-s\alpha}}{-2s\mu} \Big\{ s^2\ (\text{sign}\ \Psi - \text{sign}\ \Phi)$$

$$-4\mu^2\ (\text{sign}\ \Psi - \tfrac{1}{2}\ \text{sign}\ \Phi) \Big\} \tag{3.18a}$$

where sign Ψ means +1 (or -1) if the signature of $\Psi(s)$ is positive (or negative), so that $G_{12}(s)$ should have the behavior $K\ \frac{e^{-\alpha s}}{s}$ with K, a positive constant. This asserts that

$$G_{12}(s) = \mu \frac{e^{-s\alpha}}{s} \quad \text{for large } s \tag{3.18b}$$

confirming the choice of signs in (3.16) and (3.17).

The contact value $g_{12}(\alpha)$ is obtained in terms of μ using (3.18b)

$$\begin{aligned}
\sqrt{\rho_1\rho_2}\ g_{12}(\alpha) &= \sigma_{12}(\alpha) \\
&= \lim_{s \to \infty} [-s\, F_{12}(-s) \exp(-s\alpha)] \\
&= \sigma_{12}(\alpha^+) \\
&= \lim_{s \to \infty} [s \exp(s\alpha)\, G_{12}(s)] \\
&= \mu
\end{aligned} \tag{3.19}$$

The quantity μ in (3.16) defined in (3.14c) enters as a parameter in the solution. From (3.17)

$$\Phi(0) = \tfrac{1}{2} \sin 2\mu\alpha \tag{3.20}$$

while from (2.8)

$$\begin{aligned}
\mu^2 &= A'_{11} - A_{11}^2 \\
&= \rho_1\rho_2 - \tfrac{1}{4}(a-\rho_1-\rho_2)^2 \\
&= \rho_1\rho_2\,(1 - 4\,\Phi^2(0))
\end{aligned} \tag{3.21}$$

since

$$A_{11} = \tfrac{1}{2}\,(a-\rho_2-\rho_1)$$
$$= \rho_1\left(1+\sqrt{\frac{\rho_2}{\rho_1}}\;2\Phi(0)\right) \qquad (3.22)$$

This yields the equation for μ,

$$\mu = \sqrt{\rho_1\rho_2}\;\cos 2\mu\alpha \qquad (3.23a)$$

or simply

$$q = \eta \cos q \qquad (3.23b)$$

with $q \equiv \eta\, g_{12}(\alpha)$ and the reduced density $\eta \equiv 2\alpha\sqrt{\rho_1\rho_2}$ for the one-dimensional system. For $\eta \geq \eta_0 \cong 2.80$, the solution of (3.23) for μ is not unique. The continuity of the pressure, however, makes it possible to choose the solution along the first branch of cos q where $q \leq \frac{\pi}{2}$, that is, along the branch of the low density solution. We will see this from the expressions for pressure in the next section.

3-2. Thermodynamic properties in one dimension

Equation of state:

The virial pressure is obtained from (2.42) and (3.19), namely

$$P^V = \rho + 2\alpha\sqrt{\rho_1\rho_2}\;\mu \qquad (3.24)$$

where ρ is the total density, $\rho_1+\rho_2$, and μ is defined in (3.23a).

From the compressibility relation

$$\frac{\partial P^c}{\partial \rho_1} = 1 - \rho_2 \int_{|r|\leq\alpha} C_{12}(r)\, dr$$

$$= 1 + [\rho_2/\rho_1]^{\frac{1}{2}} \sin(2\mu\alpha) \qquad (3.25a)$$

we obtain

$$P^c = \rho + 2 \int_0^{\sqrt{\rho_1\rho_2}} \sin(2\mu\alpha)\, d(\sqrt{\rho_1\rho_2}) \qquad (3.25b)$$

The exact pressure[9] may be obtained, for $\rho_1 = \rho_2 = \frac{1}{2}\rho$, from the equation

$$\frac{P}{\rho} = 1 + \tfrac{1}{2}P/[1+\exp(\tfrac{1}{2}P)] \qquad (3.26)$$

The above three pressure are plotted in (Figure 5). From this we see that for $\rho \leq 1$ (in units in which $2\alpha = 1$), the agreement is very good, while for $\rho \to \infty$ they converge to different values;

$$\frac{P^v}{\rho} \xrightarrow{\rho \to \infty} 1 + \frac{\pi}{4} \qquad (3.27)$$

$$\frac{P^c}{\rho} \xrightarrow{\rho \to \infty} 2 \qquad (3.28)$$

$$\frac{P^{ex}}{\rho} \xrightarrow{\rho \to \infty} 1 \qquad (3.29)$$

$\sigma_{ij}(r)$ and their Fourier transforms:

Eq. (3.14b) provides the Fourier transform of $C_{12}(r)$ since

$$\tfrac{1}{2} F_{12}^{+}(s) \equiv \int_0^{\alpha} \sigma_{12}(r) \frac{e^{-sr} + e^{sr}}{2} \, dr$$

$$= \tfrac{1}{2} \int_{-\alpha}^{\alpha} \sigma_{12}(r) \, e^{-sr} \, dr \qquad (3.30a)$$

and therefore

$$\tilde{C}_{12}(k) \equiv \int_{-\alpha}^{\alpha} C_{12}(r) \, e^{-ikr} \, dr$$

$$= -F_{12}^{+}(ik) \, / \sqrt{\rho_1 \rho_2}$$

$$= -2 \, \Phi(ik) \, / \sqrt{\rho_1 \rho_2}$$

$$= \frac{-2 \, \mu}{\sqrt{\rho_1 \rho_2}} \sin\left[\alpha \sqrt{k^2 + 4\mu^2}\right] / \sqrt{k^2 + 4\mu^2} \, . \qquad (3.30b)$$

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

$$C_{12}(r) = \begin{cases} -\mu \, J_0\left[2\mu\sqrt{\alpha^2 - r^2}\right] / \sqrt{\rho_1 \rho_2} & \text{for } 0 < r < \alpha \\ 0 & \text{for } r > \alpha \end{cases} \qquad (3.31)$$

where J_0 is the Bessel function of zeroth order. It is seen from (3.31) 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 the definition (2.1), we find

$$\tilde{H}_{ij}(k) = \tilde{C}_{ij}(k) + \sum_{\ell} \rho_{\ell} \tilde{H}_{i\ell}(k) \tilde{C}_{ij}(k) \tag{3.32}$$

hence

$$\tilde{H}_{11}(k) = \left\{ \frac{1}{1-\rho_1\rho_2\tilde{C}_{12}^2(k)} - 1 \right\} \sqrt{\rho_1\rho_2} \tag{3.33a}$$

$$\tilde{H}_{12}(k) = \frac{\tilde{C}_{12}(k)}{1-\rho_1\rho_2\tilde{C}_{12}^2(k)} \cdot \rho_1\rho_2 \tag{3.33b}$$

$H_{ij}(k)$ were found numerically and are plotted in Fig. 6. The numerical calculation of the inverse Fourier transform of $\tilde{H}_{12}(k)$ in (3.33b) converges very slowly because of the slow decay of $\tilde{C}_{12}(k)$ as $k \to \infty$. We can, however, combine $\tilde{C}_{12}(k)$ and $\tilde{H}_{12}(k)$ into such a form that

$$\tilde{H}_{12}(k) - \tilde{C}_{12}(k) = \frac{\tilde{C}_{12}^3(k)}{1-\rho_1\rho_2\tilde{C}_{12}^2(k)} \tag{3.33c}$$

for which the inverse Fourier transformation is very rapidly convergent.

(3.33c) 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 (3.31).

3-3. Three dimensional solution

Similar steps are used in the three dimensional case as in the one dimensional case. The results from Chapter 2 for this

system yield

$$\sigma_{ii}^{(1)}(0) = A_{ii} \tag{3.34a}$$

$$L_{ii}(s) = 2B_i + \frac{A'_{11}}{s^2} \tag{3.34b}$$

$$\sigma_{22}(s) - \sigma_{11}(s) = G_{22}(s) - G_{11}(s)$$

$$= 2\pi(\rho_2 - \rho_1)/s^2 \tag{3.34c}$$

and

$$U_{21}^*(s) - U_{12}^*(s) = \frac{A_{21} - A_{12}}{s} + \frac{2\pi(\rho_2 - \rho_1)F_{12}^*}{s^2} \tag{3.34d}$$

The off-diagonal elements of $\underline{\underline{L}}(s)$ in (2.35) yield the following relations,

$$L_{21}(s) = G_{21}(s)\, A_{11} + G_{22}(s)\, [A_{12} - s^2\, F_{12}(-s) - sU_{12}^*(s)] \tag{3.35a}$$

$$L_{12}(s) = G_{12}(s)\, A_{22} + G_{11}(s)\, [A_{21} - s^2\, F_{12}(-s) - sU_{21}^*(s)] \tag{3.35b}$$

Their difference is

$$L_{12}(s) - L_{21}(s) = 2\pi\, (\rho_1 - \rho_2)\, F_{12}^*(s) \tag{3.35c}$$

which has the $e^{\pm\alpha s}/s$ - behavior for large $R\ell s$ in common with $U_{12}^*(s)$, and $H_{12}(s)$.

From the relation

$$\underline{\underline{H}}(-s)\ \underline{\underline{H}}(s) = \underline{\underline{L}}^T(s)\ \underline{\underline{K}}(s) \tag{3.36}$$

we get two linearly independent equations

$$H_{11}(-s)\ H_{11}(s) + H_{12}(-s)\ H_{21}(s) = L_{11}\quad s^2 - sF_{12}^{*}\ L_{21}(s) \tag{3.37a}$$

$$H_{11}(-s)\ H_{12}(s) + H_{12}(-s)\ H_{22}(s) = -s\ F_{12}^{*}\ L_{11}(s) + s^2\ L_{21}(s) \tag{3.37b}$$

The other two elements of (3.36) are the same as (3.37) after some manipulation with the help of (3.35). Using the superscript of '*' and '+' to define

$$H_{12}^{+}(s) \equiv H_{12}(s) + H_{12}(-s) = 2(A_{12}-sU_{12}^{*}) - s^2\ F_{12}^{+}(s) \tag{3.38a}$$

$$H_{12}^{*}(s) \equiv H_{12}(s) - H_{12}(-s) = -s^2\ F_{12}^{*}(s) \tag{3.38b}$$

(3.37) can be written as

$$A_{11}^{2} + \tfrac{1}{2}\ (H_{12}^{+} + s^2\ F_{12}^{*})\ [\frac{H_{12}^{+}(s)}{2} - \frac{s^2F_{12}^{*}}{2} - \frac{F_{12}^{*}}{s}\ 2\pi(\rho_2-\rho_1)] \tag{3.39a}$$

$$=(A_{11}' - B_{11}s^2)\ -sF_{12}^{*}(s)\ L_{21}(s)$$

$$A_{11}\ H_{12}^{+} + \frac{2\pi(\rho_2-\rho_1)}{2}\ (H_{12}^{+} + s^2F_{12}^{*}) = -\frac{(A_{11}' + B_{11})}{s^2}\ sF_{12}^{*}+s^2L_{21}(s) \tag{3.39b}$$

The above equations in (3.39) may be combined into one relation by eliminating $L_{21}(s)$. We find

$$\{\tfrac{1}{2} H_{12}^{+}(s) + \frac{A_{11}}{s} F_{12}^{*}(s)\}^2 - (\frac{F_{12}}{2s})^2 \{s^6 - 4(A_{11}' - A_{11}^2 + B_{11}s^2)\}$$

$$= A_{11}' - A_{11}^2 + B_{11}s^2 \tag{3.40}$$

This leads to the equation

$$\Psi^2(s) - E(s)\,\Phi^2(s) = h(s) \tag{3.41}$$

where we have defined

$$\Psi(s) \equiv \tfrac{1}{2} \cdot H_{12}^{+}(s) + \frac{A_{11}F_{12}^{*}}{s} \tag{3.42a}$$

$$\Phi(s) \equiv \frac{F_{12}^{*}(s)}{2s} \tag{3.42b}$$

$$E(s) \equiv s^6 - 4h(s) \tag{3.42c}$$

$$h(s) \equiv B_{11}\, s^2 + \mu^2 \tag{3.42d}$$

$$\mu^2 \equiv A_{11}' - A_{11}^2 \tag{3.42e}$$

We also see that from (3.34b)

$$L_{11}(s) = G_{11}A_{11} + G_{12}\,[A_{12} - s^2\, F_{12}(-s) - sU_{12}^{*}]$$

$$= \frac{A_{11}'}{s^2} + 2B_{11}$$

$$\xrightarrow{s \to \infty} - \sigma_{12}^{2}(\alpha) \tag{3.43}$$

or

$$2B_{11} = -\sigma_{12}^{2}(\alpha) \tag{3.44a}$$

$$h(s) \equiv 2B_{11}\,(s^2 - z_1^2) \tag{3.44b}$$

and

$$z_1 \equiv \mu/\sigma_{12}(\alpha) \tag{3.44c}$$

$\Psi(s)$ and $\emptyset(s)$ are both even and entire functions and have the $e^{\mp\alpha s}/s$ - behavior for large $R\ell s$, with the plus sign if $R\ell s \to +\infty$ and the minus sign if $R\ell s \to -\infty$ as can be seen from the way that they are defined.

<u>Solution of the functional equation:</u>

A functional equation of the type (3.41) was solved formally by Penrose and Lebowitz for the P.Y. equation of the system considered by Lebowitz and Zomick, i.e. $R_{11} \leq R_{12}, 0 < \alpha < \frac{1}{2}(R_{22}-R_{11})$. The P.Y. 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

$$f(s) \equiv \Psi(s) + \sqrt{E(s)}\;\Phi(s). \tag{3.45}$$

We can then rewrite the functional equation (3.41) in the form

$$f(s) \cdot f(-s) = h(s) \tag{3.46}$$

Penrose and Lebowitz have shown[13] that if E(s) and h(s) share no common zero, then a functional equation of the type (3.41) can be reduced to a Hilbert problem <u>on the arc</u>, the solution of which was found by N.I. Muskhelishvili.[21]

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

$$f(s) = \pm\sqrt{2|B_{11}|}\,(s+z_1)\exp\{I(s)\} \tag{3.47}$$

with the condition

$$\alpha = \frac{1}{2\pi i}\int_{C_1} \frac{t\ln J(t)\,dt}{\sqrt{E(t)}} \tag{3.48}$$

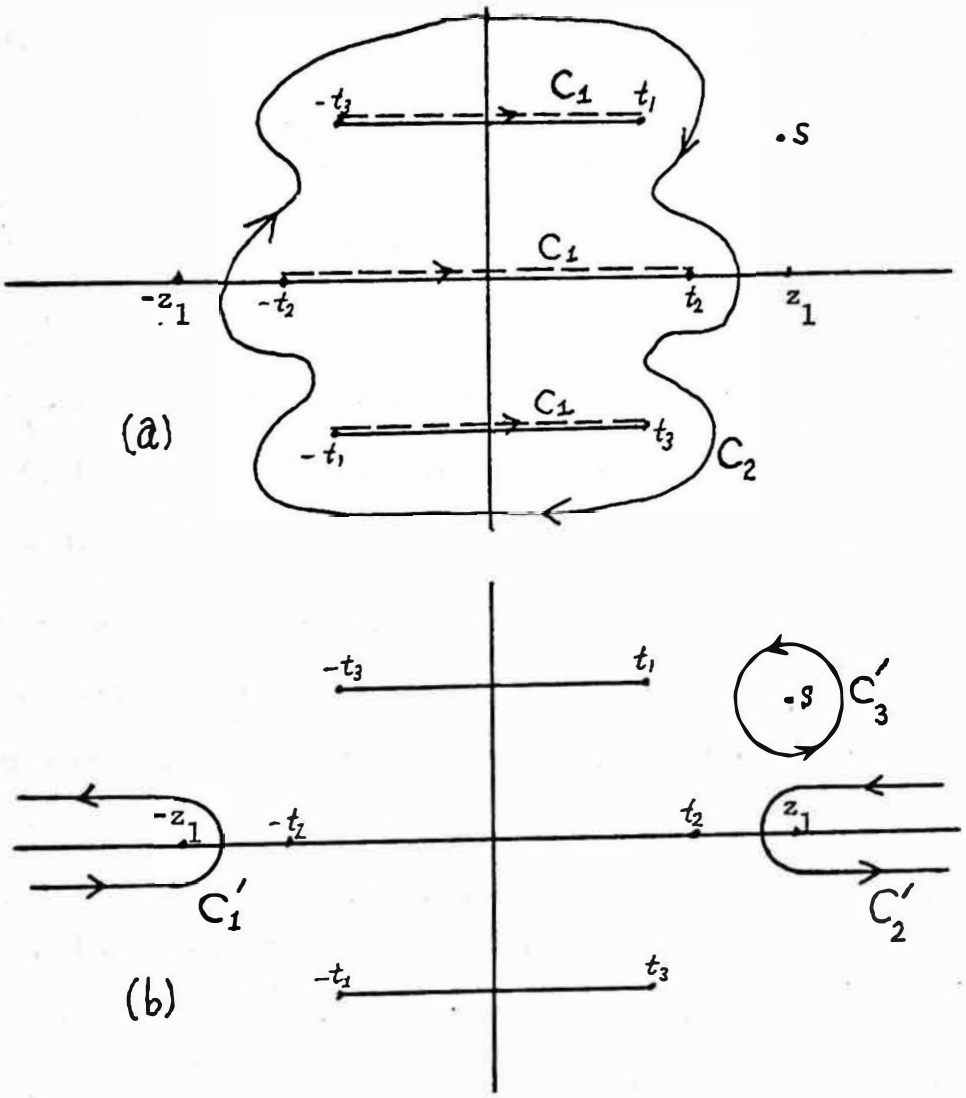


Fig. 4

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'. $\pm t_1, \pm t_2$ and $\pm t_3$ are the zeros of the sixth order polynomal $E(t)$. $\pm z_1$ are the zeros of $h(z)$.

where

$$I(s) = \frac{\sqrt{E(s)}}{2\pi i} \int_{C_1} \frac{\ell n J(t)}{\sqrt{E(t)}^{+}} \frac{dt}{(t-s)}, \tag{3.49}$$

$$J(t) \equiv \frac{t-z_1}{t+z_1}, \tag{3.50}$$

and C_1 is the system of cuts parallel to the real axis as shown in Fig. 4, branches of $\ell n J(t)$ are chosen so that $\ell n J(t)$ is an odd function, and $\sqrt{E(t)}^{+}$ means $\sqrt{E(t)}$ along the dotted positive cuts C_1 shown in Fig. 4. The integration in the right hand side of (3.49) equals to one half of the integral around the closed contour surrounding the three branch cuts, C_2. By the Cauchy theorem we can 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

$$I(s) = \frac{\sqrt{E(s)}}{2\pi i} \tfrac{1}{2} \int_{C_2} \frac{\ell n J(t)\, dt}{\sqrt{E(t)}^{+}\,(t-s)}$$

$$= \frac{\sqrt{E(s)}}{2\pi i} \tfrac{1}{2} \int_{C_1'+C_2'+C_3'} \frac{\ell n J(t)\, dt}{\sqrt{E(t)}^{+}\,(t-s)}$$

$$= \frac{\sqrt{E(s)}}{2\pi i} \frac{2\pi i}{2} \left\{ + \int_{-z_1}^{-\infty} \frac{dt}{\sqrt{E(t)}^{+}\,(t-s)} + \int_{z_1}^{\infty} \frac{dt}{\sqrt{E(t)}^{+}(t-s)} - \frac{\ell n J(s)}{\sqrt{E(s)}} \right\} \tag{3.51}$$

The function $\frac{\ell nJ(s)}{\sqrt{E(s)}}$ has discontinuities $\frac{2\pi i}{\sqrt{E(s)}}$ across the cuts (z_1,∞) and $(-z_1,-\infty)$. These are cancelled by the discontinuities in the integral which can be found from the Plemelj formulae given in Muskhelishvili.[21], [22]

Let us rewrite I(s) in the form

$$I(s) = i\, I_1(s) + \tfrac{1}{2}\, \ell nJ(s) \tag{3.52}$$

where

$$I_1(s) \equiv -i\sqrt{E(s)} \int_{z_1}^{\infty} \frac{t\,dt}{\sqrt{E(t)}\,(t^2-s^2)} \tag{3.53}$$

Having found f(s) we can write

$$\Phi(s) = \frac{f(s) - f(-s)}{2\sqrt{E(s)}} \tag{3.54}$$

$$\Psi(s) = \frac{f(s) + f(-s)}{2} \tag{3.55}$$

The sign of f(s) in (3.47) 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 $s \to \infty$.

The solutions $\Phi(s)$ and $\Psi(s)$ are, then, on the imaginary axis, $s = ik$

$$\Phi(ik) = -\sigma_{12}(\alpha) \frac{(k^2+z_1^2)^{\frac{1}{2}}}{[k^6+4\sigma_{12}^2(k^2+z_1^2)]^{\frac{1}{2}}} \sin I_1(ik) \tag{3.56a}$$

$$\Psi(ik) = -\sigma_{12}(\alpha) (k^2+z_1^2)^{\frac{1}{2}} \cos I_1(ik) \tag{3.56b}$$

where

$$I_1(ik) = [k^6+4\sigma_{12}^2(k^2+z_1^2)]^{\frac{1}{2}} \int_{z_1}^{\infty} \frac{t\,dt}{[t^6+4\sigma_{12}^2(t^2-z_1^2]^{\frac{1}{2}}(t^2+k^2)} \tag{3.56c}$$

3-4. Thermodynamic properties in three dimensions

Equation of State:

Two representations for the pressure are taken in the same way as in one dimension; from the virial theorem and compressibility relation, and their low-density expansion are found.

The virial pressure can be written in a parametric form from eqs. (2.51) and (3.56)

$$\beta P^V = \rho + \frac{4}{3}\pi\alpha^3 \rho_1\rho_2 \; g_{12}(\alpha) \tag{3.57}$$

On the other hand $g_{12}(\alpha)$ is determined as follows:

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

$$= \frac{\sqrt{\rho_1\rho_2}}{2}\left[4\pi\int_0^{\alpha}\frac{\sin kr}{k}\ C_{12}(r)dr\right]$$

$$= \frac{\sqrt{\rho_1\rho_2}}{2}\ \tilde{C}_{12}(k) \qquad (3.58)$$

where $\tilde{C}_{12}(k)$ is the Fourier Transform of $C_{12}(r)$, and

$$\tilde{C}_{12}(0) = \int C_{12}(\bar{r})\ d\bar{r} \qquad (3.59)$$

Also from (3.53), (3.54) and (3.56)

$$\Phi(0) \equiv \Phi_0 = -\tfrac{1}{2}\ \sin I_1(0) \qquad (3.60a)$$

$$\alpha = \int_{z_1}^{\infty} \frac{tdt}{\sqrt{E(t)}} \quad \text{(from (3.48))} \qquad (3.60b)$$

$$I_1 = 2\mu \int_{z_1}^{\infty} \frac{tdt}{\sqrt{E(t)}\ t^2} \qquad (3.60c)$$

By changing the variable t to z

$$t^2 = [\eta\sqrt{1-4\Phi^2(0)}]^{2/3}\ z/\alpha^2 \qquad (3.61)$$

we get

$$I_1(0) = \frac{\alpha^3}{2\eta\sqrt{1-4\Phi_0^2}} \cdot I_1 \tag{3.62a}$$

$$I_1 \equiv \int_{z_o}^{\infty} \frac{dz}{z\sqrt{z^3+\frac{4z}{z_o}-4}} \tag{3.62b}$$

$$I_2 = 2(\eta\sqrt{1-4\Phi_0^2})^{1/3} = \int_{z_o}^{\infty} \frac{dz}{\sqrt{z^3+\frac{4z}{z_o}-4}} \tag{3.62c}$$

$$z_o \equiv \left(\frac{1-4\Phi_0^2}{\eta|C_{12}^3(\alpha)|}\right)^{2/3} \tag{3.62d}$$

$$2\Phi_0 = \sin I_1 \tag{3.62e}$$

We finally obtain the contact value and the density in terms of the parameter z_o

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

$$\eta = \frac{(I_2/2)^3}{\cos I_1} \tag{3.64}$$

Therefore, with (3.57) and (3.64)

$$\beta P^{v} = \rho + \frac{4}{3}\pi\alpha^{3}\rho_{1}\rho_{2}\frac{\cos I_{1}}{\sqrt{z_{o}}\ I_{2}/2} \tag{3.65a}$$

or

$$\beta P^{v}(\pi\alpha^{3}) = (\pi\alpha^{3}\rho) + \frac{1}{3}\eta^{2}|C_{12}(\alpha)| \tag{3.65b}$$

The compressibility relation and its pressure are written

$$\beta\frac{\partial P^{c}}{\partial\rho_{1}} = 1 - \rho_{2}\int C_{12}(\bar{r})d\bar{r} \tag{3.66a}$$

$$= 1 - 2(\rho_{2}/\rho_{1})^{\frac{1}{2}}\Phi_{0} \tag{3.66b}$$

The pressures are drawn in the Fig. 8 and 9 with respect to the total density and composition respectively.

<u>Low density expansion of the pressure</u>:

The low-density expansion for pressures is obtained by expanding I_1 and I_2 in the parameter $z_o^{-\frac{1}{2}}$, then eliminating z_o in favor of η using (3.64). Let us first expand I_1 and I_2,

$$I_{1} = \sum_{n=0}^{\infty} 2\cdot(-1)^{n}\frac{4^{n}\{1\cdot3\cdot5\ldots(2n-1)\}\cdot z_{o}^{-3n+\frac{3}{2}}}{(4n+3)(4n+5)\ldots\{4n+(2n+3)\}}$$

$$= \frac{2}{3}z_{o}^{-3/2}\left[1 - \frac{12}{63}\frac{1}{z_{o}^{3}} + \frac{3\cdot6\cdot2\cdot4}{11\cdot13\cdot15}\frac{1}{z_{o}^{6}} - \frac{3\cdot20\cdot2\cdot4\cdot6}{15\cdot17\cdot19\cdot21}\frac{1}{z_{o}^{9}} + \ldots\right] \tag{3.67}$$

$$I_2 = \frac{2}{z_o^{\frac{1}{2}}} \left[1 - \left(\frac{4}{35}\right) \frac{1}{z_o^3} + \frac{6\cdot 2\cdot 4}{9\cdot 11\cdot 13} \frac{1}{z^6} - \frac{20\cdot 2\cdot 4\cdot 6}{13\cdot 15\cdot 17\cdot 19} \frac{1}{z_0^9} + \ldots\right]$$

$$= \sum_{n=0}^{\infty} 2.\ (-1)^n \frac{4^n \{1.3.5..(2n-1)\}.\ z_o^{-3n-3/2}}{(4n+3)(4n+5)\ldots\{4n\ (2n+3)\}} \tag{3.68}$$

These expansions will converge for $z_o^3 > \frac{16}{27}$.

Then with (3.62), (3.63) and (3.64) the coefficients are found for the density expansion of $\tilde{C}_{12}(k)$ at $k = 0$ and for $|C_{12}(\alpha)|$,

$$\sqrt{\rho_1\rho_2}\ \tilde{C}_{12}(0) = \frac{2}{3}\eta\ [1 - D_1\eta^2 + D_2\eta^4 - D_3\eta^6 + \ldots] \tag{3.69a}$$

$$|\tilde{C}_{12}(\alpha)| = 1 - C_1\ \eta^2 + C_2\ \eta^4 - \ldots \tag{3.69b}$$

This yields the following virial expansions for the pressure

$$\begin{aligned} \beta P^v = \rho_1 + \rho_2 + \rho_1\rho_2 \{1 &- .24285\ \rho_1^2\rho_2^2 \\ &+ .08714\ \rho_1^4\rho_2^4 - .03908\ \rho_1^6\rho_2^6 \\ &+ .01969\ \rho_1^8\rho_2^8 - .01145\ \rho_1^{10}\rho_2^{10} \\ &+ .00785\ \rho_1^{12}\rho_2^{12} - \ldots\} \end{aligned} \tag{3.70a}$$

$$\beta P^c = \rho_1+\rho_2 + \rho_1\rho_2 \{1 - .16190\, \rho_1^2\rho_2^2$$

$$+ .04665\, \rho_1^4\rho_2^4 - .01721\, \rho_1^6\rho_2^6$$

$$+ .00732\, \rho_1^8\rho_2^8 - .00386\, \rho_1^{10}\rho_2^{10}$$

$$+ .00216\, \rho_1^{10}\rho_2^{10} - \ldots\} \qquad (3.70b)$$

The fact that the direct correlation function C_{12} in the P.Y. approximation is a function only of η (and not ρ_1 and ρ_2 separately) is a consequence of the fact that only certain types[27] of Mayer diagrams are summed in this approximation and that the Mayer function for this system are

$$f_{ii}(r) = 0,\ i = 1,2,\ f_{12}(r) = f_{21}(r) = \begin{cases} -1, & r < \alpha \\ 0, & r > \alpha \end{cases} \qquad (3.71)$$

Our results can be compared directly to the first few terms in the cluster expansion for the P.Y. direct correlation function, we find

$$\tilde{C}_{12}(0) = \int C_{12}(r)\, d\bar{r} = 1 - \rho_1\rho_2 \int f_{12}\cdot f_{23}\cdot f_{34}\cdot f_{41}\, d\bar{r}_1 \ldots d\bar{r}_4$$

$$+ \text{ higher order terms of } (\rho_1\rho_2)$$

$$= 1 - (34/315)\, \rho_1\rho_2 + \ldots \qquad (3.72)$$

which agrees with the results of our solution.

Critical indices and the critical point:

Since the temperature does not play any role in hard sphere systems and may be taken as being fixed, we look into the critical indices[23] in terms of the density near the critical point. $\left(\frac{\partial^2 g}{\partial x^2}\right)_P$ and $\left(\frac{\partial^3 g}{\partial x^3}\right)_P$ vanish together at the critical point, where g is the Gibbs free energy per volume, x is the percentage of the species-1, $x = \rho_1/\rho$, $\rho = \rho_2 + \rho_2$ and P is the pressure. The symmetry of this model reduces these conditions to

$$\left(\frac{\partial^2 f}{\partial x^2}\right)_{\rho_C} = 0 \ , \quad \left(\frac{\partial^3 f}{\partial x^3}\right)_{\rho_C} = 0 \quad \text{for } x = \tfrac{1}{2} \tag{3.73}$$

where f is the Helmholtz free energy per volume and ρ_C is the critical density.

The inverse susceptibility provides a critical index γ_ρ defined as

$$\chi^{-1}(\rho) = \left(\frac{\partial^2 f}{\partial x^2}\right)_\rho \propto (\rho_c - \rho)^{\gamma_\rho}, \text{ for } \rho \leq \rho_c \tag{3.74}$$

Differentiating the free energy further we find the hypersusceptibility index ϵ_ρ

$$\left(\frac{\partial^4 f}{\partial x^4}\right)_\rho \propto (\rho_c - \rho)^{\epsilon_\rho} \tag{3.75}$$

The critical index for compressibility, α_ρ, is obtained from

$$\left[\frac{\partial}{\partial\rho}\ \rho^2\ \frac{\partial f}{\partial\rho}\right]_x = \left(\frac{\partial P}{\partial\rho}\right)_x$$

$$\propto (\rho_c - \rho)^{-\alpha_\rho} \tag{3.76}$$

The scaling hypothesis for critical indices[23] implies that

$$\alpha_\rho + \gamma_\rho + \epsilon_\rho = 2. \tag{3.77}$$

The free energy like the pressure can be obtained from the correlation function in different ways. For the exact solution both would give the same free energy. Quite generally, the free energy can be expressed in terms of the pressure as

$$f = \int^{\rho} [P/\rho^2]\, d\rho$$

$$= f^i + \frac{\eta}{\pi\alpha^3\rho} \int^{\eta} \frac{P^{\Delta}(\eta)}{\eta^2}\, d\eta. \tag{3.78}$$

where f^i, the free energy for an ideal gas, is

$$f^i = \Sigma\, x_i\, \ell n\, x_i + \ell n\rho \tag{3.79}$$

and we have for $P^{\Delta} = P - P^i$

$$(\pi\alpha^3)\ P^{\Delta} \equiv \begin{cases} \frac{1}{3}\eta^2\ |C_{12}(\alpha)| \text{ (virial expression)} & (3.80a) \\ -\int_0^{\eta} \Phi_0\, d\eta \text{ (compressibility)} & (3.80b) \end{cases}$$

where $\eta \equiv 2\,\pi\,\alpha^3\rho\,\sqrt{(x(1-x))}$.

First we see from (3.65), (3.66) and (3.76) that

$$\frac{\partial P}{\partial \rho} > 0 \quad \text{for } \rho \leq \rho_c \tag{3.81}$$

for both pressures which yields

$$\alpha_\rho = 0 \tag{3.82}$$

On the other hand, χ^{-1} is obtained by differentiating f twice with respect to the composition x by the relation

$$\chi^{-1} = \left(\frac{\partial^2 f}{\partial x^2}\right)_\rho \xrightarrow{x \to \frac{1}{2}} 4\left(1 - \frac{P^\Delta(\eta)}{\eta} - \int^\eta \frac{P^\Delta}{\eta^2}\, d\eta\right)$$

$$= \begin{cases} 4 + 4\int_0^\eta \Phi_0/\eta \cdot d\eta \quad [\text{from the compressibility}] & (3.83a) \\ 4 - \frac{4}{3}\left(\eta\, g_{12}(\alpha) + \int_0^\eta g_{12}(\alpha)\, d\eta\right) \quad [\text{from the virial theorem}] & (3.83b) \end{cases}$$

Now since Φ_0 and $g_{12}(\alpha)$ are well behaved and approach a constant value as $\eta \to \eta_c$ we see that

$$\gamma_\rho = 1 \tag{3.84}$$

Also χ^{-1} is drawn in Fig. 10.

The hyper-susceptibility is found to be

$$\frac{\partial^4 f}{\partial x^4} = 32 - 12\pi\alpha^3\rho \left\{\frac{\partial^3 f}{\partial \eta^3} + 4\frac{\partial f}{\partial \eta}\right\} \text{for } X=\tfrac{1}{2} \tag{3.85}$$

and with the help of (3.80) and (3.78) we find that

$$\frac{\partial^4 f}{\partial x^4} = C\ ,\ C > 0 \quad \text{at } \eta = \eta_c \tag{3.86a}$$

and

$$\epsilon_\rho = 0 \tag{3.86b}$$

Eqs. (3.82), (3.84) and (3.86b) show this Widom-Rowlinson model exhibits a classical phase transition in the three dimensional Percus-Yevick approximation[24]. A detailed calculation using (3.83) leads to the values of the critical density for both expressions of the free energy. They are

$$\eta_C \cong 1.6736 \tag{3.87a}$$

for the compressibility relationship and

$$\eta_C \cong 1.7876 \tag{3.87b}$$

from the virial equation. Recently Rowlinson, et al[25] obtained the critical density for the P.Y. compressibility approximation of this system

$$\eta_c \cong 1.674 \pm .003 \tag{3.87c}$$

by Pade approximant methods. This is seen to agree with the result (3.87a) obtained from the exact solution.

σ_{ij} and their Fourier Transforms

Eqs. (3.56) and (3.58) provide the Fourier transforms of the direct correlation function and radial distribution functions,

$$\tilde{C}_{12}(k) = \frac{2\Phi(ik)}{\sqrt{\rho_1\rho_2}}$$

$$= \frac{-2\sigma_{12}(\alpha)}{\sqrt{\rho_1\rho_2}} \cdot \frac{\left[k^2+z_1^2\right]^{\frac{1}{2}}}{\left[k^1+4\sigma_{12}^2(k^2+z_1^2)\right]^{\frac{1}{2}}} \sin I_1(ik)$$

$$= \frac{-2\sqrt{1+Y}}{\sqrt{\rho_1\rho_2}\sqrt{z_0^3Y^3+4Y+4}} \sin\left\{\frac{1}{2}\sqrt{z_0^3Y^3+4Y+4}\int_1^\infty \frac{dz}{(4z)\sqrt{z_0^3z^3+4z-4}}\right\} \tag{3.88a}$$

where

$$Y = 4k^2/I_2^2. \tag{3.88b}$$

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 (2.1),

$$\tilde{H}_{11}(k) = \left\{\frac{1}{1-(\sqrt{\rho_1\rho_2}\tilde{C}_{12}(k))^2} - 1\right\}\Big/\sqrt{\rho_1\rho_2} \tag{3.89a}$$

$$\tilde{H}_{12}(k) = \frac{\tilde{C}_{12}(k)}{1-(\sqrt{\rho_1\rho_2}\tilde{C}_{12}(k))^2} \tag{3.89b}$$

$H_{ij}(k)$, $C_{ij}(k)$ and $g_{ij}(r)-C_{ij}(r)$ are found with the help of machine computation and drawn in Fig. 11 and 12.

It is seen from the graphs that the P.Y. $g_{ii}(r)$ is larger than 1 and $g_{12}(r)$ is less than 1 for 'almost all' values of r. The exact radial distribution functions satisfy[14] the inequalities $g_{ii}(r) \geq 1$ and $g_{12}(r) \leq 1$ for all r.

CHAPTER 4. P.Y. EQUATION FOR A MIXTURE OF HARD SPHERES WITH $R_{11} = R_{22} = R$ and $R > \alpha > 0$

4-1. One dimensional solution

The P.Y. equation of this system with R_{ij}

$$R_{ij} = \begin{cases} R + \alpha & \text{for } i \neq j \\ R & \text{for } i = j \end{cases} \tag{4.1}$$

yields $\sigma_{ii}(R_{ii})$ directly from (2.25) in the form

$$\sigma_{ii}(R_{ii}) = A_{ii} - A'_{ii} R \tag{4.2}$$

and

$$F_{ii}(s) = \frac{A_{ii}}{s} (1 - e^{-sR}) - \frac{A'_{ii}}{s^2} (1 - e^{-sR}) + A'_{11} \frac{R}{s} e^{-sR} \tag{4.3}$$

Also for this system (2.23) holds, that is,

$$L_{ii}(s) - \frac{A'_{ii}}{s} = 0 \quad .$$

The off-diagonal elements of $\underline{\underline{L}}(s)$ in (2.19) yields

$$L_{21}(s) = G_{21}(s) [A_{11}+sF_{11}(-s)]+G_{22}(s)[A_{12}+sF_{12}(s)-sU^*_{12}(s)] \tag{4.4a}$$

$$L_{12}(s) = G_{11}(s) [A_{21}+sF_{21}(-s)-sU^*_{21}(s)]+G_{12}(s)[A_{22}+sF_{22}(-s)] \tag{4.4b}$$

Combining the above with (2.17) yields

$$L_{21}(s)-sU_{21}(s)=A_{21}+sG_{21}\left(\frac{A_{11}}{s}-F_{11}(s)\right)+sG_{22}\left[\frac{A_{12}}{s}-F_{12}(s)-U_{12}^{*}\right]$$

$$-s\sigma_{12}(s)-sU_{21}(s) \tag{4.5a}$$

$$L_{12}(s)-sU_{12}(-s)=A_{12}+sG_{12}\left[\frac{A_{22}}{s}-F_{22}(s)\right]+sG_{11}\left[\frac{A_{21}}{s}-F_{21}(s)-U_{21}^{*}\right]$$

$$-s\sigma_{12}(s)-sU_{12}(s) \tag{4.5b}$$

We introduce X(s)

$$X(s) \equiv \frac{L_{21}(s)}{s} - U_{21}(-s) - U_{12}(s) - \frac{A'_{21}}{s^2} - \frac{U_o}{s} \tag{4.6}$$

where

$$U_0 \equiv \lim_{s\to 0} \left(L_{21}(s) - \frac{A'_{21}}{s}\right), \tag{4.7}$$

We then see[26] that X(s) is entire and bounded in the right hand side of the complex s-plane since X(s) is finite as $R\ell s \to \infty$. In the left hand side of s-plane, X(s) also remains finite for $0 \leq \alpha \leq R$ since $L_{12}(s) = -L_{21}(s)$. Therefore we can say that X(s) is entire and bounded everywhere in the complex s-plane and by the Liouville theorem[18] X(s) is constant everywhere. This constant is zero as can be seen by looking at the value of X(s) at infinite $R\ell s$.

Hence, we obtain

$$L_{21}(s) = sU_{21}(-s) + sU_{12}(s) + \frac{A'_{21}}{s} + U_0 \tag{4.8a}$$

and similarly

$$L_{12}(s) = sU_{12}(-s) + sU_{12}(s) + \frac{A'_{12}}{s} - U_0 \tag{4.8b}$$

U_0 is found from (2.17) after taking inverse Laplace transform to be

$$U_0 = (A_{21} - A_{12})/2 \tag{4.9}$$

$\sigma_{12}(s)$ can therefore be rewritten as

$$\sigma_{12}(s) = \frac{A_{21}+A_{12}}{s} - \frac{A'_{21}}{s^2} - U_{21}(s) - U_{12}(s) + G_{21}(s)\left[\frac{A_{11}}{s} - F_{11}(s)\right]$$

$$+ G_{22}(s)\left[\frac{A_{12}}{s} - F_{12}(s) - U^*_{12}(s)\right] . \tag{4.10a}$$

where, if α vanishes, this reduces to the additive diameter case with equal diameters. In the case $0 < \alpha \leq R$, there will be breaks in $C_{12}(r)$ at $r = \alpha$ and at $r = R - \alpha$. Eq. (4.10) can be rewritten in the form

$$\sigma_{12}(s) = \frac{A_{21}}{s} - G_{21}(s)\left[\frac{A_{11}}{s} - F_{11}(s)\right] - U_{21}^{*} - \frac{L_{21}(s)}{s}$$

$$+ G_{22}(s)\left[\frac{A_{12}}{s} - F_{12}(s) - U_{12}^{*}(s)\right] \qquad (4.10b)$$

The last term in (4.10b) will contain terms of the form $e^{-s(R-\alpha)}$. It is therefore desirable to define a new function V(s) which has the same behavior as $L_{12}(s)$, that is, $e^{\pm\alpha s}/s$ at large s;

$$F_{12}(s) = s^{-1} A_{12} + e^{-\alpha s} V(s) - \left[\frac{L_{12}(s)}{s} + U_{12}^{*}(s)\right] = F_{21}(s) \qquad (4.11)$$

Using (4.3), we get for $\underline{\underline{H}}(s)$ defined in (2.18d)

$$H_{ii}(s) = \beta_i(s) + \gamma_i(s)\, e^{-sR}, \qquad (4.12)$$

where

$$\beta_i(s) = A'_{ii}/s \text{ and } \gamma_i(s) = -A'_{ii}/s + (A_{ii} - A'_{ii}R). \qquad (4.13)$$

Also from (4.5)

$$H_{12}(s) = -s\, e^{-Rs}\, V(s) + L_{12}(s) \qquad (4.14a)$$

$$H_{21}(s) = -s\, e^{-Rs}\, V(s) - L_{12}(-s). \qquad (4.14b)$$

Now if (2.19) is transformed to

$$\underline{\underline{H}}(-s)\ \underline{\underline{H}}(s) = \underline{\underline{L}}^{T}(s)\ [s\underline{\underline{I}} + \underline{\underline{H}}^{*}(-s)] \tag{4.15}$$

then the diagonal elements in (4.15) yield

$$L_{12}(s)\ L_{12}(-s) = V(s)\ V(-s) + \frac{\mu^2}{s^2} \tag{4.16}$$

where

$$\mu^2 \equiv A'_{ii} - (A'_{ii}R - A_{ii})^2 \tag{4.17}$$

the off-diagonal elements in (4.15) yield relations for V(s) and $L_{12}(s)$

$$L_{12}(-s) = \{s\gamma_1(-s)\ V(s) - s\gamma_2(s)\ V(-s)\}/\{s-\beta_1(s)-\beta_2(s)\} \tag{4.18a}$$

or

$$V(-s) = \{\gamma_1(-s)\ L_{12}(s)+\gamma_2(-s)L_{12}(-s)\}/s\{\beta_1(s)-\beta_2(s)\} \tag{4.18b}$$

and two relations are identities. Also

$$-\frac{\gamma_1(s)}{\beta_1-\beta_2} = b_1 s + a_1 \tag{4.19a}$$

$$\frac{\gamma_2(s)}{\beta_1-\beta_2} = b_2 s + a_2 \tag{4.19b}$$

$$a_1 = A'_{11}/(A'_{11}-A'_{22}) = \rho_1/(\rho_1-\rho_2) \tag{4.19c}$$

$$a_2 = A'_{22}/(A'_{11}-A'_{22}) = \rho_2/(\rho_2-\rho_1) \tag{4.19d}$$

$$b_1 = (A'_{11}R_{11}-A_{11})/(A'_{11}-A'_{22}) = -1/2a(1-\xi)-(1-\xi)/2(\rho_1-\rho_2) \tag{4.19e}$$

$$b_2 = (A'_{22}R_{22}-A_{22})/(A'_{11}-A'_{22}) = -1/2a(1-\xi)+(1-\xi)/2(\rho_1-\rho_2) \tag{4.19f}$$

$$\xi \equiv (\rho_1+\rho_2)\ R$$

that is

$$V(s) = (a_1 + b_1\ s)\ \frac{L_{21}(s)}{s} + (a_2 + b_2\ s)\ \frac{L_{12}(s)}{s} \tag{4.20}$$

On the other hand, $sL_{12}(s)$ is an analytic function and can be written in the form

$$sL_{12}(s) = \mu\ [\frac{P(s)}{s^2} - \frac{\Phi(s)}{s}] \tag{4.21}$$

with two even and analytic functions, P(s) and $\Phi(s)$, of s.

Finally we obtain, from (4.16) with (4.20) and (4.21), the functional relationship

$$\Psi^2(s) - E(s)\,\Phi^2(s) = A \tag{4.22}$$

with

$$\Psi(s) \equiv AP(s) + B\Phi(s) \tag{4.23a}$$

$$E(s) \equiv (s^2-4\mu^2)/a^2(\rho_1-\rho_2)^2 \tag{4.23b}$$

$$A = (b_1+b_2)^2 = \frac{1}{a^2(1-\xi)^2} \tag{4.23c}$$

$$B = 2(a_1b_2-a_2b_1) = \frac{\rho_1+\rho_2-a(1-\xi)^2}{a(1-\xi)(\rho_2-\rho_1)} \tag{4.23d}$$

$$= \sqrt{A}\,\frac{\rho_1+\rho_2}{\rho_2-\rho_1} + \frac{1-\xi}{\rho_1-\rho_2}$$

The solution of (4.22) is obtained in the following form[13]

$$\Psi(s) = \pm\sqrt{A}\ \cosh[\alpha\sqrt{s^2-4\mu^2}] \tag{4.24a}$$

$$\Phi(s) = \pm\sqrt{\frac{A}{E(s)}}\ \sinh[\alpha\sqrt{s^2-4\mu^2}] \tag{4.24b}$$

Comparing these solutions with (4.8) and (4.21) we can determine

that the signature of $\Psi(s)$ and $\Phi(s)$ are both positive. The compressibility of this system is found from the definition (2.8) with (4.2)

$$A_{11} = \frac{\rho_1-\rho_2 + a\left[(1-\rho_2 R)^2-\rho_1 R^2\right]}{2(1-\xi)} \tag{4.25}$$

where $a \equiv A_{22}+A_{11}$. The value of $\Phi(s)$ yields using (4.13)

$$2\mu\sqrt{\rho_1\rho_2}\;\Phi(0) = (\rho_2+\rho_1)\,A_{11} - \rho_1 a \tag{4.26}$$

(4.25) and (4.26) give a and A_{11} in terms of μ,

$$a = \frac{\rho + 2\sqrt{\rho_1\rho_2}\,\sin 2\mu\alpha}{(1-\xi)^2} \tag{4.27}$$

$$A_{11} = \frac{\rho_1}{kT}\frac{\partial P}{\partial \rho_1} = \rho_1\left[\frac{1}{(1-\xi)^2} + \frac{\sqrt{\rho_1\rho_2}\,\sin 2\mu\alpha}{\rho_1(1-\xi)^2}\left\{1+\rho_1-\rho_2)R\right\}\right] \tag{4.28}$$

The contact values of $g_{ij}(r)$ and $C_{ij}(r)$ are seen from (2.23) and (4.3)

$$g_{ii}(R) = -C_{ii}(R) \tag{4.29a}$$

$$= \frac{A_{ii}}{\rho_i} - \frac{A'_{ii}}{\rho_i}R\ ,$$

that is,

$$g_{11}(R) = \frac{1}{1-\xi} + \frac{\sqrt{\rho_1\rho_2}\ \sin 2\mu\alpha}{\rho_1(1-\xi)} \tag{4.29b}$$

$$g_{22}(R) = \frac{1}{1-\xi} + \frac{\sqrt{\rho_1\rho_2}\ \sin 2\mu\alpha}{\rho_2(1-\xi)} \tag{4.29c}$$

and

$$\sqrt{\rho_1\rho_2}\quad g_{12}(R_{12}) = \lim_{s\to\infty} sG_{12}(s)\ e^{\alpha s} \tag{4.30}$$

$$= \sigma_{12}(R_{12_+})$$

$$= \lim_{s\to\infty} sF_{12}(-s)\ e^{-\alpha s}$$

$$= \sigma_{12}(R_{12_-})$$

$$= \mu$$

where μ is related to $\Phi(0)$, using (4.17) by

$$\mu^2 = \frac{\sqrt{\rho_1\rho_2}^{\,2}}{(1-\xi)^2}\ (1-\sin^2 2\mu\alpha) \tag{4.31}$$

Defining

$$2\mu\alpha \equiv q \tag{4.32a}$$

(4.31) can be rewritten

$$q = \eta \cos q \tag{4.32b}$$

Here again we find the non-unique solution of the P.Y. solution, as we did in the Widom-Rowlinson model, for $\eta \geq \eta_o \cong 2.80$. We note however again that only one branch of (4.32b), that is, $0 \leq 2\mu\alpha < \pi/2$, yields a continuous pressure.

We can also verify thermodynamic stability of this solution. This requires that the matrix $M_{\ell j} = \frac{\partial \mu_\ell}{\partial \rho_j}$ be positive. In fact,

$$(\rho_1\rho_2)^2 \det (M_{ij}) = [A_{11}+\rho_1\rho_2\int C_{12}(r)dr] \times [A_{22}+\rho_1\rho_2\int C_{12}(r)dr]$$

$$- \rho_1^2\rho_2^2 [\int C_{12}(r)dr]^2 > 0 \qquad (4.33)$$

The equation of state for two different ways of getting thermodynamics are

$$\frac{P^v}{kT} = \rho_1+\rho_2+\frac{\rho_1^2+\rho_2^2}{1-\xi} \alpha + \frac{\sqrt{\rho_1\rho_2}}{1-\xi} \xi \sin (2\mu\alpha) \qquad (4.34)$$

$$+ 2(R+\alpha) \sqrt{\rho_1\rho_2} \mu$$

and $\frac{P^c}{kT}$ from (4.28).

As shown in this section, our system yields the same relation for all thermodynamic quantities with those obtained by Lebowitz and Zomick[9] regardless of the different distances of closest approach between particles.

4-2. Three dimensional solution

This system resembles very much the system considered by Lebowitz and Zomick. The results from Chapter 2 for the three dimensional case yield for this system

$$\sigma_{ii}(r) = A_{ii} R + B_{ii} R^2 + \frac{A'_{ii} R^4}{24} \tag{4.35}$$

and

$$F_{ii}(s) = \frac{A_{ii}}{s^2} + \frac{2B_{ii}}{s^3} + \frac{A'_{ii}}{s^5} - e^{-sR} \Big\{ \frac{1}{s}\Big[A_{ii}R + B_{ii}R^2 + \frac{A'_{ii}R^4}{24}\Big]$$

$$+ \frac{1}{s^2}\Big[A_{ii} + 2B_{ii}R + \frac{A'_{ii}R^3}{6}\Big] + \frac{1}{s^3}\Big[2B_{ii} + \frac{A'_{ii}R^2}{2}\Big]$$

$$+ \frac{A'_{ii}R}{s^4} + \frac{A'_{ii}}{s^5} \Big\} \tag{4.36}$$

The off-diagonal elements of (2.44) are

$$L_{12}(s) = G_{11}(s)\,[A_{21} - s^2 F_{21}(-s) - sU^*_{21}] + G_{12}(s)\,[A_{22} - s^2 F_{22}(-s)] \tag{4.37a}$$

$$L_{21}(s) = G_{22}(s)\,[A_{12} - s^2 F_{12}(-s) - sU^*_{12}] + G_{21}(s)\,[A_{11} + s^2 F_{11}(-s)] \tag{4.37b}$$

or in terms of $\sigma_{ij}(s)$

$$L_{12}(s)=G_{11}(s)\,[A_{21}-sU^{*}_{21}(s)] + G_{12}(s)A_{22}+s^{2}\sigma_{12}(s)-sA_{12}-s^{2}G_{11}(s)F_{12}(s)$$

$$-s^{2}\,G_{12}F_{22} + s^{2}U^{*}_{12} \qquad (4.38a)$$

$$L_{21}(s)=G_{22}(s)\,[A_{12}-sU^{*}_{12}(s)] + G_{21}(s)A_{11}+s^{3}\sigma_{21}(s)-sA_{21}-s^{2}G_{22}(s)F_{21}(s)$$

$$-s^{2}\,G_{12}F_{11} + s^{2}U^{*}_{21} \qquad (4.38b)$$

which make $L_{21}(s)$ and $L_{12}(s)$ related to bounded functions in such a way that

$$L_{12}(s) + s^{2}U_{12}(-s)+s^{2}U_{21}(s) \xrightarrow{s\to\infty} -sA_{12}+s^{2}U_{12}(s)$$

$$+s^{2}U_{21}(s)+s\sigma^{(1)}_{12}(o) \qquad (4.39)$$

(for $R > \alpha$)

where the super script (n) means the nth derivative with respect to the argument r.

On the other hand from the first derivative of (2.28) we get

$$U_{ij}(s) \xrightarrow{s\to\infty} \frac{A_{ij}-\sigma^{(1)}_{12}(o)}{2s} \quad (i \neq j) \qquad (4.40)$$

Noting the boundedness of $[L_{ij}(s) - A'_{ij}/s^2]$ as $s \to 0$, the $B_{ij}(s)$'s $(i \neq j)$ are bounded and entire[26] everywhere in the complex s-plane since $L_{12}(s)=L_{12}(-s)$, etc. Hence using the Liouville theorem[18] we get

$$L_{12}(s) + s^2U_{12}(-s) + s^2U_{21}(s) - \frac{A'_{12}}{s^2} - sU_0 = 2\,B_{12} \tag{4.41a}$$

$$L_{21}(s) + s^2U_{21}(-s) + s^2U_{12}(s) - \frac{A'_{12}}{s^2} + sU_0 = 2\,B_{12} \tag{4.41b}$$

where $U_0 = (A_{21} - A_{12})/2$

and

$$\sigma_{12}(s) = \frac{A_{12}}{s^2} - G_{11}(s)\left[\frac{A_{21}}{s^2} - \frac{U^*_{21}}{s^2}(s) - \frac{1}{s}\,F_{12}(s)\right] - \frac{1}{s^3}\,G_{12}(s)$$

$$\times\,[A_{22} - s^2F_{22}] - \frac{U^*_{12}}{s} + \frac{L_{12}(s)}{s^3} \tag{4.42}$$

In the first bracket in (4.42) there is a term with the asymptotic form $e^{-(R\pm\alpha)s}$ and this prompts us to define a new function $V(s)$ having the asymptotic form $e^{\pm\alpha s}$ as $|R\ell s| \to \infty$. The second bracket doesn't contribute to the $\sigma_{ij}(r)$ $(r \leq R_{12})$ or $F_{ij}(s)$.

Let us write $F_{12}(s)$ in terms of $V(s)$, $U^*_{12}(s)$ and $L_{12}(s)$ which have the asymptotic behavior $e^{\pm s\alpha}$ as $|R\ell s| \to \infty$

$$F_{12}(s) = \frac{A_{12}}{s^2} + \frac{e^{-sR}}{s^3} V(s) - \frac{U^*_{12}}{s} + \frac{L_{12}(s)}{s^3} = F_{21}(s) \tag{4.43}$$

Using the notation of (2.44) this can be transformed to

$$\underline{\underline{H}}(-s)\ \underline{\underline{H}}(s) = \underline{\underline{L}}(-s)\ [s^3 \underline{\underline{I}} + \underline{\underline{H}}^*(s)]\ /s \tag{4.44}$$

where

$$H_{ii}(s) = \beta_i(s) + \gamma_i(s)\ e^{-sR} \tag{4.45}$$

$$H_{12}(s) = -\frac{e^{-Rs}}{s} V(s) - \frac{L_{12}(s)}{s} \tag{4.46a}$$

$$H_{21}(s) = -\frac{e^{-Rs}}{s} V(s) - \frac{L_{21}(-s)}{s} \tag{4.46b}$$

$$\beta_i = -\frac{2B_{ii}}{s} - \frac{A'_{ii}}{s^3} \tag{4.47a}$$

$$\gamma_i = s\ [A_{ii}R + B_{ii}R^2 + \frac{A'_{11}R^4}{24}] + [A_{ii} + 2B_{ii}R + \frac{A'_{ii}}{6} R^3]$$
$$+ \frac{1}{s}\ [2B_{ii} + \frac{A'_{ii}}{2} R^2] + \frac{A'_{ii}}{s^2} R + \frac{A'_{ii}}{s^3} \tag{4.47b}$$

Very similarly to the one-dimensional case in the previous section, we get the diagonal components of (4.44) to yield

$$L_{12}(s)\ L_{12}(-s) = V(s)\ V(-s) - s^2\ h(s) \tag{4.48}$$

where

$$h(s) \equiv - \{\gamma_i(s)\ \gamma_i(-s) + \beta_i(s)\ [s^3 + \beta_i(s)]\}$$

$$\equiv \quad A'_{ii} - A^2_{ii} + \frac{2}{3} A'_{ii}\ A_{ii}\ R^3 + \tfrac{1}{2} B_{ii}\ A'_{ii}\ R^4 + \frac{1}{72} A'^{\,2}_{ii}\ R^6$$

$$+ s^2\ \{2B_{ii} + [A_{ii}R + B_{ii}R^2 + \frac{1}{24}\ A'_{ii}R^4]^2\} \quad (i=1,2)$$

$$\equiv \quad h_2 + h_1 \quad s^2 \tag{4.49}$$

The off-diagonal components give two identical relations

$$V(-s) = - C_1(-s)\ L_{12}(-s) - C_2(-s)\ L_{12}(s) \tag{4.50}$$

where

$$C_1(-s) = - \gamma_1(-s)\ [\beta_1(-s) + \beta_2(s)]^{-1} \tag{4.51a}$$

$$C_2(-s) = \quad \gamma_2(-s)\ [\beta_1(-s) + \beta_2(s)]^{-1} \tag{4.51b}$$

Also from (4.41) $s^2\ L_{12}(s)$ proves to be an analytic function which can be decomposed into an odd and an even part. Using the two even analytic function $P(s)$ and $\Phi(s)$ we can write

$$L_{12}(s) = \eta_-\ s\Phi(s) - \frac{P(s)}{s^2} \tag{4.52}$$

where

$$\eta_- \equiv 2\pi\,\alpha^3\,(\rho_1 - \rho_2) \tag{4.53}$$

and we have used the fact that the odd part of $L_{12}(s)$ vanishes when $\rho_1 = \rho_2$ or when $\alpha = 0$.

In fact $\Phi(s)$ and $P(s)$ are more explicitly

$$\Phi(s) = \frac{L_{12}^{*}(s)}{2s\eta_-}$$

$$= \frac{A_{21}-A_{12}}{2\eta_-} + s\int_0^R (-\sinh sr)dr \int_{r+R_{11}}^{R+R_{11}} \frac{\sigma_-(r-y)\sigma_{12}(y)dy}{\eta_-} \quad \text{(from (4.41))} \tag{4.54a}$$

$$P(s) = -\,s^2\,L_{12}^{+}(s)$$

$$= 2B_{12} + \frac{A'_{12}}{s^3} - \tfrac{1}{2}\left[s^2\,U_{12}^{*}(s) + s^2\,U_{21}^{*}(s)\right] \tag{4.54b}$$

Both the diagonal and off-diagonal elements of (4.44) yield a functional relationship, that is, from (4.48) and (4.50) using (4.52) yields,

$$\Psi^2(s) - \Phi^2(s)\,E(s) = -\,h(s)\,a(s) \tag{4.55}$$

where

$$\Psi(s) \equiv \frac{a(s)\ P(s) + b(s)\ \Phi(s)}{s^3\ \beta(s)} \tag{4.56a}$$

$$a(s) \equiv -\frac{\gamma_-(s)\ \gamma_-(-s)}{\eta_-^2} - \beta^2(s) \tag{4.56b}$$

$$\beta(s) \equiv \frac{\beta_2(s)-\beta_1(s)}{\eta_-} \tag{4.56c}$$

$$b(s) \equiv b_1 s^4 + b_2 s^2 + b_3 = \frac{s^3}{2\eta_-}\left[\gamma_+(-s)\gamma_-(s)+\gamma_+(s)\gamma_-(-s)\right] \tag{4.56d}$$

$$b_1(s) \equiv -R^2(B_-A_+-B_+A_-)/\eta_- - R^4 b_3/8 + R^5(B_-A_+'-B_+A_-')/\eta_- \tag{4.56e}$$

$$b_2(s) \equiv 2(B_-A_+-B_+A_-)/\eta_- - b_3^2 + R^3(B_-A_+'-B_+A_-')/3\eta_- \tag{4.56f}$$

$$b_3(s) \equiv 2(A_-'A_+-A_-A_+')/\eta_- = -4A_{12}'\Phi(0) \tag{4.56g}$$

$$C(s) \equiv s^6\ \{\gamma_+(s)\gamma_+(s)+[\beta_2(s)-\beta_1(s)]^2\} \tag{4.56h}$$
$$\equiv C_1 s^8 + C_2 s^6 + C_3 s^4 + C_4 s^2 + C_5$$

$$b^2(s) - a(s)\ C(s) = s^6\ \{\beta_2(s)-\beta_1(s)\}^2\ E(s)/\eta_-^2 \tag{4.56i}$$

$$E(s) \equiv s^6 - 4h(s) \tag{4.56j}$$

$$a_1 \equiv \sigma_-^2/\eta_-^2 = (A_-R+B_-R^2 + \frac{A_-'}{24}R^4)^2/\eta_-^2 \tag{4.56k}$$

$$a_2 \equiv (-A_-^2 + \frac{2}{3}A_-A_-'R^3 + \tfrac{1}{2}A_-'B_-R^4 + \frac{1}{72}A_-'^2\ R^6)/\eta_-^2 \tag{4.56l}$$

$$C_1 \equiv -\sigma_+^2 = \eta_- a_1 + 4(B_+ - h_1) \tag{4.56m}$$

$$C_2 \equiv \eta_- a_2 + 2A'_+ - 4h_2 \tag{4.56n}$$

$$C_3 \equiv - 16\ B_1B_2 = 4B_-^2 - B_+^2 \tag{4.56o}$$

$$C_4 \equiv - 4(B_+A'_+ - B_-A'_-) \tag{4.56p}$$

$$C_5 \equiv A_-'^2 - A_+'^2 = - 4\ A'_1\ A'_2 \tag{4.56q}$$

The formal solution to (4.55) can be obtained[13] in the same way as was done in the case when R = 0. Calling the two zeros of h(s) and a(s) $\pm z_1$ and $\pm z_2$ respectively we have

$$\Phi(s) = - \frac{\sigma_{12}(R) \quad (s-z_1)\ (s-z_2)\ \sin\left[I(s)\right]}{(-i)\sqrt{s^6+4\sigma_{12}^2(s^2-z_1^2)}}\ , \tag{4.57a}$$

$$\Psi(s) = - \sigma_{12}(R)\ (s-z_1)(s-z_2)\ \cos\left[I(s)\right]\ , \tag{4.57b}$$

where

$$I(s) = - i\frac{\sqrt{E(s)}}{2\pi i}\ \frac{2\pi i}{2}\left\{\int_{z_1}^{z_2} \frac{dt}{\sqrt{E(t)}^+(t-s)} + \int_{-z_1}^{-z_2} \frac{dt}{\sqrt{E(t)}^+(t-s)} - \frac{\ln J(s)}{\sqrt{E(s)}}\right\} \tag{4.58}$$

and

$$J(s) \equiv \frac{(s-z_1)\ (s-z_2)}{(s+z_1)\ (s+z_2)} \quad , \quad z_1 \equiv \sqrt{\frac{h_2}{h_1}} \quad \text{and} \quad z_2 \equiv \sqrt{\frac{a_2}{a_1}} \tag{4.59}$$

Except for s in the intervals, $z_2 > s > z_1$ and $-z_1 > s > -z_2$ we can write the above in the form

$$\Phi(s) = -\sigma_{12}(R)\ \frac{[(s^2-z_1^2)(s^2-z_2^2)]^{\frac{1}{2}}\sin[I_1(s)]}{[s^6+4\sigma_{12}^2(s^2-z_1^2)]} \tag{4.60}$$

$$I_1 = -\ i\ [s^6+4\sigma_{12}^2(s^2-z_1^2)]^{\frac{1}{2}}\int_{z_1}^{z_2} \frac{t\,dt}{[t^6+4\sigma_{12}^2(t^2-z_1^2)]^{\frac{1}{2}}(t^2+k^2)} \tag{4.61}$$

Just as in 3-3, our purpose is to get a parametric solution in terms of z_1. z_2 can be determined by considering the asymptotic behavior of the $\underline{\underline{L}}(s)$ matrix together with B_{12}. What we get immediately is

$$h_1 = 2B_{ii} + \sigma_{ii}^2(R_{ii}) \tag{4.62}$$

$$h_2 = A'_{ii} - \sigma_{ii}^{(1)2} + 2\sigma_{ii}^{(2)}\ \sigma_1 = \sigma_{12}^{(1)2} - 2\sigma_{12}\ \sigma_{12}^{(2)} \tag{4.63}$$

$$\lim_{s \to 0} P(s) = -A'_{12} = \frac{\Psi_0 A'_- - b_3\Phi_0}{a_2} \tag{4.64}$$

$$= C_4/8\ A'_{12} \tag{4.65}$$

In addition, we can derive the following relations,

$$- 4\, h_2\, A_-'^2/\eta_-^2 = b_3^2 - a_2\, C_5 \tag{4.66a}$$

$$- 4\, A_-'^2 h_1/\eta_-^2 + 16\, \frac{B_-}{\eta_-}\, \frac{A_-'}{\eta_-}\, h_2 = a_1\, C_5 + a_2 C_4 - 2b_3 b_2 \tag{4.66b}$$

$$16\, \frac{B_-}{\eta_-}\, \frac{A_-'}{\eta_-}\, h_1 + 16\, \frac{B_-^2}{\eta_-^2}\, h_2 = - b_2^2 - 2b_1 b_3 + a_1 C_4 + a_2 C_3 \tag{4.66c}$$

$$\frac{A_-'^2}{\eta_-^2} - 16\, h_1\, \frac{B_-^2}{\eta_-^2} = 2b_1 b_2 - a_1 C_3 - a_2 C_2 \tag{4.66d}$$

$$4\, \frac{A_-'}{\eta_-}\, \frac{B_-}{\eta_-} = b_1^2 - a_2\, C_1 - a_1\, C_2 \tag{4.66e}$$

$$4\, \frac{B_-'^2}{\eta_-^2} = - a_1\, C_1 \tag{4.66f}$$

From these equations we can, in principle, solve for B_-, B_+, $\frac{A_-}{\eta_-}$ and A_+ which will then determine z_2 uniquely. Because of the complexity of (4.66) we have not been able to obtain an explicit solution of these equations but hope it will be solved explicitly later.

APPENDIX 1

Graphs for Widom-Rowlinson Model

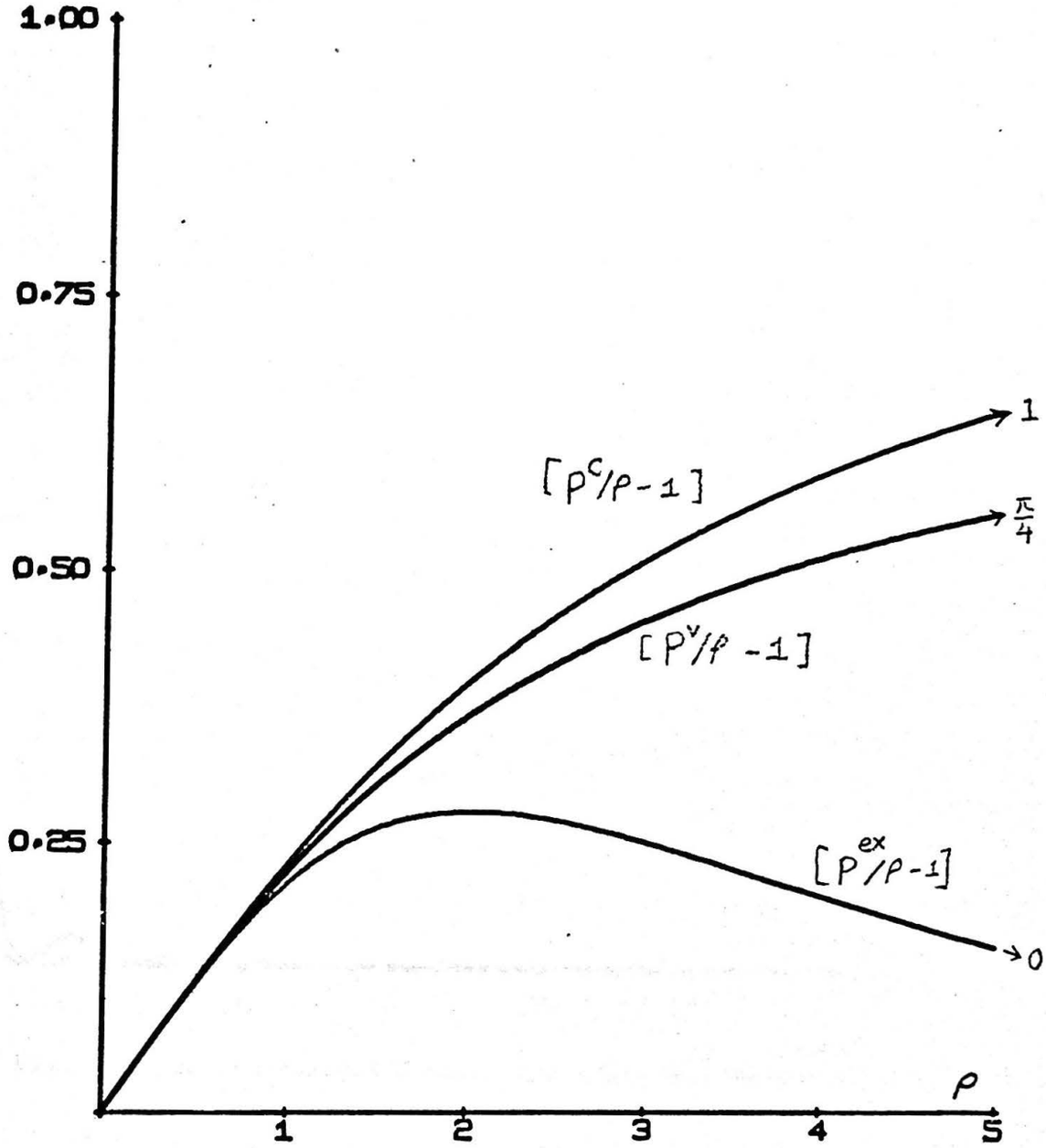


Fig. 5. One dimensional pressures for the Widom Rowlinson Model vs. the total density $\rho = \rho_1 + \rho_2$, where $\rho_1 = \rho_2$ and $2\alpha = 1$. P^{ex} is the pressure from the exact result by J. Lebowitz and D. Zomick, P^v the virial pressure and P^c the compressibility pressure. $P^{ex}/\rho \to 1 + \frac{\pi}{4}$ and $P^c/\rho \to 2$ when $\rho \to \infty$, while they are in good agreement for $\rho < 1$.

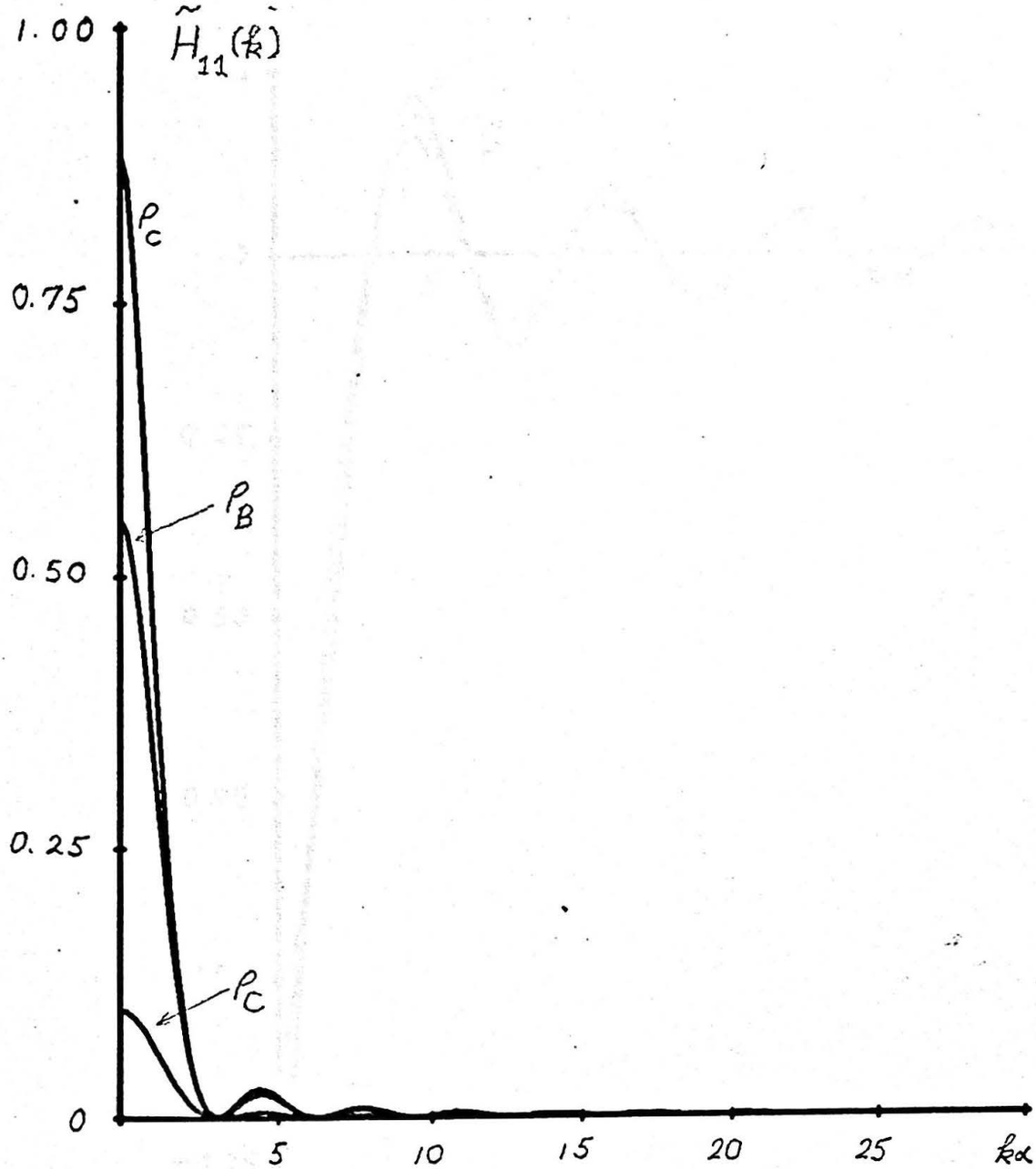


Fig. 6A. One dimensional Fourier transform of [the radial distribution function -1] between like particles for the Widom-Rowlinson model.

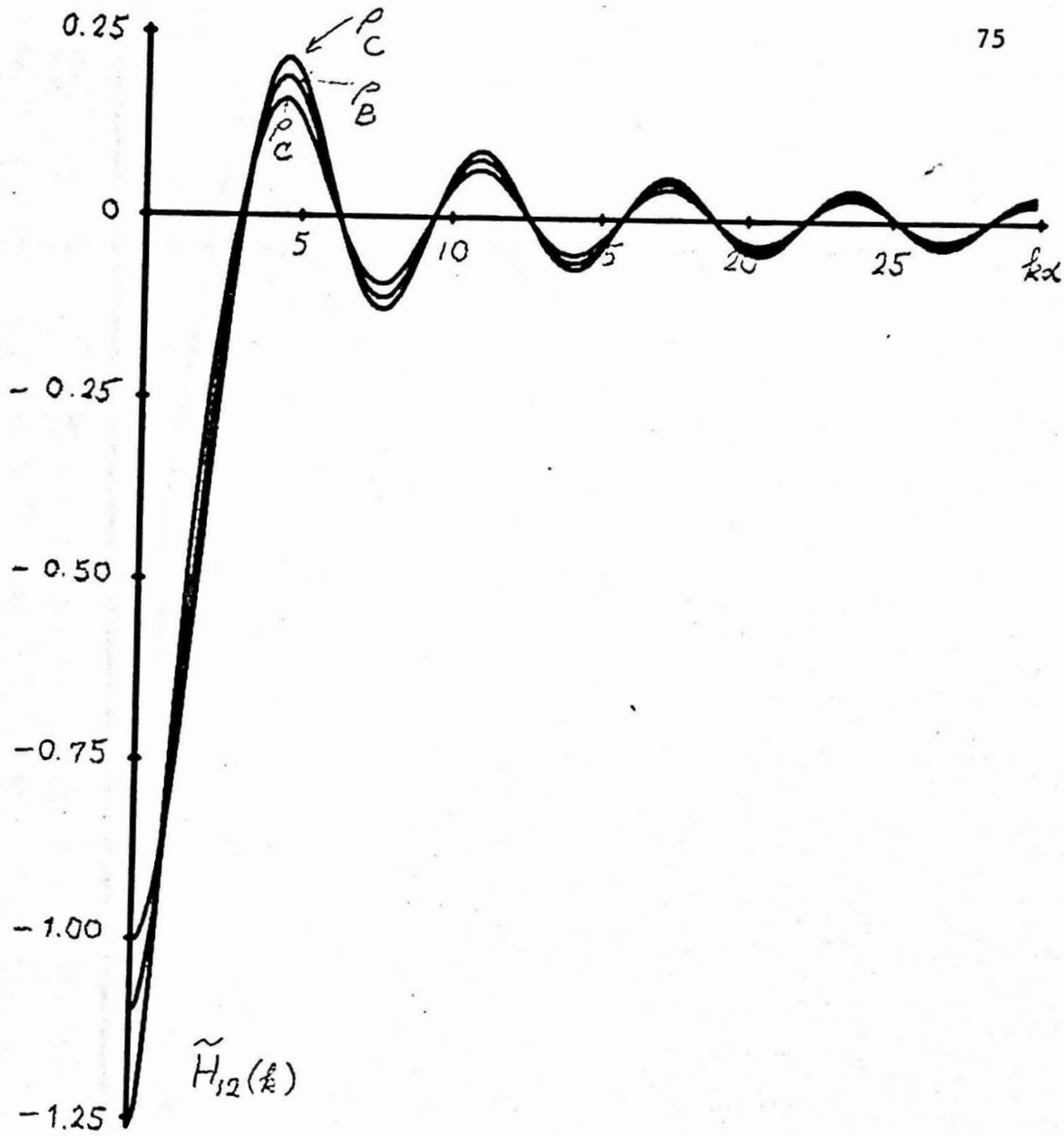


Fig. 6B. One dimensional Fourier transform of [the radial distribution function -1] between distinct particles for the Widom-Rowlinson model.

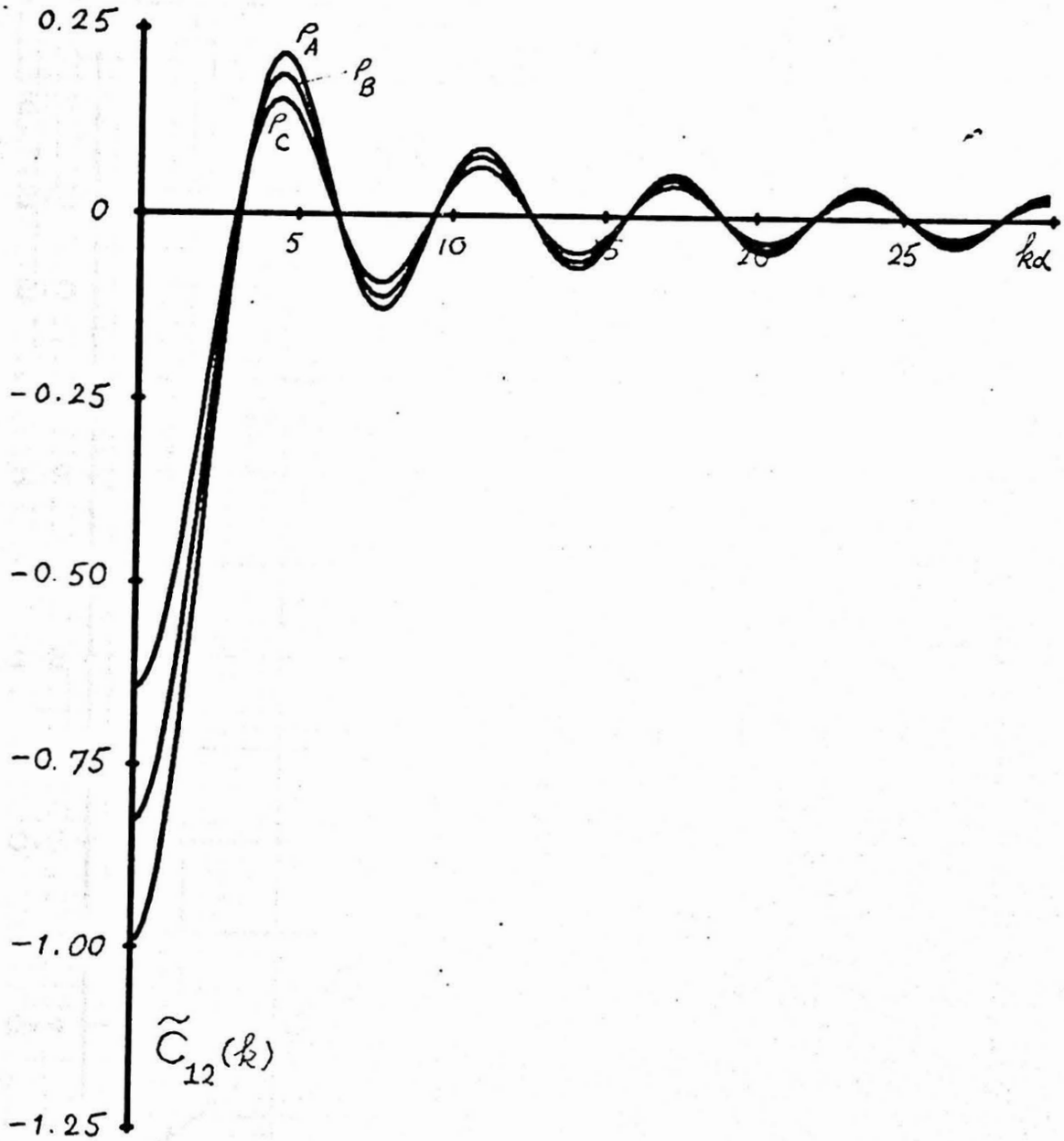


Fig. 7. One dimensional Fourier transform of the direct correlation function between distinct particles for the Widom-Rowlinson model.

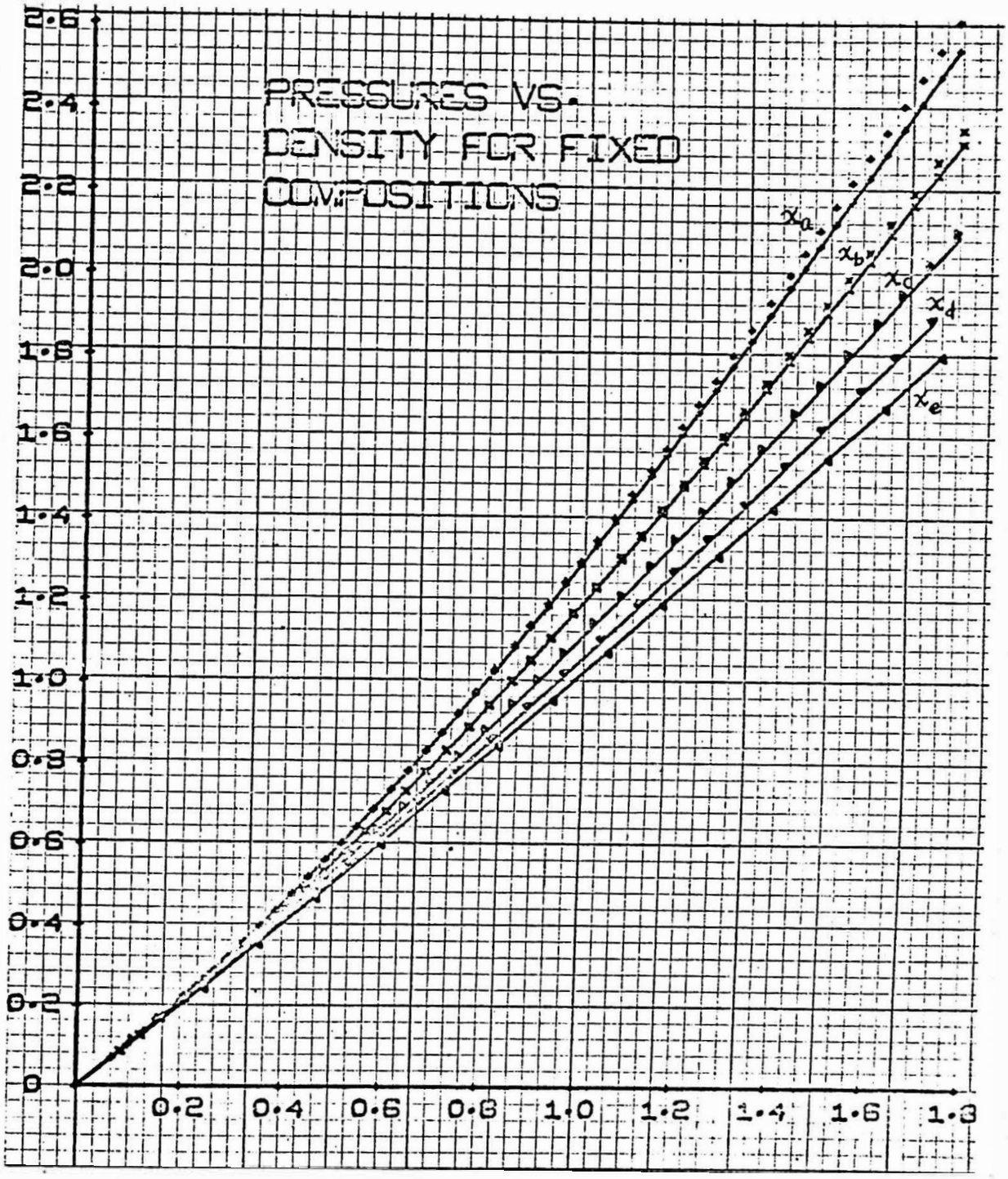


Fig. 8. Three dimensional pressures vs. the total density at fixed compositions for Widom-Rowlinson model. Disconnected points correspond to the compressibility pressure and connected points to the virial pressure. They are drawn for five values of composition ratios, $x_i = \rho_i/\rho$, that is, $x_a = 0.5$, $x_b = 0.4$, $x_c = 0.2$, $x_d = 0.1$ and $x_e = 0.05$.

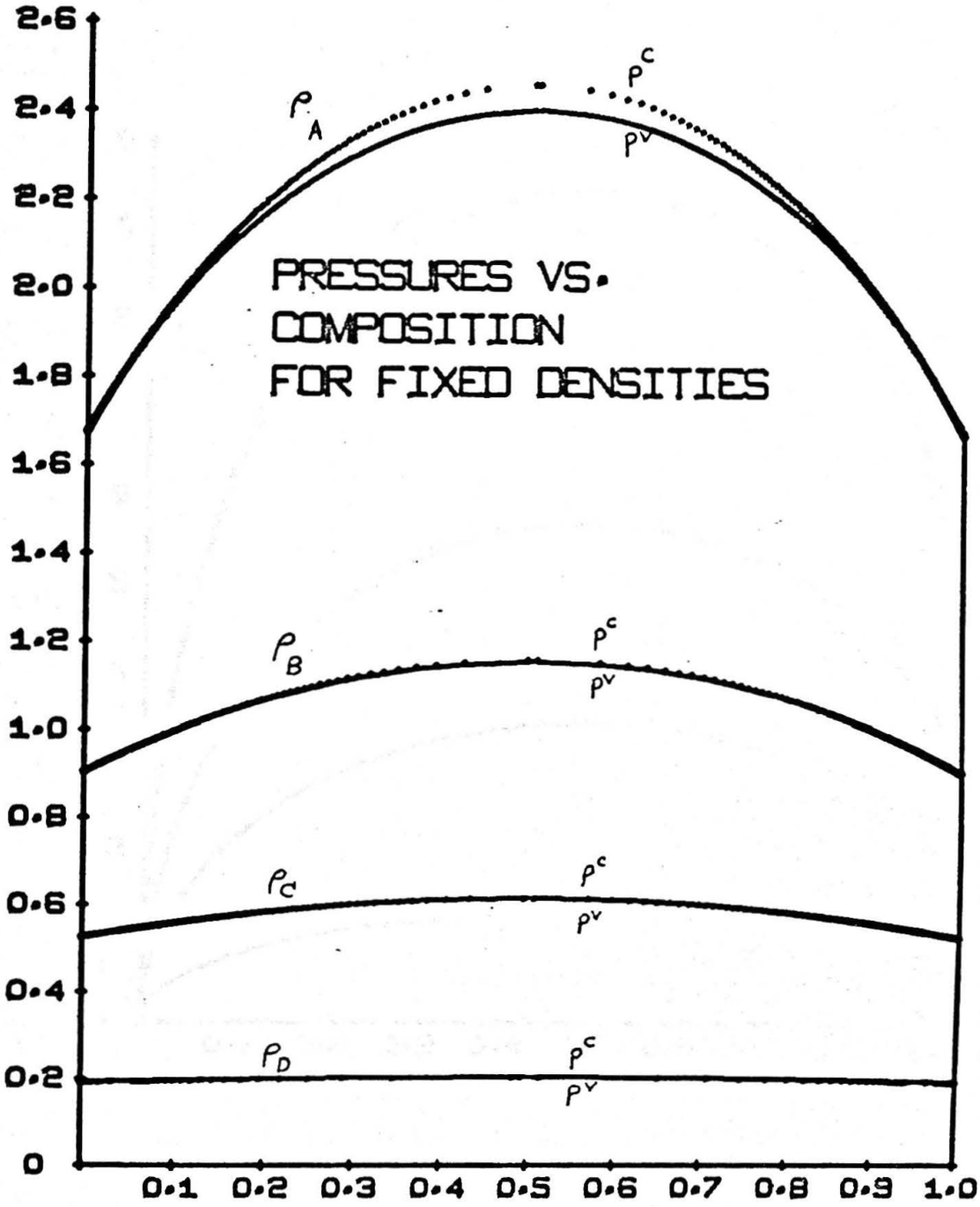


Fig. 9. Three dimensional pressures vs. composition at fixed densities for Widom-Rowlinson model. The virial and compressibility pressures, p^v and p^c are shown with connected and disconnected points respectively for four densities; $\rho_A = 1.6725$ $\rho_B = 0.9031$, $\rho_C = 0.5262$ and $\rho_D = 0.1915$ where $2\pi\alpha^3$ is set equal to unity.

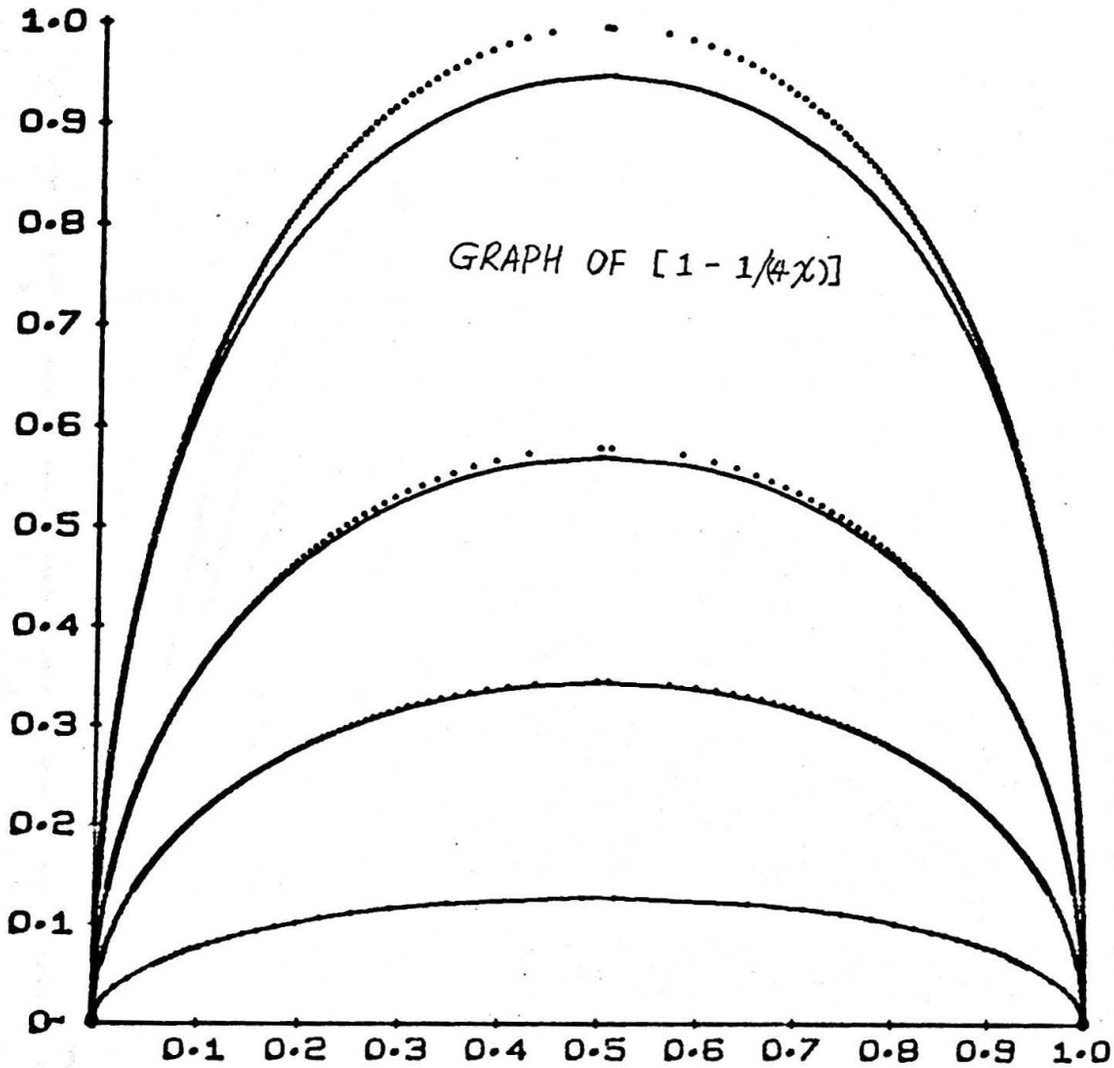


Fig. 10. $[1 - 0.25\,\chi^{-1}]$ vs. composition at fixed densities in three dimensional Widom Rowlinson model. The susceptibility, χ, diverges at the density, $\rho \cong 1.673$ for the compressibility relation and at $\rho \cong 1.78$ for the virial expression. $\rho_A = 1.6725$, $\rho_B = 0.9031$, $\rho_C = 0.5262$ and $\rho_D = 0.1915$ where $2\pi\alpha^3$ is set equal to unity.

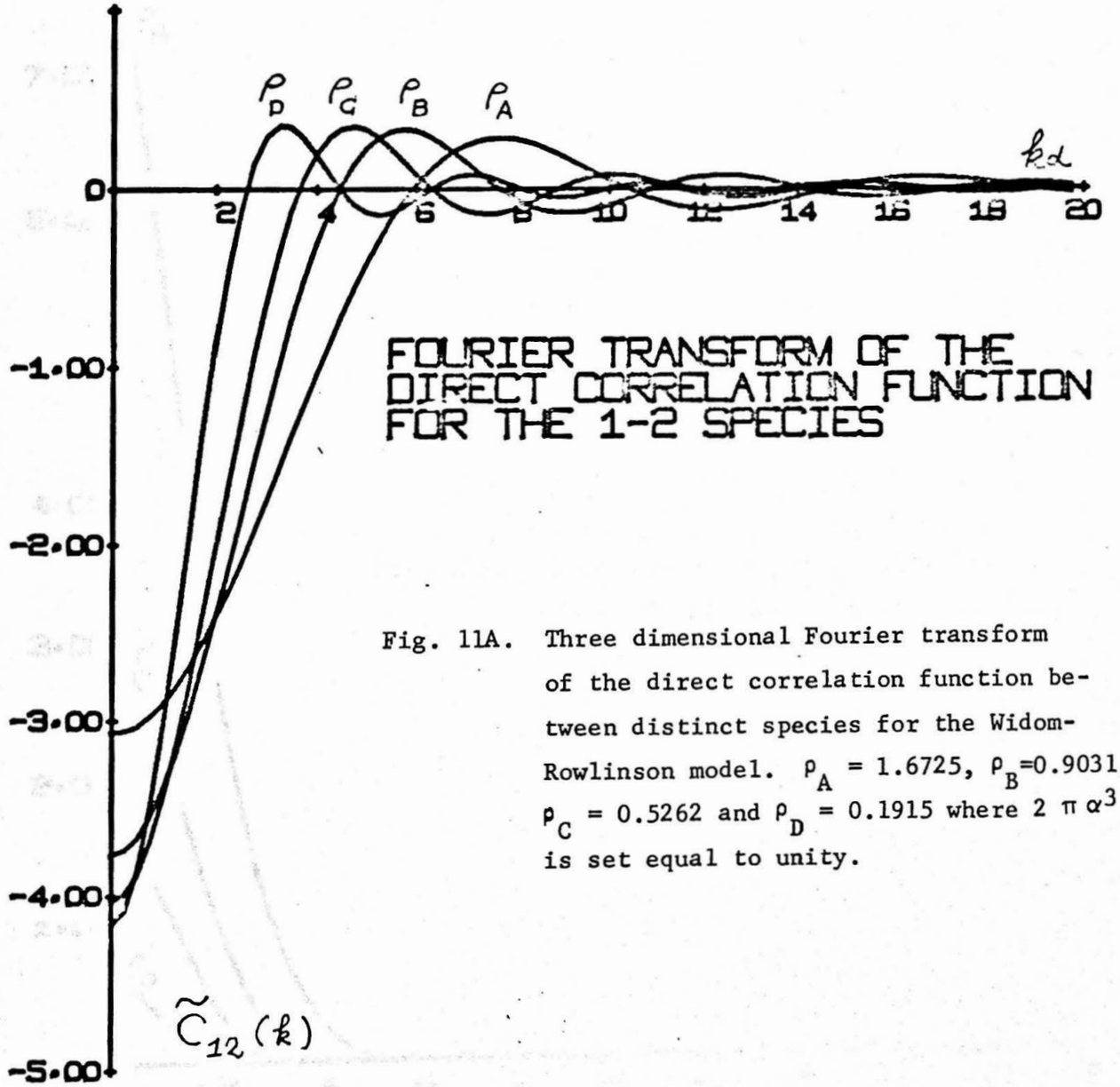
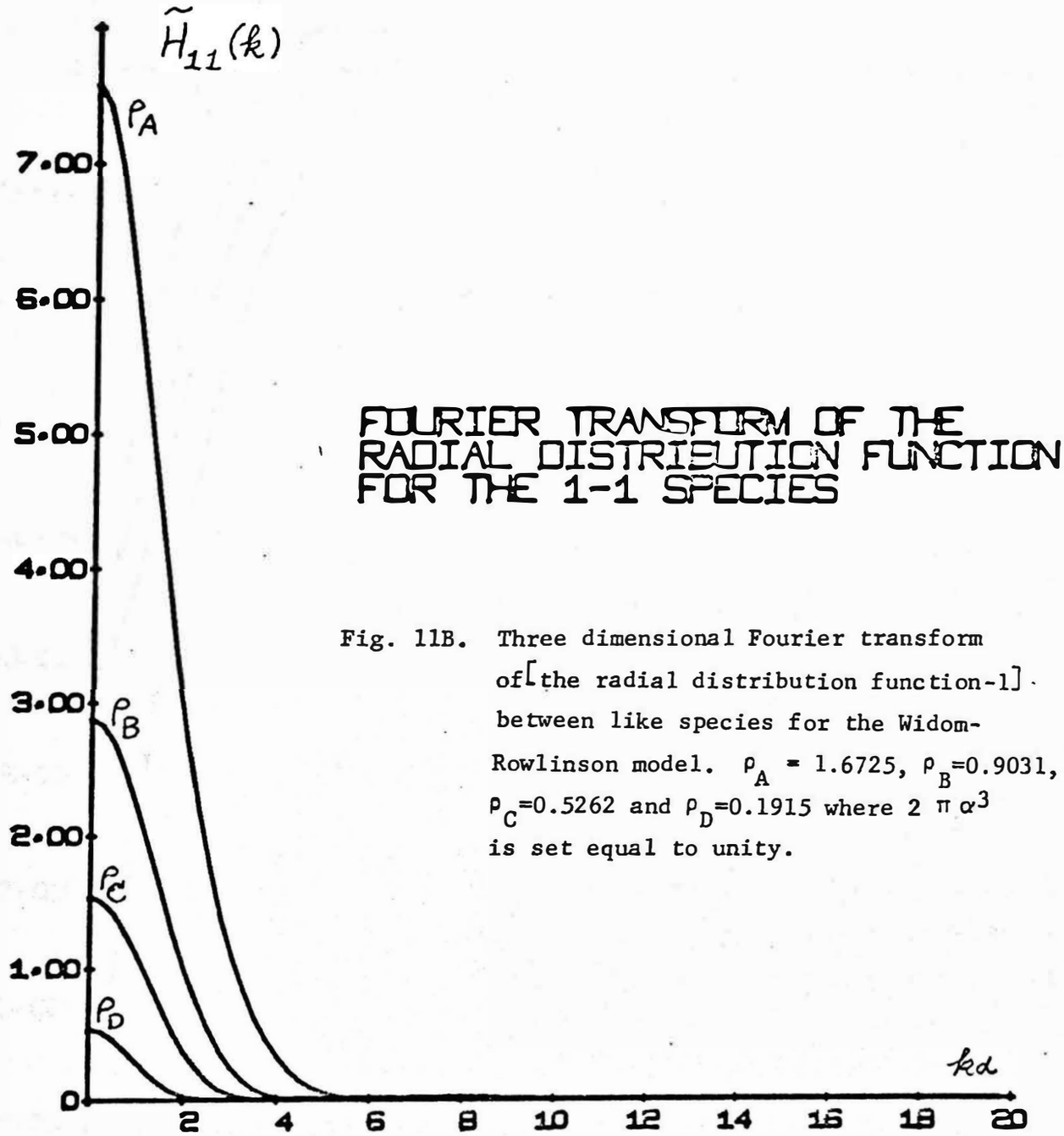
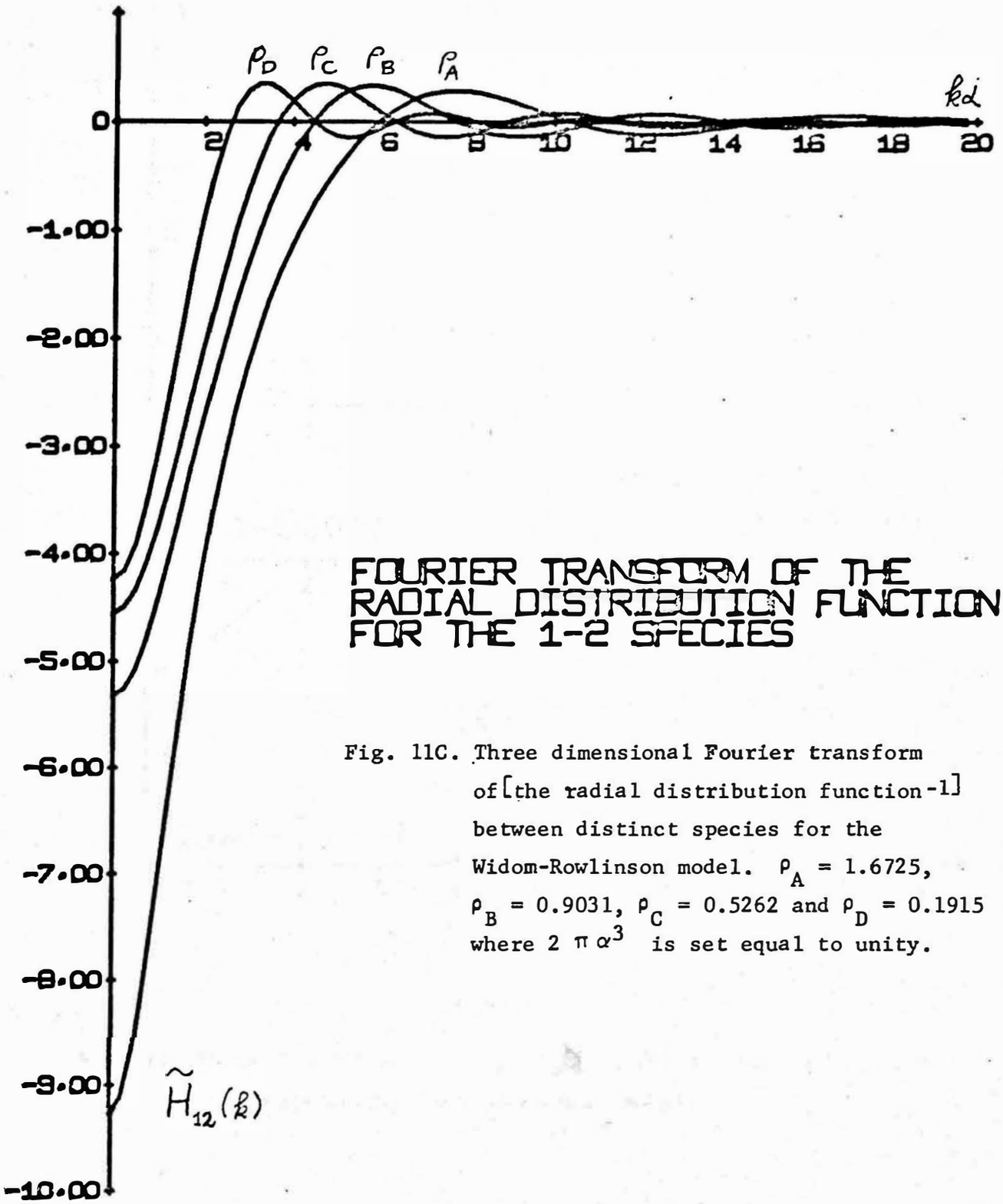


Fig. 11A. Three dimensional Fourier transform of the direct correlation function between distinct species for the Widom-Rowlinson model. $\rho_A = 1.6725$, $\rho_B = 0.9031$, $\rho_C = 0.5262$ and $\rho_D = 0.1915$ where $2\pi\alpha^3$ is set equal to unity.



FOURIER TRANSFORM OF THE RADIAL DISTRIBUTION FUNCTION FOR THE 1-1 SPECIES

Fig. 11B. Three dimensional Fourier transform of [the radial distribution function-1] between like 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.



FOURIER TRANSFORM OF THE RADIAL DISTRIBUTION FUNCTION FOR THE 1-2 SPECIES

Fig. 11C. Three dimensional Fourier transform of [the radial distribution function -1] 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.

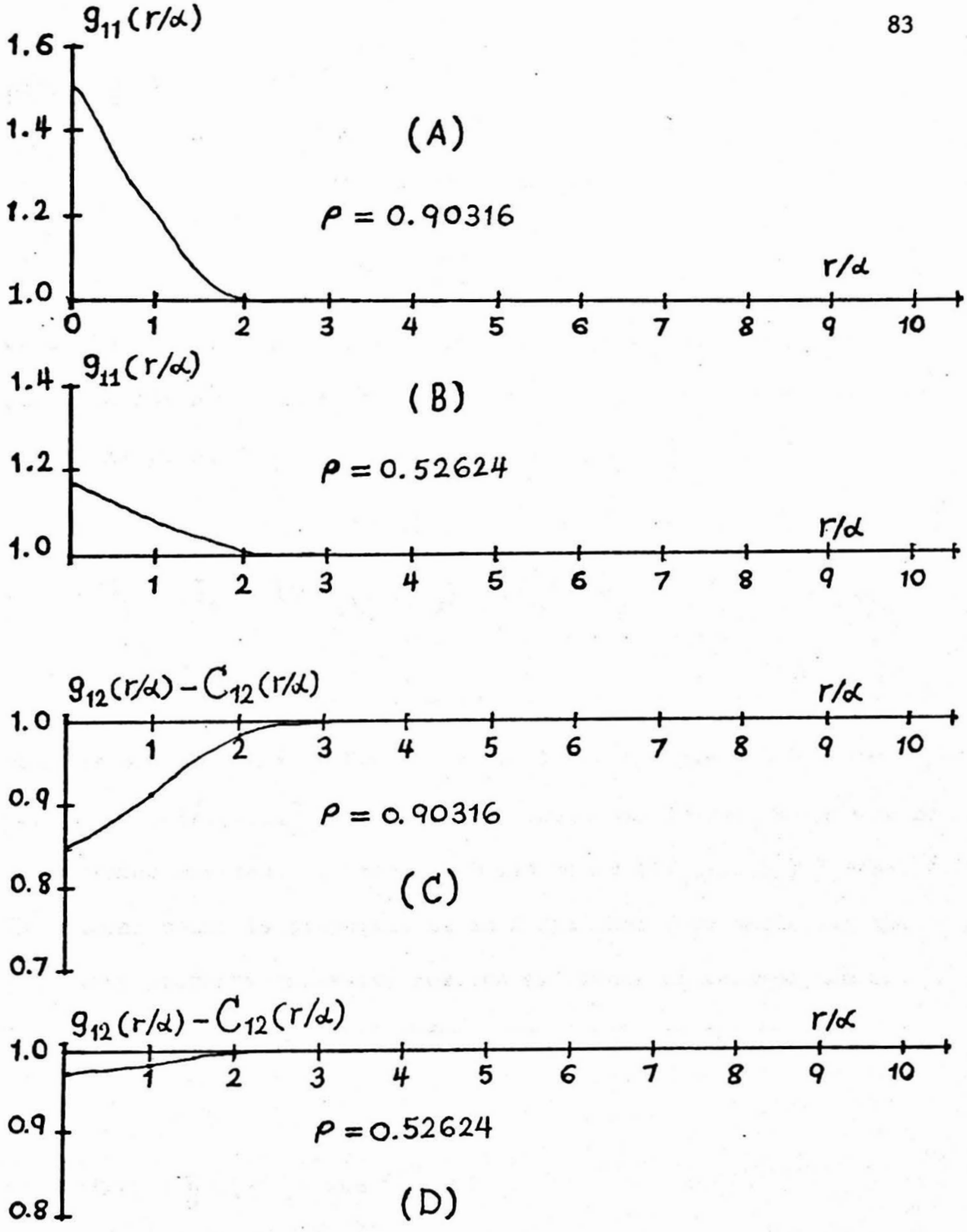


Fig. 12. Three dimensional radial distribution and direct correlation functions in the Widom-Rowlinson model.

APPENDIX 2

WIDOM-ROWLINSON MODEL

Widom and Rowlinson[10] proposed the following model system of a fluid; sometimes called the penetrable sphere model. Each particle has a volume v_o and the potential energy of a N particle system is given by

$$U(\bar{r}_1,\ldots\bar{r}_N) \equiv [W(\bar{r}_1,\ldots,\bar{r}_N) - Nv_o]\ \epsilon/v_o \qquad (A.1)$$

Where $W(\bar{r}_1,\ldots,\bar{r}_N)$ is the union of the mathematical and penetrable volumes of all the N particles in Euclidean space, and ϵ is a positive constant. $U(\bar{r}_1,\ldots,\bar{r}_N)$ is always negative and is zero when none of the volumes overlap. It has the lower bound $U(\bar{r}_1,\ldots,\bar{r}_N) \geq -(N-1)\epsilon$. This lower bound is proportional to N and therefore satisfies the stability property necessary for the existence of thermodynamics. The grand canonical partition function of this system is

$$\exp(PV/kT) = \sum_N [(z/v_o)\ \exp\theta]^N\ /N!$$

$$\times \int_V \cdots \int_V \exp[-W(\bar{r}_1,\ldots,\bar{r}_N)\ \theta/v_o]d\bar{r}_1\ldots d\bar{r}_N \qquad (A.2)$$

where $\theta \equiv \epsilon/kT$.

On the other hand the two component Widom-Rowlinson model discussed in this thesis has the interparticle potential $v_{ij}(r)$ given in eq. (1.2)

$$v_{ij}(r) = \begin{cases} \infty & (r < R_{ij}) \\ 0 & (r > R_{ij}) \end{cases} \tag{A.3}$$

$$R_{ij} = \begin{cases} \alpha & (i \neq j) \\ 0 & (i = j) \end{cases} \tag{A.4}$$

where R_{ij} is the distance of closest approach between particles of species i and j. Consider now the two component system consisting of N_1 particles of species 1 and N_2 particles of species 2 in a volume V. For any fixed configuration $\bar{r}_1,\ldots,\bar{r}_{N_2}$ of the N_2 particles of species two, the free volume accessible to the N_1 particles of species one in the total volume V is

$$V - W(\bar{r}_1,\ldots,\bar{r}_{N_2}) \tag{A.5}$$

where W is the volume excluded by the particles of species two. Summing over all particles of species one in the grand canonical partition function then yields, with proper boundary conditions,

$$\exp\,(P_{mix}\,V/kT) = \sum_{N_2} [z_2/v_o]^{N_2}/N_2!$$
$$\times \int_V \ldots \int_V \exp\,\{[V-W(\bar{r}_1,\ldots,\bar{r}_{N_2})]z_1/v_o\}d\bar{r}_1\ldots d\bar{r}_{N_2} \tag{A.6}$$

where z_1 and z_2 are the dimensionless activities of the two species normalized so as to be asymptotically equal to the dimensionless densities $\rho_1 = v_o N_1/V$ and $\rho_2 = v_o N_2/V$, $v_o = \frac{4}{3}\pi\alpha^3$ in three dimensions.

The grand partition functions (A.2) and (A.6) for the one and two component systems provide the transcription rule from two to one component systems. The pressure $P(z,\theta)$ in the one component system is related to the pressure $P_{mix}(z_1,z_2)$ in the two component system by the relation

$$v_o\,\theta\,P(z,\theta) = -\theta + v_o\,\theta\,P_{mix}(\theta, z\exp\theta) \tag{A.7}$$

Thermodynamic identities for the one component system $\rho = z \times [\partial(\theta P)/\partial z]_\theta$, $U/\epsilon V = [\partial(\theta P)/\partial\theta]_z$ and $\rho_i = z_i\,[\partial(\theta P_{mix})/\partial z_i]_\theta$ enable us to get further transcription rules

$$\rho_2 = \rho \tag{A.8}$$

$$\rho_1/z_1 = 1 - \rho - v_o\,U/\epsilon V \tag{A.9}$$

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