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Mixtures of Hard Spheres with Nonadditive Diameters: Some Exact Results and Solution of PY Equation*

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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 correlation functions as well as the solution of the Percus–Yevick integral equation for this system with $0\leq\alpha\leq\frac{1}{2}(R_{22}-R_{11})$, in one dimension. For the three-dimensional case the Percus–Yevick equation is solved partially.

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. These equations, derived on the basis of some "reasonable" physical, mathematical, or psychological hypothesis, are usually nonlinear and their solution, therefore, generally requires the use of a computer, which reduces their usefulness.[1] By some serendipity one of the more successful of these integral equations, the Percus–Yevick equation,[2] 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

$$v(r)=\infty,\qquad r<R$$
$$=0,\qquad r>R \tag{1.1}$$

was obtained by Wertheim[3] and Thiele.[4] Wertheim's method was generalized by Lebowitz[5] to yield the solution of a more general Percus–Yevick equation for mixtures of hard spheres with potential between particles of species i and j

$$v_{ij}(r)=\infty,\qquad r<R_{ij}$$
$$=0,\qquad r>R_{ij} \tag{1.2}$$

when the diameters are additive, i.e.,

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

These solutions have been used extensively in connection with x-ray and neutron scattering data from simple fluids and from liquid metals.[6] It was in connection with the latter experiments that Enderby (private communication) remarked on the "good" agreement between experiment and the results of the PY equation for some binary liquid metal mixtures, and the lack of it for others. There seemed to be a correlation between the deviations from the results of the PY equation and the degree of nonideality (excess volume) of the mixture.

Now it is well established that ions of tin, bismuth, or, for that matter, atoms of argon, do not act exactly like billiard balls. The interpretation of their structure functions in terms of those of hard spheres must therefore be thought of as "modeling," with the diameter an adjustable parameter, and not taken too literally. In particular, there is no compelling reason to assume that the best "effective" diameter between particles of different species i and j, R_{ij}, is the arithmetic mean of R_{ii} and R_{jj}. It may indeed be expected that a system in which the true interspecies potential φ_{ij} was more repulsive (attractive) than the average of the intraspecies potentials φ_{ii} and φ_{jj} would be better represented by an R_{ij} which is larger (smaller) than $(R_{ii}+R_{jj})/2$. These considerations led us to investigate the PY equation for a binary mixture of hard spheres with nonadditive diameters, i.e.,

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

with α a measure of the degree of nonadditivity. The solution of the PY equation for this system presented here is considerably more complicated than that obtained for the additive case. Indeed the complexity of the problem in three dimensions is so great that we are able to present here only part of the solution for such a system. In one dimension, however, where the solution of the PY equation has a structure very similar to that in three dimensions, the result can be given in a more explicit form.

In both cases we are led to a new kind of functional equation in the complex plane involving Laplace transforms of the direct correlation functions. The complete solution of this equation, which is used in this paper for the one dimensional case, will be given in a separate paper by Penrose and Lebowitz.[7]

For comparison we also find and give the exact results in one dimension. We find that for the case of nonadditive diameters the PY equation is no longer exact in one dimension, the exact direct-correlation function having a longer range than the interparticle potential.[8] Nevertheless the PY solution appears to be a good approximation to the exact result and we hope that this will be the case also in three dimensions where the exact result is not available.

Formulation of Problem

Let $g_{ij}(r)=g_{ji}(r)$ be the radial distribution functions, $i,j=(1,2)$, of a uniform binary mixture with densities ρ_i. The direct correlation functions $C_{ij}(r)$ are defined by the relations

$$g_{ij}(\mathbf{r})-1=C_{ij}(\mathbf{r})+\sum_{l=1}^{2}\rho_l\int[g_{il}(\mathbf{r}')-1]C_{lj}(\mathbf{r}-\mathbf{r}')d\mathbf{r}', \tag{1.5}$$

with $C_{ij}(r)=C_{ji}(r)$. As is well known, the chemical potentials of the different species may be obtained from the direct correlation functions via the relations[5]

$$\delta_{lj}-\rho_l\int C_{lj}(\mathbf{r})d\mathbf{r}=\rho_l[\partial\mu_l(\rho_1,\rho_2)/\partial\rho_j] \tag{1.6}$$

and hence

$$1-\sum\rho_l\int C_{lj}(\mathbf{r})d\mathbf{r}=\sum_l\rho_l(\partial\mu_l/\partial\rho_j)=\partial p/\partial\rho_j, \tag{1.7}$$

where μ_l is the chemical potential of the lth species and p is the pressure (we are using units in which $kT=1$).

For a system of hard spheres with interparticle potential (1.2), $g_{ij}(r)=0$ for $r<R_{ij}$. The PY approximation for this system then consists of the assumption that $C_{ij}(r)$ vanishes for $r>R_{ij}$, i.e.,

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

Finding a solution of Eq. (1.5) which satisfies (1.8) and the asymptotic conditions $g_{ij}(r)\rightarrow 1$ as $r\rightarrow\infty$ constitutes our problem.

II. ONE DIMENSION: EXACT SOLUTION

A. Equation of State

For a one-dimensional binary mixture of hard rods the exact equation of state and correlation functions can be obtained in a simple way.[9] Using the isothermal–isobaric canonical ensemble it is easily shown[10] (in the infinite volume limit) that when the position of a particle of species i is fixed then the conditional probability density, $P_{ij}^{(1)}(r)$, of finding as its *first neighbor* in some direction a particle of species j at a distance r away is given by

$$P_{ij}^{(1)}(r)=E(r-R_{ij})\rho_jK_{ij}e^{-pr}, \tag{2.1}$$

where $E(x)$ is the Heaviside function

$$E(x)=1,\quad x>0$$
$$=0,\quad x<0, \tag{2.2}$$

ρ_j is the density of particles of species j, $K_{ij}=K_{ji}$ are constants independent of r, and p is the pressure (in units of kT). The normalization of the P_{ij} yields

$$\sum_{j=1}^{2}\int_0^\infty drP_{ij}^{(1)}(r)=1=p^{-1}\sum\rho_jK_{ij}\exp(-pR_{ij}),\quad i=1,2. \tag{2.3}$$

Simple considerations of symmetry show that for $r\geq\max R_{ij}$ the ratio $P_{i1}^{(1)}(r)/P_{i2}^{(1)}(r)$ is independent of i, or

$$K_{12}=(K_{11}K_{22})^{1/2}. \tag{2.4}$$

We may relate the K_{ij} to the usual radial distribution functions $g_{ij}(r)=g_{ji}(r)$ by noting that

$$\rho_jg_{ij}(r)=P_{ij}^{(1)}(r),\quad\text{for}\quad r\leq\min_l[R_{il}+R_{lj}]. \tag{2.5}$$

Equations (2.3) and (2.4) may now be rewritten in terms of the *contact values* of the radial distribution functions; $g_{ij}(R_{ij})=K_{ij}\exp[-pR_{ij}]$,

$$p=\rho_1g_{11}(R_{11})+\rho_2g_{12}(R_{12})=\rho_1g_{21}(R_{12})+\rho_2g_{22}(R_{22}), \tag{2.6}$$

and

$$g_{12}(R_{12})=[g_{11}(R_{11})g_{22}(R_{22})]^{1/2}e^{-p\alpha}$$
$$=-p\{\rho_1+\rho_2-[(\rho_1+\rho_2)^2+4\rho_1\rho_2Q]^{1/2}\}/[2\rho_1\rho_2Q], \tag{2.7}$$

where $Q=(e^{2p\alpha}-1)$ and α, defined in (1.4), measures the nonadditivity of the diameters. To obtain the equation of state, we now make use of the virial theorem

$$p=\rho_1+\rho_2+\rho_1^2R_{11}g_{11}(R_{11})+2\rho_1\rho_2R_{12}g_{12}(R_{12})+\rho_2^2R_{22}g_{22}(R_{22})$$
$$=[\rho_1+\rho_2+2\rho_1\rho_2\alpha g_{12}(R_{12})]/(1-\xi), \tag{2.8}$$

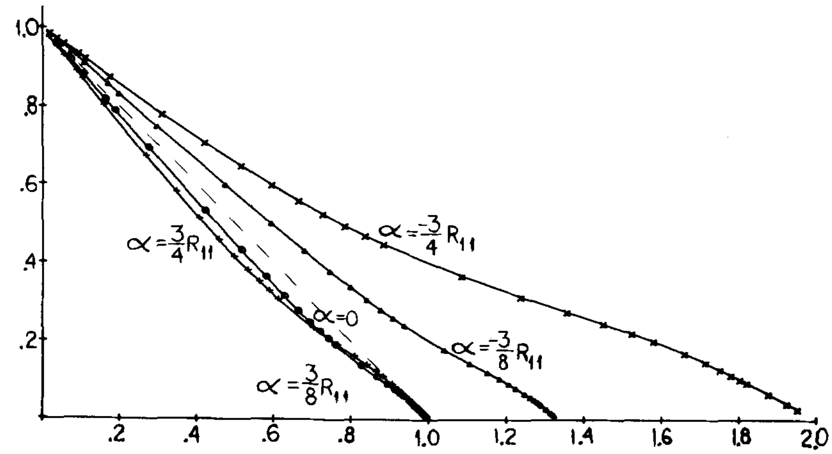

FIG. 1. Exact equations of state. Plots of ρ/p vs $\xi=\frac{3}{2}\rho\ R_{11}$ for a one-dimensional mixture of hard rods; $\rho_1=\rho_2=\frac{1}{2}\rho$, $R_{22}=2R_{11}$.

where $\xi=\rho_1R_{11}+\rho_2R_{22}$ and we have used (2.6) to obtain the second equality in (2.8). Using now (2.7) yields the equation of state

$$\rho=pQ/\{pQ[R_{11}+y(R_{22}-R_{11})]+Q-p\alpha+p\alpha[1+4y(1-y)Q]^{1/2}\}, \quad (2.9)$$

where

$$\rho=\rho_1+\rho_2, \qquad y=\rho_2/\rho=1-\rho_1/\rho. \quad (2.10)$$

The excess volume of the mixture is given by[11]

$$(\rho^{-1})^{Ex}=\alpha\{[1+4y(1-y)Q]^{1/2}-1\}/Q, \quad (2.11)$$

which, as expected, has the same sign as α.

It is interesting to look at (2.7) and (2.9) as the pressure increases. For α positive the states of small volume correspond to a segregation of the components, while for α negative a smaller volume is obtained for a thorough mixing. Hence as the pressure increases the state of the system will change, for $y\neq 0$ or 1, from a random one to an "ordered" one. (The difference between the orderings for $\alpha>0$ and $\alpha<0$ is very similar to the different orderings found in ferro- and antiferromagnetic states.[12]) A quantitative measure of this effect is provided by the ratio

$$g_{12}(R_{12})/[g_{11}(R_{11})g_{22}(R_{22})]^{1/2}=e^{-p\alpha}$$

according to (2.7). For our one-dimensional system the transition from a random state at low pressure to an ordered state at high pressure proceeds in a smooth way, whereas in three dimensions we expect there to be a phase transition.

As $p\rightarrow\infty$ the system will go to a state of close packing which for $\alpha>0$, when there is segregation, clearly corresponds to $\xi\equiv\rho_1R_{11}+\rho_2R_{22}\rightarrow 1$, yielding, for fixed y, a maximum density

$$\rho_{\max}=[R_{11}+y(R_{22}-R_{11})]^{-1}, \qquad \alpha\geq 0 \quad (2.12)$$

(the same density as for $\alpha=0$). For $\alpha<0$ the maximum value of ρ for fixed y can be obtained from (2.9) as

$$\rho_{\max}=[R_{11}+y(R_{22}-R_{11})+\alpha(1+|(y-\tfrac{1}{2})|)]^{-1}, \qquad \alpha\leq 0. \quad (2.13)$$

In Fig. 1, we plot ρ/p vs ξ for $y=\frac{1}{2}$, $R_{22}=2R_{11}$, and $\alpha=\pm\frac{3}{8}R_{11}$, $\alpha=\pm\frac{3}{4}R_{11}$. The expected behavior of $\xi=\frac{3}{2}\rho R_{11}$ as $p\rightarrow\infty$ is clearly seen.

B. Correlation Functions

Let $P_{ij}^{(n)}(r)$ be the probability density that the nth neighbor of a given particle of species i is a particle of species j located a distance r away. Then clearly[10,13]

$$P_{ij}^{(n)}(r)=\sum_{l=1}^{2}\int_0^r P_{il}^{(n-1)}(r')P_{lj}^{(1)}(r-r')dr', \quad (2.14)$$

and

$$\rho_j g_{ij}(r)=\sum_{n=1}^{\infty}P_{ij}^{(n)}(r). \quad (2.15)$$

Hence, defining the symmetric Laplace transforms

$$G_{ij}(s)=\int_0^\infty e^{-sr}(\rho_i\rho_j)^{1/2}g_{ij}(r)dr, \quad (2.16)$$

$$P_{ij}(s)=\int_0^\infty e^{-sr}(\rho_i/\rho_j)^{1/2}P_{ij}^{(1)}(r)dr = (\rho_i\rho_j)^{1/2}K_{ij}\exp(-sR_{ij})(s+p)^{-1}, \quad (2.17)$$

TABLE I. Values of $(k_{ij}^{\max})$ and τ_{ij} from Figs. 2–4: $k_0=3\pi/(R_{11}+R_{22})$, $\tau_0=4\pi/(R_{11}+R_{22})$, $\rho_1=\rho_2$, $p=0.991/(R_{11}+R_{22})$.

(i,j)	$(R_{11}+R_{22})/2R_{ij}$	$(k_{ij}^{\max})/k_0$	τ_{ij}/τ_0
$\alpha=0$			
(1, 1)	1.12	1.12	1.12
(2, 2)	0.90	0.91	0.90
(1, 2)	1.00	1.00	1.00
$\alpha=(35/39)\lambda$			
(1, 1)	1.12	1.15	1.12
(2, 2)	0.90	0.93	0.90
(1, 2)	0.91	0.93	0.91
$\alpha=-(35/39)\lambda$			
(1, 1)	1.12	1.15	1.12
(2, 2)	0.90	0.93	0.90
(1, 2)	1.11	1.11	1.09

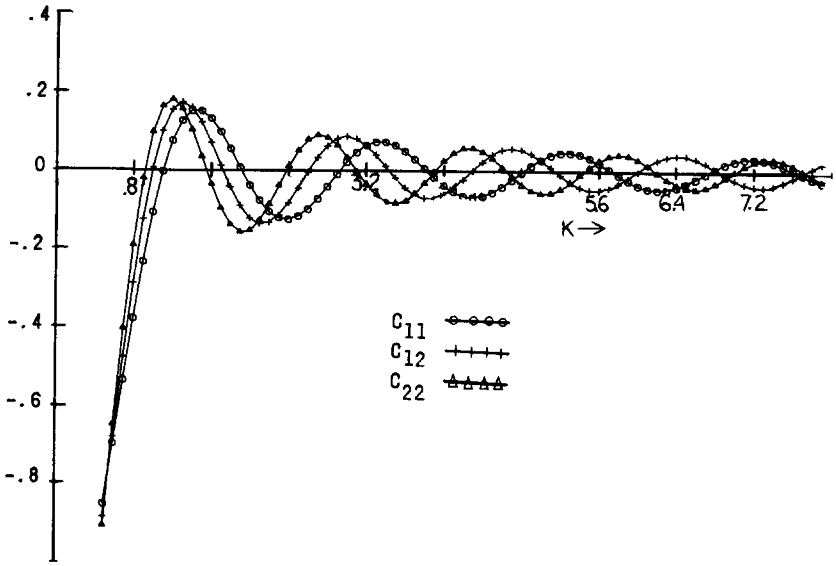

FIG. 2. Exact one-dimensional $C_{ij}(k)$ (additive diameters). Plots of the Fourier transforms of the direct correlation functions for $\alpha=0$. Values of the other parameters are given in Table I; k is in units of k_0.

we have, in matrix notation,

$$\mathbf{G}(s)=\mathbf{P}(s)[\mathbf{I}-\mathbf{P}(s)]^{-1}, \qquad (2.18)$$

where $\mathbf{I}$ is the unit matrix. The Fourier transform of $(\rho_i\rho_j)^{1/2}[g_{ij}(r)-1]$, $\tilde{H}_{ij}(k)$, is given by

$$\tilde{\mathbf{H}}(k)=\mathbf{G}(ik)+\mathbf{G}(-ik), \qquad (2.19)$$

while from (1.5) the Fourier transform of $(\rho_i\rho_j)^{1/2}C_{ij}(r)$, $\tilde{C}_{ij}(k)$, is given by

$$\tilde{\mathbf{C}}(k)=\tilde{\mathbf{H}}(k)[\mathbf{I}+\tilde{\mathbf{H}}(k)]^{-1}$$
$$=\mathbf{I}-[\mathbf{I}+\mathbf{G}(ik)+\mathbf{G}(-ik)]^{-1}. \qquad (2.20)$$

Explicit calculation gives

$$\tilde{C}_{11}(k)=1-\{[p^2+k^2-K^2-K_2^2]\times[p^2+k^2+K_1^2-2K_1(p\cos kR_{11}-k\sin kR_{11})]-2K^2[pK_1\cos kR_{11}-kK_1\sin kR_{11}+pK_2\cos k(2\alpha+R_{11})-K_2k\sin k(2\alpha+R_{11})-K_1^2-K_1K_2\cos 2k\alpha]+K^2[p^2+k^2-K_1^2-K^2]\}/D, \qquad (2.21)$$

$$\tilde{C}_{12}(k)=\tilde{C}_{21}(k)=-2K\{[p^2+k^2][(K_1+K_2)\cos 2k\lambda-p\cos kR_{12}+k\sin kR_{12}]+K^2[p\cos kR_{12}-k\sin kR_{12}]-K_1K_2[p\cos k(R_{12}-2\alpha)-k\sin k(R_{12}-2\alpha)]\}, \qquad (2.22)$$

where

$$K_i=\rho_ig_{ii}(R_{ii}),\quad K=(\rho_1\rho_2)^{1/2}g_{12}(R_{12}),\quad \lambda=(R_{22}-R_{11})/2, \qquad (2.23)$$

$$D=[p^2+k^2]\det[\mathbf{I}-\mathbf{P}(ik)\mathbf{P}(-ik)]$$
$$=[p^2+k^2-K_1^2-K^2][p^2+k^2-K_2-K^2]-2K_1K_2K^2\cos 2k\alpha-K^2(K_1^2+K_2^2). \qquad (2.24)$$

The expression for $\tilde{C}_{22}(k)$ is obtained from that of $\tilde{C}_{11}(k)$ by interchanging the subscripts 1 and 2. It is readily seen that for $\alpha\neq 0$ the range of $C_{ij}(r)$ extends beyond R_{ij} so that the PY equation is not exact even in one dimension when $\alpha\neq 0$. Graphs of $\tilde{C}_{ij}(k)$ for various α are plotted in Figs. 2–4. The values of k for which $\tilde{C}_{ij}(k)$ has its maximum, $k_{\max}{}^{ij}$, and the approximate distance between successive maxima, τ_{ij}, the "period" of $\tilde{C}_{ij}(k)$, are presented in Table I together with the values of $1.5\pi/R_{ij}$ and $2\pi/R_{ij}$, with which they are seen to agree closely. Assuming that a similar simple relation holds also in three dimensions permits us then to deduce an "effective" parameter α for binary mixtures of liquid metals, etc., from the difference between $(k_{\max}{}^{12})^{-1}$ and $\frac{1}{2}[(k_{\max}{}^{11})^{-1}+(k_{\max}{}^{22})^{-1}]$. The latter quantities are accessible to experiment via neutron scattering.[6]

III. PY SOLUTION: ONE DIMENSION

We now describe the solution of the PY equation for a mixture of hard rods with diameters $R_{22}>R_{11}$ and $R_{12}=\frac{1}{2}(R_{22}+R_{11})+\alpha$. Our method follows along the lines of Ref. 5. Using the basic PY approximation (1.8) we can define a function

$$\sigma_{ij}(r)=-(\rho_i\rho_j)^{1/2}C_{ij}(r),\qquad r\leq R_{ij}$$
$$=(\rho_i\rho_j)^{1/2}g_{ij}(r),\qquad r\geq R_{ij} \qquad (3.1)$$

in terms of which Eq. (1.5) can be written in bipolar coordinates

$$\sigma_{ij}(r)=A_{ij}-\sum\int dy\,\sigma_{il}(y)\sigma_{lj}(r-y),$$
$$|y|\geq R_{il},\ |r-y|\leq R_{lj}, \qquad (3.2)$$

where

$$A_{ij}=(\rho_i\rho_j)^{1/2}[1-\sum_{l=1,2}\rho_l\int C_{lj}(r)dr]$$
$$=(\rho_i/\rho_j)^{1/2}A_{jj}=(\rho_i\rho_j)^{1/2}(\partial p/\partial\rho_j). \qquad (3.3)$$

The last equality relating the direct correlation func-

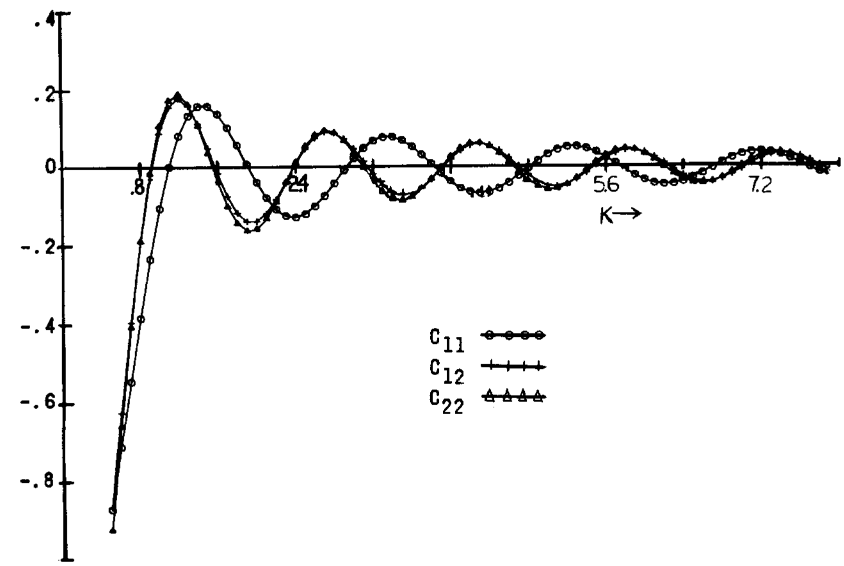

FIG. 3. Exact one-dimensional $C_{ij}(k)$ (positive α). Plots of the Fourier transforms of the direct correlation functions for $\alpha=+(35/39)\lambda$.

tion to the pressure is exact for the correct functions (1.6)-(1.7). When the PY correlations are used in (1.6) and (1.7) they define approximate chemical potentials μ_l^c and a "compressibility pressure" for the PY equation.[5]

Define the following integrals:

$$G_{ij}(s)=\int_{R_{ij}}^{\infty} e^{-sr}\sigma_{ij}(r)dr=G_{ji}(s), \tag{3.4}$$

$$F_{ij}(s)=\int_0^{R_{ij}} e^{-sr}\sigma_{ij}(r)dr=F_{ji}(s), \tag{3.5}$$

$$U_{ij}(r)=\delta_{i1}\delta_{j2}\sum\int_{R_{1l}+r}^{R_{l2}}\sigma_{1l}(r-z)\sigma_{l2}(z)dz, \quad r\leq\lambda+\alpha$$
$$=0, \quad r>\lambda+\alpha\equiv\tfrac{1}{2}(R_{22}-R_{11})+\alpha, \tag{3.6}$$

$$U_{ij}(s)=\int_0^{\lambda+\alpha} e^{-sr}U_{ij}(r)dr. \tag{3.7}$$

Taking the Laplace transform of (3.2) and rearranging, we can write in matrix form

$$s\boldsymbol{\sigma}(s)=\mathbf{A}-s\mathbf{G}(s)[\mathbf{F}(s)+\mathbf{F}(-s)]-s[\mathbf{U}(s)-\mathbf{U}(-s)], \tag{3.8a}$$

or

$$\mathbf{G}(s)=\mathbf{H}(s)\mathbf{K}^{-1}(s). \tag{3.8b}$$

Here, $\boldsymbol{\sigma}(s)=\mathbf{G}(s)+\mathbf{F}(s)$,

$$\mathbf{H}(s)=\mathbf{A}-s\mathbf{F}(s)-s\mathbf{U}(S)+s\mathbf{U}(-s), \tag{3.9}$$

$$\mathbf{K}(s)=s[\mathbf{I}+\mathbf{F}(s)+\mathbf{F}(-s)], \tag{3.10}$$

and $\mathbf{I}$ is the unit matrix. We also define

$$\mathbf{L}(s)=\mathbf{G}(s)\mathbf{H}^T(-s)=\mathbf{H}(s)\mathbf{K}^{-1}(s)\mathbf{H}^T(-s)=-\mathbf{L}^T(-s), \tag{3.11}$$

where the superscript T denotes the transpose of a matrix and the last equality follows since $\mathbf{K}(s)$ is an odd function of s and is symmetric in its indices.

As mentioned at the end of Sec. I, we look for solutions of Eq. (2.1) such that $g_{ij}(r)\rightarrow1$ as $r\rightarrow\infty$. More specifically, we require that $\int|g_{ij}(r)-1|dr<\infty$. This implies that $G_{ij}(s)-(\rho_i\rho_j)^{1/2}s^{-1}$ can have no singularities in the closed right half-plane. $\mathbf{F}(s)$ and $\mathbf{U}(s)$, being Laplace transforms over a finite interval, are entire functions of s and thus, from (3.9), $\mathbf{H}(s)\rightarrow\mathbf{A}$ as $s\rightarrow0$. Therefore, letting

$$A_{ij}'=\sum(\rho_i\rho_l)^{1/2}A_{jl}=(\rho_i\rho_j)^{1/2}[A_{11}+A_{22}]\equiv(\rho_i\rho_j)^{1/2}a, \tag{3.12}$$

the function

$$\mathbf{G}(s)\mathbf{H}^T(-s)-s^{-1}\mathbf{A}'=\mathbf{L}(s)-s^{-1}\mathbf{A}' \tag{3.13}$$

has no singularities in the closed right half-plane. Using now (3.11), $\mathbf{L}(s)=-\mathbf{L}^T(-s)$, we have that $\mathbf{L}(s)-s^{-1}\mathbf{A}'$ is entire.

We now examine the growth of $\mathbf{L}(s)$ as $s\rightarrow\infty$. Looking first at the diagonal elements of $\mathbf{L}(s)$, $L_{ii}(s)=-L_{ii}(-s)$,

$$L_{11}(s)=G_{11}(s)[A_{11}+sF_{11}(-s)]+G_{12}(s)\times[A_{12}+sF_{12}(-s)+sU_{12}(-s)-sU_{12}(s)], \tag{3.14}$$

$$L_{22}(s)=G_{21}(s)[A_{21}+sF_{21}(-s)]+G_{22}(s)[A_{22}+sF_{22}(-s)]. \tag{3.15}$$

When $\mathrm{Re}s\rightarrow\infty$, $G_{ij}(s)\sim s^{-1}\exp(-sR_{ij})$, $F_{ij}(-s)\sim s^{-1}\times\exp(-sR_{ij})$, and $U_{12}(-s)\sim s^{-1}\exp[-s(\lambda+\alpha)]$, so that $[L_{ii}(s)-A_{ii}'s^{-1}]$ is entire and everywhere bounded and thus by Liouville's theorem equal to a constant[14],

$$L_{11}(s)-A_{11}'s^{-1}=B_{11}, \tag{3.16}$$

$$L_{22}(s)-A_{22}'s^{-1}=B_{22}. \tag{3.17}$$

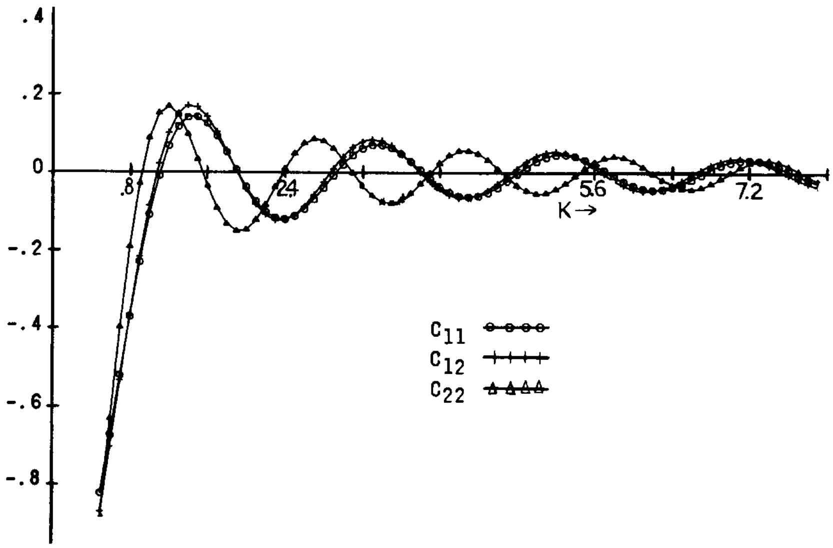

FIG. 4. Exact one-dimensional $C_{ij}(k)$ (negative α). Plots of the Fourier transforms of the direct correlation functions for $\alpha=-(35/39)\lambda$.

By looking at $\mathbf{L}(s)$ as $s\to 0$ we have that $B_{11}=B_{22}=0$. Writing out explicitly the diagonal terms of $\boldsymbol{\sigma}(s)$ and using (3.16) and (3.17) we find that

$$\sigma_{11}(s)=s^{-1}A_{11}-s^{-2}A_{11}'+G_{12}(s)\times[s^{-1}A_{12}-F_{12}(s)+U_{12}(-s)-U_{12}(s)]+G_{11}(s)[s^{-1}A_{11}-F_{11}(s)], \quad (3.18)$$

$$\sigma_{22}(s)=s^{-1}A_{22}-s^{-2}A_{22}'+G_{21}(s)[s^{-1}A_{21}-F_{21}(s)]+G_{22}(s)[s^{-1}A_{22}-F_{22}(s)]. \quad (3.19)$$

Looking at the PY equation, directly in r space we find that for $\alpha>0$, the case we shall consider here, $\sigma_{21}(r)=A_{21}=\sigma_{12}(r)$ for $r\leq\lambda-\alpha$. We shall assume also that $\alpha\leq\lambda$, i.e., $R_{11}\leq(R_{11}+R_{22})/2\leq R_{12}\leq R_{22}$. Taking the inverse transform of (3.19) for $r\leq R_{22}$, the last two terms vanish. In a similar manner, $U_{12}(-s)$ in (3.18) does not grow faster than $\exp[(\lambda+\alpha)s]$ as s goes to plus infinity so again the last two terms will vanish. Hence,

$$\sigma_{11}(r)=A_{11}-A_{11}'r, \qquad r\leq R_{11}, \quad (3.20a)$$

$$\sigma_{22}(r)=A_{22}-A_{22}'r, \qquad r\leq R_{22}. \quad (3.20b)$$

The result for the diagonal elements, for $\alpha\geq 0$, is seen to be of the same form as for the case of additive radii, that is, where $\alpha=0$. Using (3.20) in (3.3) we can express the A_{ij} in terms of $a=A_{11}+A_{22}$. We find

$$A_{11}=\{(\rho_1-\rho_2)+a[(1-\rho_2R_{22})^2-\rho_1^2R_{11}^2]\}/2(1-\rho_1R_{11}-\rho_2R_{22}) \quad (3.21)$$

and a similar expression for A_{22}.

The off-diagonal terms of $\mathbf{L}(s)$, Eq. (3.11), we have the form

$$L_{21}(s)=G_{21}(s)[A_{11}+sF_{11}(-s)]+G_{22}(s)[A_{12}+sF_{12}(-s)+sU_{12}(-s)-sU_{12}(s)], \quad (3.22)$$

$$L_{12}(s)=G_{11}(s)[A_{21}+sF_{21}(-s)]+G_{12}(s)[A_{22}+sF_{22}(-s)]. \quad (3.23)$$

Combining (3.23) with (3.8) yields

$$s^{-1}L_{12}(s)-U_{12}(-s)=s^{-1}A_{12}-G_{11}(s)F_{12}(s)-G_{12}(s)F_{22}(s)-U_{12}(s)+s^{-1}[A_{21}G_{11}(s)+A_{22}G_{12}(s)]-\sigma_{12}(s). \quad (3.24)$$

Defining the function

$$f(s)=-s^{-1}L_{12}(s)+U_{12}(-s)+s^{-2}A_{12}'+s^{-1}U_0, \quad (3.25)$$

where $U_0=\lim_{s\to 0}[L_{12}(s)-A_{12}'s^{-1}]$, we see from (3.13) that $f(s)$ is entire and from (3.24) that it is bounded in the right half-plane. Using (3.11) we find that,

$$f(-s)=-s^{-1}L_{21}(s)+U_{12}(s)+s^{-2}A_{12}'-s^{-1}U_0. \quad (3.26)$$

But, from (3.22), $L_{21}(s)$ is also bounded as $s\to+\infty$ so $f(s)$ is entire and bounded and, by Liouville's theorem, equal to a constant, which in this case, too, is found to be equal to zero. Hence,

$$L_{21}(s)=sU_{12}(s)+s^{-1}A_{12}'-U_0\equiv e^{-\lambda s}sY(s)=-L_{12}(-s), \quad (3.27)$$

where we have introduced the new function $Y(s)$. $Y(s)$ will increase as $s^{-1}e^{\pm\alpha s}$ as $\text{Re}\,s\to\pm\infty$. Taking the inverse Laplace transform of (3.27), using (3.22) gives $U_{12}(r)=U_0-A_{12}'r$ for $r<\lambda-\alpha$ and by looking at $\sigma_{12}(r)$ at $r=0$, we find that $U_0=(A_{21}-A_{12})/2$. When $\alpha=0$, $U_0=\lambda A_{12}'$, then $Y(s)=A_{21}'/s^2$ is entire and bounded leading to the results of Footnote 14 in Ref. 5; $\sigma_{12}(r)=\text{constant}$, for $r<\lambda$; $\sigma_{12}(r)=C+d(r-\lambda)$ for $\lambda<r<R_{12}$. For our case, $0\leq\alpha<\lambda$, there will be breaks in $C_{12}(r)$ at $r=\lambda\mp\alpha$, and at $R_{12}-2\alpha$. This can be seen by using (3.27) to rewrite (3.24) in the form

$$\sigma_{12}(s)=s^{-1}[A_{12}+2U_0]-G_{11}(s)[F_{12}(s)-s^{-1}A_{21}]-G_{12}(s)[F_{22}(s)-s^{-1}A_{22}]-e^{-\lambda s}Y(s) \quad (3.28)$$

and noting that the second term on the right will contain expressions of the form $\exp[-s(R_{11}+\lambda-\alpha)]=\exp[-s(R_{12}-2\alpha)]$ while the last term will have exponentials of $[-s(\lambda\pm\alpha)]$. This suggests defining a new function $U(s)$, [to be distinguished from $\mathbf{U}(s)$ and $U_{12}(s)$], such that it has the same asymptotic behavior as $Y(s)$;

$$F_{12}(s)=s^{-1}A_{21}-e^{-\lambda s}Y(s)+\exp[-s(R_{12}-\alpha)]U(s)$$
$$=F_{21}(s). \qquad (3.29)$$

We now proceed to express $\mathbf{H}(s)$ in (3.9) in terms of $Y(s)$ and $U(s)$ and substitute them and (3.27) into (3.11) to obtain equations for Y and U. We find, using (3.20),

$$H_{ii}(s)=\beta_i(s)+\gamma_i(s)\exp(-sR_{ii}), \qquad (3.30)$$

where

$$\beta_i(s)=s^{-1}A_{ii}', \qquad \gamma_i(s)=-A_{ii}'s^{-1}+(A_{ii}-A_{ii}'R_{ii}). \qquad (3.31)$$

Also

$$H_{21}(s)=se^{-\lambda s}Y(s)-s\exp[-s(R_{12}-\alpha)]U(s), \qquad (3.32a)$$

$$H_{12}(s)=se^{\lambda s}Y(-s)-s\exp[-s(R_{12}-\alpha)]U(s). \qquad (3.32b)$$

Now, from (3.8) and (3.11),

$$\mathbf{G}(s)=\mathbf{H}(s)\mathbf{K}^{-1}(s)=\mathbf{L}(s)[\mathbf{H}^T(-s)]^{-1}$$
$$=-\{[\mathbf{H}(-s)]^{-1}\mathbf{L}(-s)\}^T, \qquad (3.33)$$

but since $\mathbf{G}^T(s)=\mathbf{G}(s)$ and $\mathbf{L}^T(s)=-\mathbf{L}(-s)$, we have

$$\mathbf{H}(-s)\mathbf{H}(s)=-\mathbf{L}(-s)[s\mathbf{I}+\mathbf{H}(-s)-\mathbf{H}(s)], \qquad (3.34)$$

where (3.10) has been used to eliminate $K(s)$.

Expressing everything in terms of $U(s)$ and $Y(s)$ yields for the diagonal elements of (3.34),

$$U(s)U(-s)=Y(s)Y(-s)+s^{-2}\{\gamma_i(s)\gamma_i(-s)$$
$$-\beta_i(s)[s-\beta_i(s)]\}$$
$$=Y(s)Y(-s)-s^2\mu^2, \qquad (3.35)$$

with $i=1$ *or* 2 (no summation), and

$$\mu^2=A_{ii}'-(A_{ii}'R_{ii}-A_{ii})^2=q^2-y^2, \quad i=1 \text{ or } 2 \qquad (3.36)$$

where we have used (3.21) for the second equality with

$$q=(\rho_1\rho_2)^{1/2}/(1-\xi), \qquad (3.37)$$

$$y=[(\rho_1+\rho_2)-a(1-\xi)^2]/2(1-\xi), \qquad (3.38)$$

$$\xi=\rho_1R_{11}+\rho_2R_{22}. \qquad (3.39)$$

From the off-diagonal terms in (3.34) we find the relation

$$\exp[(R_{12}-\alpha)]\{[\beta_2(s)-\beta_1(s)]U(-s)+\gamma_1(-s)Y(-s)$$
$$-\gamma_2(-s)Y(s)\}+e^{-\lambda s}\{-\gamma_1(-s)U(s)+\gamma_2(s)U(-s)$$
$$+Y(s)[\beta_1(s)+\beta_2(s)-s]\}=0. \qquad (3.40)$$

Equation (3.40) is true as s goes to plus or minus infinity and thus each of the bracketed expressions must separately be equal to zero. We thus find from the first bracket

$$U(-s)=[\gamma_1(-s)Y(-s)-\gamma_2(-s)Y(s)]/[\beta_1(s)-\beta_2(s)] \qquad (3.41)$$

or

$$U(s)=(a_1+b_1s)Y(s)+(a_2+b_2s)Y(-s), \qquad (3.42)$$

where

$$a_1=-A_{11}'(A_{22}'-A_{11}')^{-1}=-\rho_1/(\rho_2-\rho_1), \qquad (3.43)$$

$$a_2=A_{22}'(A_{22}'-A_{11}')^{-1}=\rho_2/(\rho_2-\rho_1), \qquad (3.44)$$

$$b_1=(A_{11}-A_{11}'R_{11})/(A_{22}'-A_{11}')$$
$$=-[2a(1-\xi)]^{-1}+(1-\xi)/2(\rho_2-\rho_1), \qquad (3.45)$$

$$b_2=(-A_{22}+A_{22}'R_{22})/(A_{22}'-A_{11}')$$
$$=-[2a(1-\xi)]^{-1}+(1-\xi)/2(\rho_1-\rho_2). \qquad (3.46)$$

The second bracket in (3.40) yields the same relationship as (3.41). Substituting (3.42) in (3.35) yields a functional equation involving $Y(s)$ and $Y(-s)$ which we now have to solve. Before doing that, we note that it follows from the definition, Eq. (3.27), that $s^2Y(s)$ is entire. We can therefore write

$$Y(s)=\mu[s^{-2}P(s)+s^{-1}Q(s)], \qquad (3.47)$$

where $P(s)$ and $Q(s)$ are even and entire functions of the variable s. Substituting (3.47) in (3.42) yields

$$U(s)=\mu[(a_1+a_2)s^{-2}P(s)+(b_1-b_2)Q(s)$$
$$+(b_1+b_2)s^{-1}P(s)+(a_1-a_2)s^{-1}Q(s)]. \qquad (3.48)$$

Using this last expression in (3.35), multiplying by $-s^2$, and noting that $a_1+a_2=1$, gives

$$(b_1+b_2)^2P^2(s)-4(a_2b_1-a_1b_2)P(s)Q(s)$$
$$+[(a_1-a_2)^2-1-(b_1-b_2)^2s^2]Q^2(s)=1. \qquad (3.49)$$

Letting

$$A=(b_1+b_2)^2, \qquad (3.50)$$

$$B=2(b_2a_1-a_2b_1), \qquad (3.51)$$

$$C(s)=(a_1-a_2)^2-1-(b_1-b_2)^2s^2=-4a_1a_2-(b_1-b_2)^2s^2, \qquad (3.52)$$

then (3.49) becomes simply

$$AP^2(s)+2BP(s)Q(s)+C(s)Q^2(s)=1 \qquad (3.53)$$

Multiplying by A and defining

$$D(s)=B^2-AC(s)=-4(a_2b_1^2+a_1b_2^2)+(b_1^2-b_2^2)^2s^2$$
$$=[s^2-4\mu^2]/(\rho_1-\rho_2)^2a^2, \qquad (3.54)$$

(3.49) takes the form

$$[AP(s)+BQ(s)]^2-D(s)Q^2(s)=A. \qquad (3.55)$$

Setting

$$AP(s)+BQ(s)=\varphi(s) \qquad (3.56)$$

the final form of our functional equation is

$$\varphi^2(s)-D(s)Q^2(s)=A. \qquad (3.57)$$

Equation (3.57) is a functional equation for the two entire even functions of s, $\varphi(s)$, and $Q(s)$, whose growth as $s\rightarrow\infty$ is $e^{\alpha s}$. The solutions of a general equation of the form of (3.57), which will be needed also for the three dimensional case will be given in Ref. 7. For (3.57) it can be readily checked that there is a solution of the form

$$\varphi(s)=\pm(A)^{1/2}\cosh\alpha(s^2-4\mu^2)^{1/2} \quad (3.58)$$

$$Q(s)=\pm[A/D(s)]^{1/2}\sinh\alpha(s^2-4\mu^2)^{1/2}, \quad (3.59)$$

with

$$(A)^{1/2}=|b_1+b_2|, \quad \text{and} \quad D^{1/2}(s)=(s^2-4\mu^2)^{1/2}(\rho_1-\rho_2)a \quad (3.60)$$

an odd function of s with a cut on the real axis between $\pm2\mu$.

IV. PROPERTIES OF THE PY SOLUTION

Having obtained the solution of (3.57) satisfying the proper symmetry and asymptotic conditions, i.e., having found a solution of the PY equation, our problem is now reduced to finding the parameter a and the correct signs for $\varphi(s)$ and $Q(s)$ in (3.58) and (3.59). This can be obtained by substituting our expressions for $P(s)$ and $Q(s)$ in (3.47) and then comparing the resulting $Y(s)$ as $s\rightarrow0$ with its defining equation, (3.27). This leads to the choice of the negative sign for φ in (3.58) and the positive sign for Q in (3.59) and yields the following implicit equation for $a=A_{11}+A_{22}=\rho_1\partial p/\partial\rho_1+\rho_2\partial p/\partial\rho_2$,

$$2\alpha q=-[1-x^2]^{-1/2}\arcsin x=-\theta/\cos\theta, \quad (4.1)$$

where q is given in (3.37) and

$$\sin\theta=x\equiv y/q\equiv\tfrac{1}{2}[\rho_1+\rho_2-a(1-\xi)^2]/(\rho_1\rho_2)^{1/2} \quad (4.2)$$

or

$$a=[\rho_1+\rho_2-2x(\rho_1\rho_2)^{1/2}]/(1-\xi)^2. \quad (4.3)$$

For a given value of α and q (4.1) is solved for θ and/or x which is then used in (4.3) to find the "compressibility" a. When $\alpha\rightarrow0$, $x\rightarrow0$, and $a\rightarrow(\rho_1+\rho_2)/(1-\xi)^2$ the correct result for the additive-diameter case. Expanding the right side of (4.3) in a power series in x and solving for a as a power series in αq we find

$$a=[1-\xi]^{-2}\{\rho_1+\rho_2+[4\rho_1\rho_2\alpha/(1-\xi)]\times[1-(8/3)q^2\alpha^2+(64/5)q^4\alpha^4+\cdots]\}, \quad (4.4)$$

which agrees up to $O(\alpha^2)$ with the exact result. As $\xi\rightarrow1$, the maximum possible density, $q\rightarrow\infty$ and $x\rightarrow-1$ giving

$$\lim_{\xi\rightarrow1}(1-\xi)^2a=[(\rho_1)^{1/2}+(\rho_2)^{1/2}]^2, \quad (4.5)$$

showing that at very high densities the compressibility $a=\rho_1\partial p/\partial\rho_1+\rho_2\partial p/\partial\rho_2$ is independent of α. This agrees with the exact result and corresponds to a complete separation of the two components at high pressure as would be expected intuitively. (A comparison of the PY and exact compressibilities show that they agree well over the whole density range.)

We now show that the thermodynamic state obtained from our solution of the PY equation via the relations (1.7), defining "compressibility" chemical potentials μ_l, is stable. As shown elsewhere,[15] the thermodynamic stability of a mixture of hard spheres requires that the matrix $M_{lj}=\partial\mu_l/\partial\rho_j$ be positive definite. Since the diagonal elements of $\mathbf{M}$ are positive in our case we need only look at the determinant. Using (3.2), (3.20), (3.21), and (4.3) we find[16]

$$\begin{aligned}(\rho_1\rho_2)^2\det(M_{ij})&=\{[A_{11}+\rho_1\rho_2\textstyle\int C_{12}(r)dr]\\&\quad\times[A_{22}+\rho_1\rho_2\textstyle\int C_{12}(r)dr]\\&\quad-\rho_1^2\rho_2^2[\textstyle\int C_{12}(r)dr]^2\}\\&=[A_{11}A_{22}+\rho_1\rho_2a\textstyle\int C_{12}(r)dr]\\&=(A_{11}A_{22}+\tfrac{1}{2}\rho_1\rho_2a\{-a+\textstyle\sum\rho_i\\&\quad\times[1-\rho_i\textstyle\int C_{ii}(r)dr]\})\\&=\rho_1\rho_2(1-x^2)/(1-\xi)^2\\&=[\arcsin x]^2/4\alpha^2\underset{\xi\rightarrow1}{\rightarrow}(\pi/8)^2/4\alpha^2. \quad (4.6)\end{aligned}$$

For $\alpha=0$, x is also zero and (4.6) coincides with the exact result. For $\alpha>0$ the PY solution, like the exact result, yields a smooth transition to a phase-separated system. This separation proceeds smoothly, without any phase transition, *if* we follow in (4.1) the branch of arcsin$x$ which vanishes for $x=0$.

A particularly instructive way of seeing the separation of the components is to examine, as we did for the exact solution, the contact values of the radial distribution functions $g_{ij}(R_{ij})=-C_{ij}(R_{ij})$. For additive diameters, the PY solution agrees with the exact one, $g_{ij}(R_{ij})=(1-\xi)^{-1}$, i.e., there is complete mixing. For our case, $\alpha\geq0$, we find from (3.20), (3.21), and (4.3),

$$g_{11}(R_{11})=[1-(\rho_2/\rho_1)^{1/2}x](1-\xi)^{-1}, \quad (4.7)$$

$$g_{22}(R_{22})=[1-(\rho_1/\rho_2)^{1/2}x](1-\xi)^{-1}. \quad (4.8)$$

To obtain $g_{12}(R_{12})$ we use the general relation

$$\begin{aligned}\sigma_{ij}(R_{ij}^-)&=\lim_{s\rightarrow\infty}[-sF_{ij}(-s)\exp(-sR_{ij})]\\&=\sigma_{ij}(R_{ij}^+)\\&=\lim_{s\rightarrow\infty}[s\exp(sR_{ij})G_{ij}(s)], \quad (4.9)\end{aligned}$$

where the second equality follows from the continuity of $\sigma_{ij}(r)$ at $r=R_{ij}$. Substituting our expression for $F_{12}(s)$ in (4.9) we obtain,

$$\begin{aligned}g_{12}(R_{12})&=(1-x^2)^{1/2}[1-\xi]^{-1}\\&=-[\arcsin x][2\alpha(\rho_1\rho_2)^{1/2}]^{-1}\\&=\mu(\rho_1\rho_2)^{-1/2}. \quad (4.10)\end{aligned}$$

This agrees with (3.36) which may now be rewritten in the form

$$\sigma_{12}^2(R_{12})=\rho_ia-\sigma_{ii}^2(R_{ii}), \qquad i=1 \text{ or } 2 \quad (4.11)$$

a relation which can also be derived by taking the limit as $s\to\infty$ of $sL_{ii}(s)$ in (3.14) and (3.15). As $\xi\to 1$, $x\to -1$, $g_{12}(R_{12})$ goes to a finite value whereas $g_{ii}(R_{ii})\to\infty$.

The contact values of the radial distribution functions also furnish us with a "virial pressure" p^v, Eq. (2.8),

$$p^v=\rho_1+\rho_2+\sum \rho_i\rho_j R_{ij} g_{ij}(R_{ij})$$
$$=\{\rho_1+\rho_2+2\rho_1\rho_2 R_{12}[(1-x^2)^{1/2}-1] + (\rho_1\rho_2)^{1/2}[2\alpha(\rho_1\rho_2)^{1/2}-x\xi]\}/(1-\xi) \quad (4.12)$$

Due to the approximate nature of the PY equation for hard rods with nonadditive diameters, p^v agrees with the compressibility pressure only to order α.

V. PY SOLUTION: THREE DIMENSIONS

The solution of the Percus–Yevick approximation in three dimensions for $0\leq\alpha\leq\lambda$, follows closely the one-dimensional solution of Sec. III. To facilitate the comparison we use the same symbols for functions which play a similar mathematical role although their definitions in terms of the g_{ij} and C_{ij} are different. We define, as in Ref. 5,

$$\sigma_{ij}(r)=-12(\eta_i\eta_j)^{1/2} r C_{ij}(r), \qquad r\leq R_{ij}$$
$$=12(\eta_i\eta_j)^{1/2} r g_{ij}(r), \qquad r\geq R_{ij} \qquad \eta_i=\pi\rho_i/6. \quad (5.1)$$

With this definition of σ_{ij} the PY equation for hard spheres in three dimensions takes a form similar to Eq. (3.2),

$$\sigma_{ij}(r)=A_{ij}-\sum_{l=1}\int_{R_{ij}}^{\infty} dy\,\sigma_{il}(y)\int_{|r-y|}^{\min[r+y,R_{lj}]}\sigma_{lj}(x)dx \quad (5.2)$$

with

$$[(12)^2\eta_i\eta_j]^{-1/2}A_{ij}=[1-\sum_{l=1,2}\rho_l\int C_{lj}(\mathbf{r})d\mathbf{r}]$$
$$=\sum \rho_l\partial\mu_l/\partial\rho_j=\partial p/\partial\rho_j, \quad (5.3)$$

using (1.6) and (1.7) to define compressibility μ_l's and pressure. Defining $\mathbf{G}(s)$, $\mathbf{F}(s)$, $\mathbf{U}(r)$, and $\mathbf{U}(s)$ in terms of the three-dimensional σ_{ij}, (5.1), by Eqs. (3.4)–(3.8), we find upon taking the Laplace transform of (5.2),

$$s^2[\mathbf{G}(s)+\mathbf{F}(s)]=\mathbf{A}-s\mathbf{G}(s)[\mathbf{F}(-s)-\mathbf{F}(s)] +s[\mathbf{U}(s)-\mathbf{U}(-s)], \quad (5.4a)$$

or

$$\mathbf{G}(s)=\mathbf{H}(s)\mathbf{K}^{-1}(s), \quad (5.4b)$$

$$\mathbf{H}(s)=\mathbf{A}-s^2\mathbf{F}(s)-s\mathbf{U}(s)+s\mathbf{U}(-s), \quad (5.5)$$

$$\mathbf{K}(s)=s^2\mathbf{I}+s\mathbf{F}(-s)-s\mathbf{F}(s). \quad (5.6)$$

As in one dimension we define

$$\mathbf{L}(s)=\mathbf{G}(s)\mathbf{H}^T(-s)=\mathbf{H}(s)\mathbf{K}^{-1}(s)\mathbf{H}^T(-s)=\mathbf{L}^T(-s), \quad (5.7)$$

where the last term differs in sign from that in Eq. (3.11) since $\mathbf{K}(s)$ is now an even function of s.

The requirement that $g_{ij}(r)\to 1$ as $r\to\infty$ in such a way that $\int r\,|\,g_{ij}(r)-1\,|\,dr<\infty$ implies that $G_{ij}(s)-12\times(\eta_i\eta_j)^{1/2}s^{-2}$ has no singularities in the closed right half-plane. This in turn implies that $\mathbf{L}(s)-s^{-2}\mathbf{A}'$, where

$$A_{ij}'=12(\eta_i\eta_j)^{1/2}(A_{11}+A_{22})=(12)^2(\eta_i\eta_j)^{1/2}a \quad (5.8)$$

is analytic in the right half-plane and hence, by (5.7), is entire.

Explicitly, the diagonal terms of $\mathbf{L}(s)$ are

$$L_{11}(s)=G_{11}(s)[A_{11}-s^2F_{11}(-s)] +G_{12}(s)[A_{12}-s^2F_{12}(-s)+sU_{12}(-s)-sU_{12}(s)] =L_{11}(-s), \quad (5.9)$$

$$L_{22}(s)=G_{21}(s)[A_{21}-s^2F_{21}(-s)] +G_{22}(s)[A_{22}-s^2F_{22}(-s)] =L_{22}(-s). \quad (5.10)$$

Both expressions are bounded as $\mathrm{Re}s\to+\infty$ so that using Liouville's theorem we can, as in the additive-diameter case, set $L_{ii}(s)-A_{ii}'/s^2$ equal to a constant which we call $2B_{ii}$. We may then write

$$G_{11}(s)[A_{11}-s^2F_{11}(-s)]+G_{12}(s) \times[A_{12}-s^2F_{12}(-s)+sU_{12}(-s)-sU_{12}(s)] =2B_{11}+s^{-2}A_{11}', \quad (5.11)$$

$$G_{21}(s)[A_{21}-s^2F_{21}(-s)]+G_{22}(s)[A_{22}-s^2F_{22}(-s)] =2B_{22}+s^{-2}A_{22}'. \quad (5.12)$$

Combining (5.11) and (5.12) with (5.4) to eliminate the $G(s)F(-s)$ terms leads to the following equations for $\sigma_{ii}(s)=G_{ii}(s)+F_{ii}(s)$:

$$s\sigma_{11}(s)=A_{11}s^{-1}+2B_{11}s^{-2}+A_{11}'s^{-4} +[F_{11}(s)-A_{11}s^{-2}]G_{11}(s) +[F_{12}(s)-A_{12}s^{-2}-U_{12}(-s)s^{-1}+U_{12}(s)s^{-1}]G_{12}(s). \quad (5.13)$$

$$s\sigma_{22}(s)=A_{22}s^{-1}+2B_{22}s^{-2}+A_{22}'s^{-4} +[F_{21}(s)-A_{21}s^{-2}]G_{21}(s)+[F_{22}(s)-A_{22}s^{-2}]G_{22}(s). \quad (5.14)$$

Looking at the PY equation directly in r space gives

$$\sigma_{21}(r)=\sigma_{12}(r)=A_{21}r, \qquad r\leq\lambda-\alpha \quad (5.15)$$

so that taking the inverse transform of (5.13) and (5.14) for $r<R_{ii}$, and noting that since $U_{12}(-s)$ does not grow faster than $\exp[(\lambda+\alpha)s]$ as $s\to\infty$ the last two terms in (5.13) and (5.14) vanish, yields

$$\sigma_{ii}(r)=A_{ii}r+B_{ii}r^2+(1/24)A_{ii}'r^4, \qquad r\leq R_{ii}, \qquad i=1,2 \quad (5.16)$$

and

$$F_{ii}(s)=A_{ii}s^{-2}+2B_{ii}s^{-3}+A_{ii}'s^{-5}-\exp(-sR_{ii})\times\{s^{-1}[A_{ii}R_{ii}+B_{ii}R_{ii}^2+(1/24)A_{ii}'R_{ii}^4]+s^{-2}(A_{ii}+2B_{ii}R_{ii}+\tfrac{1}{6}A_{ii}'R_{ii}^3)+s^{-3}(2B_{ii}+\tfrac{1}{2}A_{ii}'R_{ii}^2)+s^{-4}(A_{ii}'R_{ii})+s^{-5}A_{ii}'\}. \quad (5.17)$$

The results for the diagonal elements are again seen to be of exactly the same form as for the additive diameter case; the coefficients, of course, are different. As in one dimension we shall see that the off-diagonal elements have a considerably different form.

The off-diagonal terms of $\mathbf{L}(s)$ are

$$L_{12}(s)=G_{11}(s)[A_{21}-s^2F_{21}(-s)]+G_{12}(s)[A_{22}-s^2F_{22}(-s)], \quad (5.18)$$

$$L_{21}(s)=G_{21}(s)[A_{11}-s^2F_{11}(-s)]+G_{22}(s)[A_{12}-s^2F_{12}(-s)-sU_{12}(s)+sU_{12}(-s)]. \quad (5.19)$$

Eliminating the $F_{ij}(-s)$ from (5.18) via (5.4) yields

$$L_{12}(s)+s^2U_{12}(-s)=s^3\sigma_{12}(s)-sA_{12}+s^2[G_{11}(s)F_{12}(s)+G_{12}(s)F_{22}(s)-U_{12}(s)]+A_{21}G_{11}(s)+A_{22}G_{12}(s) \quad (5.20)$$

As $\mathrm{Re}s\to+\infty$ the right side of (5.20) goes as $-sU_0$, where $U_0=U_{12}(r=0)=\frac{1}{2}(A_{21}-A_{12})$ as in (3.26), while as $s\to0$ the left side of (5.20) goes as $s^{-2}A_{12}'$. We can therefore define the function $f(s)$,

$$f(s)=L_{12}(s)+s^2U_{12}(-s)-s^{-2}A_{12}'+sU_0, \quad (5.21)$$

where $f(s)$ is entire and bounded in the closed right half-plane. But

$$f(-s)=L_{21}(s)+s^2U_{12}(s)-s^{-2}A_{12}'-sU_0 \quad (5.22)$$

is also bounded in the right half-plane so that $f(s)$ is entire and bounded everywhere and hence equal to a constant which we designate as $2D$. We have thus

$$L_{21}(s)=2D-s^2U_{12}(s)+s^{-2}A_{12}'+sU_0=L_{12}(-s)\equiv-e^{-\lambda s}Y(s), \quad (5.23)$$

where we have again introduced the auxiliary function $Y(s)$: $s^2Y(s)$ is entire and grows as $\exp[\alpha\,|\,\mathrm{Re}s\,|]$ when $s\to\pm\infty$. The structure of $F_{21}(s)$ will be similar to that found in one dimension. We therefore introduce the function $U(s)$ with the same asymptotic behavior as $Y(s)$ by

$$F_{21}(s)=F_{12}(s)=s^{-2}A_{21}-s^{-3}e^{-\lambda s}Y(s)+s^{-3}\exp[-s(R_{12}-\alpha)]U(s). \quad (5.24)$$

To find equations for $Y(s)$ and $U(s)$ we manipulate Eqs. (5.4)–(5.7) to obtain

$$\mathbf{H}(-s)\mathbf{H}(s)=\mathbf{L}(-s)[s^2\mathbf{I}+s^{-1}\mathbf{H}(s)-s^{-1}\mathbf{H}(-s)]. \quad (5.25)$$

Using (5.5), (5.9)–(5.12), and (5.17) we can write

$$H_{ii}(s)=\beta_i(s)+\gamma_i(s)\exp(-sR_{ii}), \qquad i=1,2 \quad (5.26)$$

$$L_{ii}(s)=-s\beta_i(s), \quad (5.27)$$

where

$$\beta_i(s)=-2B_{ii}s^{-1}-A_{ii}'s^{-3} \quad (5.28)$$

and

$$\gamma_i(s)=s[A_{ii}R_{ii}+B_{ii}R_{ii}^2+(1/24)A_{ii}'R_{ii}^4]+[A_{ii}+2B_{ii}R_{ii}+(1/6)A_{ii}'R_{ii}^3]+s^{-1}(2B_{ii}+\tfrac{1}{2}A_{ii}'R_{ii}^2)+s^{-2}(A_{ii}'R_{ii})+s^{-3}A_{ii}'. \quad (5.29)$$

For the off-diagonal terms of $\mathbf{H}(s)$, (5.4) combined with (5.24) yields

$$H_{21}(s)=s^{-1}e^{-\lambda s}Y(s)-s^{-1}\exp[-(R_{12}-\alpha)s]U(s), \quad (5.30)$$

$$H_{12}(s)=s^{-1}e^{\lambda s}Y(-s)-s^{-1}\exp[-(R_{12}-\alpha)s]U(s), \quad (5.31)$$

where we have used the relation

$$A_{12}-A_{21}=2U_0. \quad (5.32)$$

We can now write out (5.25) with the only unknown functions being $U(s)$ and $Y(s)$.

The diagonal terms in (5.25) yield the relation (no summation on i)

$$Y(s)Y(-s)=U(s)U(-s)-s^2\{\gamma_i(s)\gamma_i(-s)+\beta_i(s)[s^3+\beta_i(s)]\}, \qquad i=1,2. \quad (5.33)$$

From the 1–2 term of (5.25) we obtain the equation

$$s^{-1}\exp[(R_{12}-\alpha)s]\{[\beta_2(s)+\beta_1(-s)]U(-s)+\gamma_1(-s)Y(-s)-\gamma_2(-s)Y(s)\}+s^{-1}e^{-\lambda s}\{-[\beta_1(-s)+\beta_2(-s)-s^3]Y(s)-\gamma_1(-s)U(s)-\gamma_2(s)U(-s)\}=0. \quad (5.34)$$

This equation is true as s goes to plus or minus infinity and thus each of the bracketed expressions must separately be equal to zero. From the first bracket,

$$U(-s)=C_1(-s)Y(-s)+C_2(-s)Y(s), \quad (5.35)$$

where

$$C_1(-s)=-\gamma_1(-s)[\beta_1(-s)+\beta_2(s)]^{-1}, \quad (5.36)$$

$$C_2(-s)=\gamma_2(-s)[\beta_1(-s)+\beta_2(s)]^{-1}. \quad (5.37)$$

Letting

$$h(s)=-(\gamma_i(s)\gamma_i(-s)+\beta_i(s)[s^3+\beta_i(s)])=([A_{ii}'-A_{ii}^2+\tfrac{2}{3}A_{ii}A_{ii}'R_{ii}^3+\tfrac{1}{2}B_{ii}A_{ii}'R_{ii}^4+(1/72)A_{ii}'^2R_{ii}^6]+s^2\{2B_{ii}+[A_{ii}R_{ii}+B_{ii}R_{ii}^2+(1/24)A_{ii}'R_{ii}^4]^2\})=[h_2+h_1s^2], \qquad i=1\text{ or }2, \quad (5.38)$$

we are left with the functional equation

$$U(s)U(-s)=Y(s)Y(-s)-s^2h(s), \quad (5.39)$$

where

$$U(s)=C_1(s)Y(s)+C_2(s)Y(-s). \quad (5.40)$$

As in one dimension, we divide $Y(s)$ into an even and odd part by defining $P(s)$ and $\Phi(s)$, both even entire functions of s such that

$$Y(s)=s^{-2}P(s)+s^{-1}\Phi(s). \quad (5.41)$$

Substituting (5.35) into (5.39) and multiplying by $s^8[\beta_2(s)-\beta_1(s)]^2$, we obtain

$$A(s)P^2(s)+2B(s)P(s)\Phi(s)+C(s)\Phi^2(s)$$
$$=-s^{10}h(s)[\beta_2(s)-\beta(s)]^2. \quad (5.42)$$

Here $A(s)$, $B(s)$, and $C(s)$ are even polynomials,

$$A(s)=-s^4[\gamma_1(s)\gamma_1(-s)+\gamma_2(s)\gamma_2(-s)-\gamma_1(s)\gamma_2(-s)$$
$$-\gamma_1(-s)\gamma_2(s)]-s^4[\beta_2(s)-\beta_1(s)]^2$$
$$=a_1s^6+a_2s^4+a_3s^2+a_4, \quad (5.43)$$

$$B(s)=s^5[\gamma_1(s)\gamma_2(-s)-\gamma_2(s)\gamma_1(-s)]$$
$$=b_1s^6+b_2s^4+b_3s^2+b_4, \quad (5.44)$$

$$C(s)=s^6[\gamma_1(s)+\gamma_2(s)][\gamma_2(-s)+\gamma_1(-s)]$$
$$+s^6[\beta_2(s)-\beta_1(s)]^2$$
$$=c_1s^8+c_2s^6+c_3s^4+c_4s^2+c_5, \quad (5.45)$$

where[17]

$$a_4=-\lambda b_4=\lambda^2c_5=-4\lambda^2\eta_1\eta_2(12^2a)^2, \quad (5.46)$$

$$b_3=24a[4\lambda(\eta_1B_{22}+\eta_2B_{11})+(\eta_1A_{22}-\eta_2A_{11})+16a\lambda^3\eta_1\eta_2], \quad (5.47)$$

$$c_4=-96a[\eta_1B_{22}+\eta_2B_{11}+6a\lambda^2\eta_1\eta_2], \quad (5.48)$$

$$a_3=-\lambda[2b_3+\lambda c_4]=c_3+16B_{11}B_{22}, \quad (5.49)$$

and $a=A_{11}+A_{22}$ has been defined in (5.8). Multiplying (5.42) by $A(s)$, and noting from (5.38), which is valid for $i=1$ or 2, that

$$B^2(s)-A(s)C(s)=s^{10}[\beta_2(s)-\beta_1(s)]^2[s^6-4h(s)], \quad (5.50)$$

we can set

$$A(s)P(s)+B(s)\Phi(s)=s^5[\beta_2(s)-\beta_1(s)]\Psi(s) \quad (5.51)$$

to obtain an equation of the form

$$\Psi^2(s)-E(s)\Phi^2(s)=V(s), \quad (5.52)$$

$$E(s)=s^6-4h(s), \qquad V(s)=-h(s)A(s), \quad (5.53)$$

with $\Psi(s)$ an entire even function of s since the other terms in (5.52) are.

Equation (5.52) is a function equation for the entire even functions $\Psi(s)$ and $\Phi(s)$ whose asymptotic behavior at infinity is of $O(e^{\alpha s})$. It is of the same general form albeit more complicated than the corresponding equation in one dimension, Eq. (3.57), where the polynomials corresponding to $E(s)$ and $V(s)$, [i.e., $D(s)$ and A], were of orders 2 and 0, respectively.

The solution of (5.52) will be given in Ref. 7. It will be shown there that a solution having the required asymptotic behavior will exist only if the coefficients of polynomials $E(s)$ and $V(s)$ satisfy certain conditions. This will give us relationships and hopefully permit us to determine explicitly[18] the coefficients A_{11}, A_{22}, B_{11}, and B_{22} appearing in $\sigma_{ii}(r)$ in (5.16) and consequently the correlation functions and equations of state of our system. [The A_{ij}' are related to the A_{ii} via (5.8)].

The situation is analogous, but more complicated than in one dimension where there were only two constants A_{11} and A_{22} in $\sigma_{ii}(r)$. One relation among our constants, similar to Eq. (3.21), may be obtained from the definition of the A_{ij} in (5.3) and the symmetry $C_{12}(r)=C_{21}(r)$:

$$24(\eta_1\eta_2)^{1/2}\int_0^{R_{12}} r\sigma_{12}(r)dr$$
$$\equiv K=12\eta_1(1+B_{11}R_{11}^4)+A_{11}(16\eta_1R_{11}^3-1)$$
$$+4(A_{11}+A_{22})\eta_1^2R_{11}^6$$
$$=12\eta_2(1+B_{22}R_{22}^4)+A_{22}(16\eta_2R_{22}^3-1)$$
$$+4(A_{11}+A_{22})\eta_2^2R_{22}^6. \quad (5.54)$$

Further relations between the A_{ii} and B_{ii} may be obtained by looking at the asymptotic form of (5.11) and (5.12) as $s\rightarrow\infty$. Using the continuity of $\sigma_{ij}(r)$ and its first two derivatives[5] at R_{ij}, we have

$$G_{ij}(s)\underset{s\rightarrow\infty}{\longrightarrow}s^{-1}\exp(-sR_{ij})[\sigma_{ij}+s^{-1}\sigma_{ij}'$$
$$+s^{-2}\sigma_{ij}''+\cdots]+\cdots, \quad (5.55)$$

$$F_{ij}(-s)\underset{s\rightarrow\infty}{\longrightarrow}+s^{-1}\exp(sR_{ij})[\sigma_{ij}-s^{-1}\sigma_{ij}'$$
$$+s^{-2}\sigma_{ij}''+\cdots]+\cdots, \quad (5.56)$$

where $\sigma_{ij}\sigma_{ij}'$ and σ_{ij}'' are the zeroth, first, and second derivatives of $\sigma_{ij}(r)$ evaluated at $r=R_{ij}$. This yields

$$-\sigma_{12}^2=2B_{11}+\sigma_{11}^2=2B_{22}+\sigma_{22}^2, \quad (5.57)$$

$$(\sigma_{21}')^2-2\sigma_{21}''\sigma_{21}=A_{11}'-[(\sigma_{11}')^2-2\sigma_{11}''\sigma_{11}]$$
$$=A_{22}'-[(\sigma_{22}')^2-2\sigma_{22}''\sigma_{22}], \quad (5.58)$$

where σ_{ii}, σ_{ii}', and σ_{ii}'' are expressible in terms of A_{ii} and B_{ii} via (5.16). It is to be noted that (5.54) and (5.57) do not contain α explicitly. They are indeed equivalent to the relations obtainable from Eq. (5.38) when the constants h_1 and h_2 appearing there are expressed in terms of $i=1$ or $i=2$,

$$h_1=-\sigma_{12}^2, \qquad (5.59)$$

$$h_2=A_{11}A_{22}+(A_{11}+A_{22})K$$
$$=(2\pi\rho_1\rho_2)^2\det(\partial\mu_i/\partial\rho_j), \qquad (5.60)$$

where the last equality was derived along the lines of Eq. (4.6). We expect that $h_1<0$ and $h_2>0$, at least for small densities,[18] so that $E(s)$ would have a pair of real roots and two pairs of complex roots. A phase transition, corresponding to a separation of the two components, might then show up as a locus of points where $h_2=0$.

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[1] See, for example, G. S. Rushbrooke, in *Statistical Mechanics of Equilibrium and Non-Equilibrium*, edited by J. Meixner (North-Holland, Amsterdam, 1965), p. 222.

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[7] O. Penrose and J. L. Lebowitz (to be published).

[8] The vanishing of the exact direct correlation functions $C_{ij}(r)$ for $r>R_{ij}$, in the additive-diameter case, can be understood from an analysis of the Mayer graphs entering the virial expansion of these functions. Using some theorems due to Andrew Locket (private communication) it is seen that only "complete" f graphs contribute to $C_{ij}(r)$. We believe that the difference between the additive and nonadditive cases is related to the fact that in the former the Mayer graphs can be transformed into "interval graphs."

[9] The thermodynamic functions for the nonadditive case were also found by C. C. Carter, "On the van der Waal's Theory of Binary Mixtures", thesis, Rockefeller University, 1966.

[10] See, for example, A. Muenster, *Statistical Thermodynamics* (Wiley, New York, 1962); E. Helfand, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. **34**, 1037 (1961).

[11] J. S. Rowlinson, *Liquids and Liquid Mixtures* (Academic, New York, 1959).

[12] The symmetry inherent in this analogy has been very interestingly used by B. Widom and J. Rowlinson, J. Chem. Phys. **52**, 1670 (1970), in their analysis of a one-component system "isomorphic" to our binary mixture with $R_{11}=R_{22}=0$ 0, $\alpha>0$. The existence of a phase transition in lattice gases of this type was proven recently by J. L. Lebowitz and G. Gallavotti, J. Math. Phys. (to be published).

[13] J. L. Lebowitz, J. K. Percus, and I. J. Zucker, Bull. Am. Phys. Soc. **7**, 415 (1962).

[14] See, e.g., E. C. Titchmarsh, *The Theory of Functions* (Oxford U.P., London, 1939).

[15] J. L. Lebowitz and J. S. Rowlinson, J. Chem. Phys. **41**, 133 (1964).

[16] The final simplicity of the expression for the det (M_{ij}), which happens also in the 3-D additive-diameter case, c.f., Eqs. (4.2) and (4.3) in Ref. 15, is mystifying. We are particularly interested in this for our, $\alpha\neq0$, 3-D case, where we expect a phase transition and this determinant appears explicitly in Eq. (5.60).

[17] Calling σ_{ij}, σ_{ij}' and σ_{ij}'' the values of $\sigma_{ij}(r)$ and its first two derivatives (which are continuous) at $r=R_{ij}$ we have

$$a_1=[\sigma_{22}-\sigma_{11}]^2, \qquad b_1=2[\sigma_{11}\sigma_{22}'-\sigma_{22}\sigma_{11}'], \qquad c_1=-[\sigma_{11}+\sigma_{22}]^2,$$

$$b_2=-2[\sigma_{22}R_{11}A_{11}'-\sigma_{11}R_{22}A_{22}'+\sigma_{22}''\sigma_{11}'-\sigma_{11}''\sigma_{22}'],$$

$$\begin{aligned}c_2=&(12)^2[\eta_1+\eta_2]a-2h_2+2A_{11}A_{22}+4(R_{22}-R_{11})[A_{11}B_{22}-A_{22}B_{11}]\\&+12a[\eta_2A_{11}(4R_{22}^3-12R_{22}^2R_{11})+\eta_1A_{22}(4R_{11}^3-12R_{11}^2R_{22})]\\&-4B_{11}B_{22}(R_{11}-R_{22})^2+6(12)^2a^2\eta_1\eta_2[R_{11}^2+R_{22}^2-\tfrac{3}{2}R_{11}R_{22}]\\&+12a[2\eta_2B_{11}(4R_{11}R_{22}^3-6R_{11}^2-R_{22}^4)\\&+2\eta_1B_{22}(4R_{22}R_{11}^3-6R_{11}^2R_{22}^2-R_{11}^4)]\\=&a_2+2(12)^2a[\eta_1+\eta_2]-4h_2.\end{aligned}$$

[18] The existence of unique solutions of the PY equation, having a convergent virial expansion, for the type of system considered here has been proven, for small values of the densities $\rho_iR_{ii}^3$, by J. Groeneveld, J. Chem. Phys. **53**, 3193 (1970).