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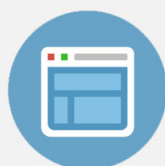
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A simple equilibrium statistical mechanical theory of dense hard sphere fluid mixtures

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The equilibrium statistical mechanical theory of Andrews for a hard core fluid is reformulated generally from simple, rigorous probability theory and is shown to apply to multicomponent systems. A simple expression is rigorously derived for the third virial coefficient of a mixture of nonadditive hard spheres. In the cases of additive potentials or binary systems, the expression is a great simplification of the previously known result. The exact theory of mixtures of not necessarily additive one-dimensional hard lines is developed simply for uniform mixing. Expressions for the reciprocal of the activity and the pressure in mixtures of additive hard spheres are determined approximately by similar methods. Calculations for binary mixtures with diameter ratios of 1.1 to 1, 1.667 to 1, and 3 to 1 are compared with computer experiments. The theory is significantly better than either the equation of state obtained from the Percus-Yevick equation or from the scaled particle theory. Indeed, it is about as accurate as the best empirical equation of Mansoori, Carnahan, Starling, and Leland. The physical origin of the decrease in pressure with diameter ratio at constant volume is discussed. Equations are listed, permitting calculation of various excess functions and excess functions of mixing for hard spheres.

I. INTRODUCTION

Almost certainly, modern statistical mechanical theories of liquids will represent the positions of the molecules, at least to a first approximation, by the positions of an equally dense collection of hard particles of appropriate dimensions. Outside the critical region, the molecules' attractive wells have little effect on the structure of the fluid, even though they profoundly affect the values of the thermodynamic properties. Thus, as a starting point for a theory of liquids, a theory of hard cores is needed which is relatively simple, accurate, and pictorial, so that it leads naturally to extension by grafting attractive wells on to the hard core potentials (of a possibly temperature-dependent diameter).

It is possible to describe the challenge in developing a successful theory of hard particles in the following manner: All we need to do is to describe an array of N particles placed "randomly" in a space S (where S is the length, area, or volume of the system in one, two, or three dimensions, respectively). If the particles are points, the meaning of the word random is perfectly clear. The probability per unit space of finding a particle is always $\rho = N/S$, regardless of what we know about the region of interest. The presence of a particle at \mathbf{r} in no way affects the probability of finding particles nearby. There is absolutely no correlation between positions of the N point particles. However, as soon as the particles are allowed to have finite hard cores, the meaning of a random distribution becomes more complicated. The presence of one particle at \mathbf{r} implies that no other could lie within σ of \mathbf{r} , where σ is the diameter of a single particle. This feature destroys the simple mathematical consequences of "randomness" found with points. The centers of the N particles are not distributed at random in S . They are held apart from each other by at least the distance σ . The meaning of random in this case does not relate to the centers of the particles, but is instead related in some way to their edge-to-edge separations. How it relates mathematically is unclear. True, we can use a Monte Carlo or

molecular dynamics treatment to mimic actual experiments which create random configurations. However, as the hard core diameters increase, the correlation among particle centers increases. The positions of the particles become increasingly uniform; significant fluctuations in density, either clusters or voids, become less and less common. This can be seen clearly in contrasting the uncorrelated centers of point particles with the highly correlated centers of crystalline close-packed spheres. Similarly, one can imagine the distribution of centers of N one-dimensional hard lines of length σ on a line of length L . When $N\sigma \ll L$, the essentially point particles are randomly arrayed. As $N\sigma$ increases, the effect of the particle centers' being held apart from each other becomes more and more significant. The distances separating particle centers become more and more uniform until finally, as $N\sigma$ approaches L , the particle separation distances approach the constant value of σ .

The meaning of a random distribution of hard particles is easy to determine in the case of one-dimensional systems. For them, it is equivalent to reducing the length of a hard particle from σ to a point, provided one simultaneously reduces the length of the box by σ . The meaning of a random distribution of hard lines is the same as a random distribution of points in a box of length $L - N\sigma$. When the problem dimensionality exceeds one, however, no equivalence exists between the distribution of edge-to-edge separations and the distribution of point-to-point separations in a collection of points in a vessel of some size less than S . This is because there then exist multiple paths from one particle to another involving different numbers of intermediate particles, so the particle diameters cannot simply be reduced from σ to 0 while preserving edge-to-edge separations.

The essence of the problem of describing hard particles theoretically is, then, capturing the essence of this subtle correlation of the particle centers as the fraction of S occupied by the hard cores increases. In previous publications,¹⁻³ one of us has formulated a

theory which approaches the problem in a physically pictorial manner. The approach involves, of course, an approximation, but one made at such a place that the results of the theory are highly insensitive to it, so long as it is reasonable. We have reformulated that theory since it was first published for single component hard spheres, disks, and lines, so that its basis is more transparent, and we present that reformulation in Sec. II. In Sec. III we cite a few general results needed for a multicomponent theory. In Sec. IV we use our general approach to calculate the exact third virial coefficient for mixtures of not necessarily additive hard spheres. We use third virial coefficients, or an approximation thereto, in our general theory. In Sec. V we give an exact treatment of mixtures of not necessarily additive one-dimensional hard lines for the case of uniform mixing. In Sec. VI, we formally develop our expression for the reciprocal of the activity (and ultimately for the pressure) of one component in a three-dimensional mixture of hard spheres. In Sec. VII we compare the results of our theory with the three sets of computer-generated experimental data on binary hard sphere mixtures that exist in the literature. We observe that our results are significantly better than those generated by either the Percus-Yevick theory or the scaled particle theory, and indeed are about as accurate as the results offered by the best empirical equations which claim no basis in a molecular theory. We also discuss the decrease in pressure with diameter ratio in binary hard sphere mixtures at constant volume fraction occupied. In Sec. VIII we summarize the thermodynamic formulas one can use in going from quantities generated by the theory to various excess properties for both single component hard particles and for the process of mixing them. In Sec. IX we discuss the work reported here and attempt to evaluate it.

II. GENERAL FORMULATION OF OUR THEORY FOR SINGLE-COMPONENT HARD PARTICLES

Let there be a total of N particles in a total space S (where $S=L$, the box length, in one dimension; $S=A$, the system area, in two dimensions; $S=V$, the system volume, in three dimensions). We fix these particles in a typical equilibrium configuration, reflecting the most probable distribution of interparticle separations. Our theory generates an expression for the reciprocal of the activity a^{-1} of the fluid, where the standard state used is an ideal gas of molecules of the type being considered at the temperature and density of the system. For hard particles, Sa^{-1} is simply the total space through which an $(N+1)$ st particle could move without overlapping one of the N fixed particles. This means that a^{-1} is simply the probability that at a point r chosen at random an $(N+1)$ st particle could be inserted. We calculate this probability as the product of two terms $a^{-1} = I \cdot II$. The first term is the probability that the point r does not overlap one of the N particles of diameter σ , i. e., that none of the N fixed particles has its center within $\frac{1}{2}\sigma$ of r . The space occupied by each hard core we denote by s_c , where $s_c = \sigma$ in one dimension, $s_c = \pi(\frac{1}{2}\sigma)^2 = \frac{1}{4}\pi\sigma^2$ in two dimensions, and $s_c = \frac{4}{3}\pi(\frac{1}{2}\sigma)^3 = \frac{1}{6}\pi\sigma^3$ in three dimensions. The value of I is simply the ratio of empty space

$S - Ns_c$ to total space S :

$$I = \frac{\text{empty space}}{\text{total space}} = \frac{S - Ns_c}{S} = 1 - \frac{Ns_c}{S} \quad (1)$$

The second term is the probability, conditional on the first, that no particle lies in the rest of the space that needs to be empty if the $(N+1)$ st is to be accommodated. That space is an annulus whose size we denote by s_a . In one dimension $s_a = 2\sigma - \sigma = \sigma$. In two dimensions $s_a = \pi\sigma^2 - \frac{1}{2}\pi\sigma^2 = \frac{1}{2}\pi\sigma^2$. In three dimensions $s_a = \frac{4}{3}\pi\sigma^3 - \frac{1}{6}\pi\sigma^3 = \frac{1}{2}\pi\sigma^3$. No member of the ensemble that contributes to I has a particle center inside the region s_c located about the point r . We now expand the size of the region by moving out further away from r ; II is the fraction of the remaining members that have the additional region s_a empty of particle centers. It is here that we can exploit the meaning of the random distribution imposed on the N hard cores, as discussed in Sec. I. Once we know that r does not overlap a core, the random positions of the N particles and the fact that r was chosen at random assure that there is a constant probability density w for finding the nearest particle center as we increase the annular region. There is nothing which could cause correlation with position, and no physical cause of such correlation. Thus, the randomness in the N particles' positions enters the theory: The probability $w d\alpha$, conditional on there being no particle inside the annulus α , that the first neighbor lies within the infinitesimal annulus of space $d\alpha$ between α and $\alpha + d\alpha$ is independent of position:

$$w d\alpha = \text{probability, conditional on no particle inside } \alpha, \text{ that one lies between } \alpha \text{ and } \alpha + d\alpha \quad (2)$$

We are certain that $N-1$ of the particles are outside $d\alpha$ in the members of the ensemble still being counted. At most, one of them could be within $d\alpha$. The probability that one of them is inside and the other $N-1$ outside is $w d\alpha$.

The functional dependence of $II(\alpha)$ on annulus size α follows immediately from Eq. (2). The product $II(\alpha)$ times $w d\alpha$ from Eq. (2) is the probability, conditional on no particle center in s_c , that the closest particle to r has its center in the annulus between α and $\alpha + d\alpha$. The negative of this $wII(\alpha) d\alpha$ is thus identical to the change dII in II on increasing the annulus from α to $\alpha + d\alpha$. Thus, II is the solution of the equation

$$dII(\alpha) = -wII(\alpha) d\alpha \quad (3)$$

Thus, the form $II(\alpha) = c \exp(-w\alpha)$ follows immediately, where c and w are independent of annular size. If $\alpha = 0$, all N particles must lie outside it; thus, $II(0) = 1$, from which we conclude that $c = 1$ and

$$a^{-1} = I \cdot II = \left(1 - \frac{Ns_c}{S}\right) \exp(-ws_a) \quad (4)$$

A different way to view w , equivalent to that of Eq. (2), is obtained by noting that the probability density of Eq. (2) is normalized to unity in the range $\alpha = 0$ to $\alpha = \infty$, as it should be. We thus can calculate the average empty annulus A before a nearest particle is encountered:

$$A = \int_0^\infty \alpha w e^{-w\alpha} d\alpha = \frac{1}{w}. \quad (5)$$

Thus, w is the reciprocal of the average size of the empty annulus found about the empty hard core space (of radius $\frac{1}{2}\sigma$) of the particle.

With these interpretations of w , and with w the only thing undetermined in Eq. (4), we are in a position to proceed. In the picture afforded by Eq. (4), all N particles are together in the system; the center of none of them lies within the region $s_c + \alpha$; and we want the probability that one of them lies in $d\alpha$. This is N times the probability that a particular one lies in $d\alpha$. This is the ratio of $d\alpha$ to the effective empty space available to a particular particle in the fluid as that space has been reduced from S by the presence of the $N-1$ other particles. If we call the average amount by which each such other particle reduces the effective empty space ω , then $w = N/(S - N\omega)$, and we can write

$$a_i^{-1} = \left(1 - \frac{NS_c}{S}\right) \exp\left(\frac{-NS_a}{S - N\omega}\right) = (1 - s_c\rho) \exp\left(\frac{-s_a\rho}{1 - \omega\rho}\right). \quad (6)$$

This equation is the basis of our theory. It is simple, derived rigorously from statistical mechanics and probability theory, and intuitive. Everything in Eq. (6) is determined except ω , and the values of important quantities are highly insensitive to the choice of ω . Any reasonable choice of ω , guided by minimal physical insight into what it represents, leads in the cases where we have applied Eq. (6) to excellent results. This is the picture we follow in order to calculate ω : We imagine the N particles originally in their equilibrium configuration in S to begin to attract each other and thus all to move gently, without jostling, together toward the center of the vessel. Ultimately, they will reach a condition where they are packed so closely that further packing would require jostling and thus increasing their order. In this close-packed condition (which still represents the particles' original disorder) molecular sized holes would not exist (except in mixtures of particles of widely differing sizes; see Sec. VI). The volume of this resulting cluster of the N particles is $N\omega$. The value of ω in more than one dimension would be a weak function of density, because the increase in order with density discussed in Sec. I will result in a decrease in ω with density. In one dimension, the close-packed cluster has the length $N\sigma$ regardless of the starting density of the hard lines. In two or three dimensions ω will always be greater than s_c , because there is no way to pack circles or spheres without trapping empty space along with each hard core occupying s_c . For example, in three dimension $s_c = 0.5236\sigma^3$, while crystalline close packing, which yields the smallest possible value of ω , has $\omega = 0.7071\sigma^3$. This extra empty space lies in the interstices between hard spheres, even when they are close packed. It is effectively removed from the empty part of the system through the combined interactions of the set of particles by virtue of their round shapes when they cluster together in the center, in the condition out of which we view the actual equilibrium condition to have been reached through expansion. We therefore expect ω to start fairly large, perhaps a bit larger than the value consistent with simple

cubic (square) packing, and then to decrease with increasing density. At the maximum fluid density ω should lie around $0.8225\sigma^3$ (in three dimensions), which is the well-known average volume occupied by close-packed spheres which are forced to stay random and not allowed to jostle into crystalline structure.⁴

Any theory based on Eq. (6) which builds the above considerations into the value of ω will predict results within a couple of percent of computer experimental data on spheres. Different choices could be made, trading off simplicity against precision. In Sec. VII of this paper, we use a particular approximation to ω that is extremely simple, yet that catches the important elements of the physical picture for mixtures of spheres in three dimensions.

III. THE RECIPROCAL OF THE ACTIVITY

Let there be a total of N particles in a space S , where N_1 are of component 1, N_2 of component 2, ..., N_n of component n . We let $\rho \equiv N/S$, $\beta \equiv 1/kT$, $X_k \equiv N_k/N$, and a_i^{-1} = the reciprocal of the activity of component i , defined by

$$\mu_i(\rho, T, \mathbf{X}) \equiv \mu_i^0(X_i \rho, T) - kT \ln a_i^{-1}(\rho, T, \mathbf{X}), \quad (7)$$

where μ_i^0 is the chemical potential of i in an ideal gas of density $X_i\rho$ and temperature T . The set of mole fractions is denoted by \mathbf{X} .

A procedure parallel to that of Sec. II of Ref. 1 is valid for semiclassical mixtures, as well as for single-component fluids. The same useful starting point is obtained in a multicomponent theory:

$$Sa_i^{-1} = \int d\mathbf{r}_{N+1,i} \exp(-2\beta u_{N+1,i}). \quad (8)$$

The subscript $N+1$, i on $d\mathbf{r}$ means the space element for the $(N+1)$ st particle, which is of type i . Equation (8) means that in order to perform the integration, we first fix the N particles in a most likely configuration, then let the $(N+1)$ st (of type i) wander throughout the system, weighting each space element by the exponential in the total potential energy introduced by that particle. Thus, $2u_{N+1,i}$ is the difference in total intermolecular potential energy when the N particles are at a typical \mathbf{r}^N in the presence of an $(N+1)$ st of type i at \mathbf{r}_{N+1} and when the N particles are at \mathbf{r}^N in the absence of the $(N+1)$ st.

It is an exercise in thermodynamics to express the pressure of a mixture in a form analogous to Eq. (6) of Ref. 1, as an integral over a_i^{-1} for each component:

$$\frac{p}{\rho kT} = \sum_{i=1}^n X_i \left[1 - \ln a_i^{-1} + \frac{1}{\rho} \int_0^\rho \ln a_i^{-1}(T, \rho', \mathbf{X}) d\rho' \right]. \quad (9)$$

IV. EXACT THIRD VIRIAL COEFFICIENTS FOR MIXTURES OF NOT NECESSARILY ADDITIVE HARD SPHERES

The advantages of Eq. (8) as a starting point for a theory of fluids are that it is both exact and pictorial. Andrews has used it for a pedagogically attractive formulation of the formal expressions for virial coefficients.⁵ The ideal gas appears when the N particles are com-

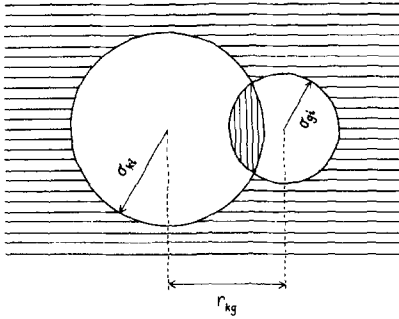


FIG. 1. Particles of types g and k , when separated by less than $\sigma_{ki} + \sigma_{gi}$, exclude between them the vertically shaded region from particle i . If they were further apart, they would each exclude the region separately.

pletely ignored; the second virial coefficient enters when the N particles are admitted but separated by large distances so there are no interactions among them [only between them and the $(N+1)$ st]; the third virial coefficient corrects for the fact that some pairs among the N would typically lie close together. Let us follow this procedure for a mixture of hard spheres of different sizes. We will develop a_i^{-1} in a power series in the density

$$a_i^{-1} = 1 + A_{2i} \rho + A_{3i} \rho^2 + \dots \quad (10)$$

through developing Eq. (8) in the form

$$V a_i^{-1} = V + N A_{2i} + \frac{N^2}{V} A_{3i} + \dots \quad (11)$$

In three dimensions, the rhs of Eq. (8) is the volume in which the wandering $(N+1)$ st particle of type i could fit, given that the N hard spheres of appropriate sizes were fixed in the vessel in some typical equilibrium configuration. If these spheres were nonexistent, $u=0$ and the rhs of Eq. (8) would simply be V , the leading term of Eq. (11). If these spheres are taken in the first approximation to lie a long way from each other, then in the region of each of them we must replace the $d\mathbf{r}_{N+1,i}$ that contributed to V by $\exp(-\beta U) d\mathbf{r}_{N+1,i}$, where U is the potential between the wanderer and the fixed particle. The N such fixed particles generate N separate regions in which this replacement must occur:

$$A_{2i}(n) = \sum_{k=1}^n X_k \int d\mathbf{r}_{ki} f_{ki}, \quad (12)$$

where we introduce the formal notation

$$f_{ki} \equiv e_{ki} - 1, \quad e_{ki} \equiv \exp[-\beta U_{ki}(r_{ki})], \quad (13)$$

where the subscripts refer to the components of the pair

of particles concerned. For hard spheres, the negative of the integral in Eq. (12) is simply the volume $\frac{4}{3}\pi\sigma_{ki}^3$ excluded to the wanderer (of type i) by the presence of an isolated particle of type k . We denote the hard-core diameter for a $k-i$ pair by σ_{ki} . Thus, for hard sphere mixtures,

$$A_{2i} = -\frac{4}{3}\pi \sum_{k=1}^n X_k \sigma_{ki}^3. \quad (14)$$

The second virial coefficient is computed in terms of the A_2 's by expanding Eq. (9) in a power series in ρ :

$$B_{\text{mix}} = -\frac{1}{2} \sum_{i=1}^n X_i A_{2i}, \quad (15)$$

and for hard sphere mixtures it is the well-known result

$$B_{\text{mix}} = \frac{2}{3}\pi \sum_{i,k=1}^n X_i X_k \sigma_{ki}^3. \quad (16)$$

Now let us consider the next correction term in Eq. (11). Some pairs of the N fixed particles will lie near each other, in which case the overlap of their annuli with each other and the wanderer demands a correction. To the lowest order in density, the probability that a particle of type k lies in $d\mathbf{r}_k$ and a particle of type g nearby in $d\mathbf{r}_g$ is $d\mathbf{r}_k d\mathbf{r}_g e_{kg}/V^2$. If they do lie there, the $d\mathbf{r}_i$ that contributed to the V term in Eq. (11) must be changed to $e_{ki} e_{gi} d\mathbf{r}_i$, and the contributions they make to Eq. (12) must be subtracted, since their contributions are given already. Manipulations which parallel those of Ref. 5 lead to the general result

$$A_{3i} = \frac{1}{2} \sum_{k,g=1}^n X_k X_g \int d\mathbf{r}_{kg} d\mathbf{r}_{gi} e_{kg} f_{ki} f_{gi}. \quad (17)$$

For hard sphere mixtures, the physical interpretation of the integral in Eq. (17) is as follows: If the particles of type k and g were truly a long way apart, they would keep the wanderer out of the two spheres of total volume $\frac{4}{3}\pi(\sigma_{ki}^3 + \sigma_{gi}^3)$. That excluded volume is handled correctly by the A_2 term. If the particles of type k and g are within the distance $(\sigma_{ki} + \sigma_{gi})$ of each other, however, the volume available to the wanderer is increased, as shown by the horizontally shaded region in Fig. 1. The vertically shaded region is excluded to the $(N+1)$ st by both when they are widely separated, but excluded only once by them jointly when they are close together. Thus, evaluating Eq. (17) for hard sphere mixtures is simply computing the lens-like vertically shaded volume in Fig. 1 (the integral over $d\mathbf{r}_{gi}$) and then integrating it over all relative positions of the particles of type k and g (the integral over $d\mathbf{r}_{kg}$). For hard spheres, the result is

$$A_{3i} = \frac{1}{2}\pi^2 \sum_{k,g=1}^n X_k X_g \left(-\frac{1}{9}\sigma_{ki}^6 - \frac{1}{18}\sigma_{kg}^6 + \sigma_{ki}^4 \sigma_{gi}^2 + \sigma_{ki}^4 \sigma_{kg}^2 + \sigma_{kg}^4 \sigma_{ki}^2 + \frac{8}{9}\sigma_{ki}^3 \sigma_{gi}^3 - \frac{16}{9}\sigma_{ki}^3 \sigma_{kg}^3 - \sigma_{ki}^2 \sigma_{gi}^2 \sigma_{kg}^2 \right). \quad (18)$$

The third virial coefficient is computed in terms of the A_2 's and A_3 's by expanding Eq. (9) in a power series in ρ :

$$C_{\text{mix}}(T) = -\sum_{i=1}^n X_i \left(\frac{2}{3} A_{3i} - \frac{1}{3} A_{2i}^2 \right). \quad (19)$$

For mixtures of an arbitrary number of components of hard spheres whose diameters are not necessarily additive, the resulting exact third virial coefficient is

$$C_{\text{mix}} = \frac{\pi^2}{54} \sum_{i,k,g=1}^n X_i X_k X_g (3\sigma_{ki}^6 - 54\sigma_{ki}^4 \sigma_{gi}^2 + 48\sigma_{ki}^3 \sigma_{gi}^3 + 18\sigma_{ki}^2 \sigma_{gi}^2 \sigma_{gk}^2) . \quad (20)$$

In two special cases, Eq. (20) simplifies. For additive potentials, $\sigma_{gh} = \frac{1}{2}(\sigma_{gg} + \sigma_{hh})$, and we can define dimensionless diameter ratios y_g by $\sigma_{gg} = y_g \sigma$. Here, we are letting σ be the diameter of the smallest spheres, so $y_1 = 1$. In this case the exact third virial coefficient becomes

$$\begin{aligned} C_{\text{mix}} &= \frac{\pi^2}{6} \sigma^6 \sum_{i,k,g=1}^n X_i X_k X_g (y_i^3 y_k^2 y_g + \frac{1}{2} y_i^2 y_k^2 y_g^2 + \frac{1}{6} y_i^3 y_k^3) \\ &= \frac{\pi^2}{6} \sigma^6 \left[\left(\sum_{k=1}^n y_k X_k \right) \left(\sum_{k=1}^n y_k^2 X_k \right) \left(\sum_{k=1}^n y_k^3 X_k \right) + \frac{1}{2} \left(\sum_{k=1}^n y_k^2 X_k \right)^3 + \frac{1}{6} \left(\sum_{k=1}^n y_k^3 X_k \right)^2 \right] . \end{aligned} \quad (21)$$

This is a simplified expression of the conventional result⁶; the conventional result is also obtained from the Percus-Yevick approximation applied to the compressibility (but not the virial) expression.⁷ For binary mixtures of hard sphere fluids, the exact third virial coefficient has long been available,⁸ but Eq. (20) or (21) permits a dramatic simplification in its formulation:

$$C_{\text{binary}}(T) = \frac{\pi^2 \sigma^6}{36} \{ X^2 [(1-X)(8y^3 + 15y^2 + 6y + 1) + 10X] + (1-X)^2 y^3 [X(y^3 + 6y^2 + 15y + 8) + (1-X)10y^3] \} . \quad (22)$$

Here, σ is the diameter of the smaller spheres, and $y\sigma$ the diameter of the larger; X is the mole fraction of the smaller, and $(1-X)$ the mole fraction of the larger.

V. ONE-DIMENSIONAL MIXTURE OF NOT NECESSARILY ADDITIVE HARD LINES

Consider a one-dimensional mixture of N hard lines in a box of length L , each component k having mole fraction X_k . Let the intermolecular potential between particles of types g and k be ∞ for separation distances less than σ_{gk} and 0 for distances greater. We evaluate the rhs of Eq. (8) in a manner parallel to that developed in Sec. II for single-component fluids. We place the N lines in a configuration typical of equilibrium, and identify a_i^{-1} as the probability that at a randomly chosen point x an extra particle of type i could be accommodated.

Allowing nonadditive potentials raises two interesting questions: (1) What is a configuration typical of equilibrium, and (2) what is the meaning of the probability that x does not overlap one of the lines when the length of a line depends on the nature of its neighbor? It is easy to see that it is not enough to scatter the N particles at random on the line L , with uniform density $\rho_k = X_k \rho$ of each component throughout the vessel. That would maximize the entropy. However, suppose, for example, that $\sigma_{gk} = \frac{1}{2}(\sigma_{gg} + \sigma_{kk}) + \Delta$, where Δ is a large positive quantity. As the density is increased in a mixture of g and k particles, there must come a time when the g 's clump together and the k 's clump separately. Indeed, one could jam so many particles into the box that the only way they could be accommodated would be for the g 's and k 's to separate completely with only a single interface between the pure g 's and the pure k 's. Nonadditive lines have been studied,⁹ and we anticipate using the pictorial nature of Eq. (8) to explore the nonuniformity of the distribution in a future paper. For now, we simply place the N particles randomly on L , acknowledging that this is not truly the equilibrium structure, but noting that unless the nonadditivity and density are both large, this will be an excellent approximation.

The second question raises the ambiguous nature of "the length of a particle," since particles' lengths are not intrinsic, but depend on the nature of their neighbors. These lengths, however, are independent of the nature i of the $(N+1)$ st particle; thus, they are a feature of the distribution of the N particles on L . If this distribution is random, the probability of a kl pair in that order is $X_k X_l$. The length within which the point x would overlap a particle's core is thus $N \sum_{k,l} X_k X_l \sigma_{kl}$, and the value of I in Eq. (1) is $1 - \rho \sum_{k,l} X_k X_l \sigma_{kl}$. For additive potentials for which $\sigma_{kl} = \frac{1}{2}(\sigma_{kk} + \sigma_{ll})$ and $\sigma_{kk} \equiv y_k \sigma$, this expression reduces to $1 - \rho \sigma \sum_k X_k y_k$. The value of I is obtained from Eq. (6), where s_a is the total empty space needed to accommodate a particle of type i minus the amount of empty space we know already exists about x . The former is $\sigma_{ki} + \sigma_{ii}$, and the latter is σ_{ki} , so $s_a = \sigma_{ki} + \sigma_{ii} - \sigma_{ki}$. The value of ω is the average length per particle when all N are jammed together; in this case that is $\sum_{k,l} X_k X_l \sigma_{kl}$, so we can write the reciprocal of the activity of component i in a one-dimensional mixture of not necessarily additive randomly distributed hard lines:

$$\begin{aligned} a_i^{-1} &= \left(1 - \rho \sum_{k,l=1}^n X_k X_l \sigma_{kl} \right) \\ &\times \exp \left[\frac{-\rho \sum_{k,l} X_k X_l (\sigma_{kl} + \sigma_{li} - \sigma_{ki})}{1 - \rho \sum_{k,l} X_k X_l \sigma_{kl}} \right] . \end{aligned} \quad (23)$$

The analog of Eq. (23) for additive potentials is

$$a_i^{-1} = \left(1 - \rho \sigma \sum_k X_k y_k \right) \exp \left(\frac{-\rho y_i \sigma}{1 - \rho \sigma \sum_k X_k y_k} \right) . \quad (24)$$

From Eq. (23), the pressure for nonadditive lines follows from the use of Eq. (9):

$$\frac{p}{\rho k T} = \frac{1}{1 - \rho \sum_{k,l} X_k X_l \sigma_{kl}} . \quad (25)$$

For additive potentials the equivalent of Eq. (25) is

$$\frac{p}{\rho kT} = \frac{1}{1 - \rho \sum_k X_k \sigma_k} \quad (26)$$

These expressions are in strict analogy to the single-component result.¹⁰ The simple Eq. (25) catches the leading term in the expansion in powers of the nonadditive part of the potential where the equilibrium configuration of the N particles is allowed to vary.

VI. HARD SPHERE FLUID MIXTURE

We calculate a_i^{-1} for a hard sphere mixture in the manner described in Sec. II. The first probability term I is the probability that \mathbf{r} lies in empty space and not inside the core of one of the N fixed particles. This is unambiguous for additive potentials and is the fraction $1 - \frac{1}{6} \pi \rho \sum_k X_k \sigma_{kk}^3$ of the vessel that is not taken up by cores. It is the probability that no particle of type k has its center within $\frac{1}{2} \sigma_{kk}$ of \mathbf{r} . The second term is the probability, conditional on the first, that free space surrounds \mathbf{r} not just out to a distance $\frac{1}{2} \sigma_{kk}$, but beyond that by a further distance $\frac{1}{2} \sigma_{ii}$. The volume of this spherical shell which must additionally be empty is

$$s_a = \frac{4}{3} \pi \left[\left(\frac{1}{2} (\sigma_{ii} + \sigma_{kk}) \right)^3 - \frac{4}{3} \pi \left(\frac{1}{2} \sigma_{kk} \right)^3 \right] = \frac{\pi}{6} [(\sigma_{ii} + \sigma_{kk})^3 - \sigma_{kk}^3]. \quad (27)$$

Use of these results in Eq. (6) gives the reciprocal of the activity in a mixture of additive hard cores:

$$a_i^{-1} = \left(1 - \frac{1}{6} \pi \rho \sum_k X_k \sigma_{kk}^3 \right) \times \exp \left\{ \frac{-\frac{1}{6} \pi \rho \sum_k X_k [(\sigma_{ii} + \sigma_{kk})^3 - \sigma_{kk}^3]}{1 - \rho \omega_i} \right\}. \quad (28)$$

This may be written for additive potentials in terms of y 's defined by $\sigma_{kk} \equiv y_k \sigma$:

$$a_i^{-1} = \left(1 - \frac{1}{6} \pi \rho \sigma^3 \sum_k X_k y_k^3 \right) \times \exp \left\{ \frac{-\frac{1}{6} \pi \rho \sigma^3 \sum_k X_k [(y_i + y_k)^3 - y_k^3]}{1 - \rho \omega_i} \right\}. \quad (29)$$

For nonadditive potentials, an analogy to Eq. (23) may also be written:

$$a_i^{-1} = \left(1 - \frac{1}{6} \pi \rho \sum_{k,l} X_k X_l \sigma_{kl}^3 \right) \times \exp \left[\frac{-\frac{1}{6} \pi \rho \sum_{k,l} X_k X_l (8\sigma_{kl}^3 - \sigma_{kl}^3)}{1 - \rho \omega_i} \right]. \quad (30)$$

The integration over density to obtain the pressure can be done for Eq. (28), (29), or (30) only after the value of ω_i is estimated, and this estimate is all that remains in order to complete the theory.

The value of ω_i is the average volume effectively excluded to a type i particle by each sphere in the mixture when they are jammed together gently as described in Sec. II. The nature of this jamming is unambiguous only for crystals or for one-dimensional systems. The strength of our approach to fluids, however, is that the results are insensitive to choice of ω_i . Any realistic choice can catch the essence of the fluid. The second virial coefficient is given correctly, regardless of the choice of ω_i . The simplest possible choice of ω for single component spheres is probably the constant value

$0.8225\sigma^3$, the "random close packed" volume of such spheres.^{4,10} Further refinements in the choice of ω involve imagining or calculating the nature of the jam structure into which the system can be viewed as being gently squeezed. In previous work we have not bothered to refine ω by some complex process such as fitting a lot of known virial coefficients. The virtue of our approach is that physical transparency and simplicity accompany a theory whose precision is the equal of the most complicated existing theories. Indeed, replacing ω by the constant $0.7071\sigma^3$, its value for crystalline close-packed spheres, generates chemical potential and pressure as a function of density in remarkable agreement with computer experiments on crystalline spheres.¹ The volume increase on going from $0.7071\sigma^3$ to $0.8225\sigma^3$ is 15%, precisely the fractional volume increase observed experimentally in melting a host of simple substances. An intuitive understanding of the cause of crystallization is offered: By changing from random to ordered arrangement, the jam volume is decreased. This increases the effective empty volume and thereby the likelihood that the $(N+1)$ st particle can be accommodated in the system. Thus, the chemical potential in the crystal is decreased, despite the crystal's lowered entropy.

The low-density value of ω_i could be obtained exactly from Eq. (18). As we discussed in Sec. II, we would expect $\omega_i(\rho)$ to be a maximum at low density. As ρ increases and the correlations among the particle centers described in Sec. I become more significant, the value of ω_i should decrease. Here we follow the simplest reasonable procedure for determining $\omega_i(\rho, \mathbf{X})$, a procedure parallel to what we previously employed for single components.¹ We take high- and low-density values ω_{iH} and ω_{iL} , respectively, from simple considerations of what these values must be. We then let ω_i be a linear interpolation between them over the density range from zero to crystalline jam density. Although this procedure could be refined, we are buoyed by knowing how insensitive the results are to the details of the approach, and we let $\omega_i = \omega_{iL} + \rho A$, such that $\omega_i = \omega_{iH}$ at jam density ρ_0 : $\omega_{iH} = \omega_{iL} + \rho_0 A$. Thus, A must equal $(\omega_{iH} - \omega_{iL})/\rho_0$ and

$$\omega_i = \omega_{iL} + \frac{\rho}{\rho_0} (\omega_{iH} - \omega_{iL}). \quad (31)$$

We will write ω_{iL} and ω_{iH} formally by adding contributions from each component present, weighted by their mole fractions:

$$\omega_{iL} \equiv \sum_{k=1}^n X_k \omega_{iLk}, \quad \omega_{iH} \equiv \sum_{k=1}^n X_k \omega_{iHk}. \quad (32)$$

Here, ω_{iLk} is the average volume effectively excluded to a type i particle by spheres of type k in the mixture when all N spheres are crowded into the center of the box from an initial low density by the condensation process described in Sec. II. A natural choice for ω_{iLk} would be that which gives the exact third virial coefficient on using Eqs. (14) and (18). Examination of Eq. (18) in light of the insensitivity of results to the choice of ω suggests that it is needlessly complex. We would expect when particles i and k are about the same size that ω_{iLk} will

be the value of ω_L for single-component fluids: $(29/84)\pi\sigma^3 \approx 1.0846\sigma^3$. This evokes a picture of the type k particles jammed together in a structure some 2% expanded (linearly) from a simple cubic lattice. Such a picture also makes sense when $\sigma_{ii} > \sigma_{kk}$. On the other hand, when $\sigma_{ii} < \sigma_{kk}$ a different value of ω_{iL} is obtained. This can be seen in the limit where $\sigma_{ii}/\sigma_{kk} = 0$, where particle i is a point. In this case it makes no difference how the k particles jam together; they simply exclude the volumes of their cores, and ω_{iLk} is $\frac{4}{3}\pi(\frac{1}{2}\sigma_{kk})^3 = (\pi/6)\sigma_{kk}^3 = (\pi/6)\sigma^3 y_k^3$. These considerations are enough for us to catch the essence of the low-density ω_i for additive potentials (nonadditive spheres will be treated in a separate publication): (1) If $\sigma_{ii} \geq \sigma_{kk}$ (i.e., $y_i/y_k \geq 1$), $\omega_{iLk} = (29/84)\pi\sigma_{kk}^3 = (29/84)\pi(\sigma y_k)^3$. (2) If $\sigma_{ii}/\sigma_{kk} = 0$ (i.e., $y_i/y_k = 0$), $\omega_{iLk} = (\pi/6)\sigma_{kk}^3 = (\pi/6)(\sigma y_k)^3$. (3) In the range between $\sigma_{ii}/\sigma_{kk} = 0$ and $\sigma_{ii}/\sigma_{kk} = 1$, we interpolate linearly between the appropriate values of ω_{iLk} from (1) and (2) above:

$$\omega_{iLk} = \frac{29\pi}{84} a_{ik} \sigma_{kk}^3 = \frac{29\pi}{84} a_{ik} (\sigma y_k)^3, \quad (33)$$

where

$$a_{ik} = 1, \quad \text{for } y_i/y_k \geq 1 \text{ (i.e., } i \geq k), \quad (34)$$

$$a_{ik} = \frac{14}{29} + \frac{15y}{29y_k}, \quad \text{for } y_i/y_k \leq 1 \text{ (i.e., } i \leq k). \quad (35)$$

The last parentheses in Eqs. (34) and (35) apply when the component subscripts are ordered in increasing size of the particles. Use of Eqs. (34) and (35) leads to third virial coefficients for $X=0.5$ that are off from the exact values, given by Eq. (18), by only -1.09% , -2.66% , and $+1.01\%$ at $y=1.1$, $5/3$, and 3 , respectively.

In the high-density limit, similar considerations apply. The single-component analog of ω_{iH} would be simply $\omega_{iHk} = \sigma_{kk}^3/\sqrt{2} \approx 0.7071\sigma_{kk}^3$. The same complication arises here as in the low-density case for $\sigma_{ii} < \sigma_{kk}$; however, the effect of this complication on the value of ω_i is much less at high density where the molecules are closer together. We have found that correcting for this effect on ω_{iHk} in binary 50–50 mixtures of hard spheres has almost no effect at σ_{22}/σ_{11} = either 1.1 or 1.667. At $\sigma_{22}/\sigma_{11} = 3$, only slight improvement in the results ($< 1\%$) was found and only at high densities ($\rho > 0.48\rho_0$). Physically, this is just where one would expect the correction to be useful. We consider the added complexity of correcting ω_{iHk} to be unjustified. We have therefore settled on the following simple expression for a_i^{-1} for hard sphere mixtures:

$$a_i^{-1}(z, X, y) = (1 - \theta z) \exp\left(\frac{-\beta_i z}{1 - \gamma_i z + \Delta_i z^2}\right). \quad (36)$$

Here, z is the dimensionless density scaled by the crystalline multiphase close-packed density ρ_0 :

$$z \equiv \frac{\rho}{\rho_0} \equiv \frac{\sigma^3}{\sqrt{2}} \rho \sum_k X_k y_k^3 \equiv \frac{\sigma^3}{\sqrt{2}} \epsilon \rho, \quad (37)$$

$$\theta \equiv \frac{\sqrt{2}\pi}{6}, \quad (38)$$

$$\beta \equiv \frac{\theta}{\epsilon} \sum_k X_k [(y_i + y_k)^3 - y_k^3], \quad (39)$$

$$\gamma \equiv \frac{29\theta}{14\epsilon} \sum_k X_k a_{ik} y_k^3 \equiv \Delta_i + 1, \quad (40)$$

where a_{ik} is given by Eqs. (34) and (35), and ϵ is defined in Eq. (37). If Eq. (36) is used with Eq. (9), the resulting pressure is

$$\frac{p}{\rho kT} = \sum_{i=1}^n X_i \left[\frac{\beta_i z}{1 - \gamma_i z + \Delta_i z^2} - \frac{1}{\theta z} \ln(1 - \theta z) - \frac{\beta_i \gamma_i}{2\Delta_i(1 - \Delta_i)z} \ln\left(\frac{1 - \Delta_i z}{1 - z}\right) - \frac{\beta_i}{2\Delta_i z} \ln(1 - \gamma_i z + \Delta_i z^2) \right]. \quad (41)$$

This is analogous to the simple result found in Ref. 1 for single-component hard spheres.

VII. NUMERICAL RESULTS FOR BINARY MIXTURES

For binary mixtures with $X_1 = X$, $X_2 = (1 - X)$, $y_1 = 1$, and $y_2 = y$, the coefficients in Eq. (41) reduce to

$$z = \frac{\sigma^3}{\sqrt{2}} \rho [X + (1 - X)y^3] \equiv \frac{\sigma^3}{\sqrt{2}} \epsilon \rho, \quad (42)$$

$$\beta_1 = \frac{\theta}{\epsilon} \{7X + (1 - X)[(1 + y)^3 - y^3]\}, \quad (43)$$

$$\beta_2 = \frac{\theta}{\epsilon} \{X[(y + 1)^3 - 1] + 7(1 - X)y^3\}, \quad (44)$$

$$\gamma_1 = \frac{29\theta}{14\epsilon} \left[X + (1 - X) \left(\frac{14}{29} + \frac{15}{29y} \right) y^3 \right] \equiv \Delta_1 + 1, \quad (45)$$

$$\gamma_2 = \frac{29\theta}{14\epsilon} \equiv \Delta_2 + 1, \quad (46)$$

where the recurring quantity $X + (1 - X)y^3$ is defined in Eq. (42) to be ϵ .

The tables of this section compare the results for binary hard sphere mixtures using these parameters in Eq. (41) with the three known computer experiments on such mixtures.^{11–13} We compare our theoretical calculations with the two different results stemming from the Percus–Yevick integral equation for the radial distribution function,¹⁴ extended to mixtures by Lebowitz.⁷ The P–Y theory is still the standard of comparison, despite the frustrating fact that the compressibility and virial equation routes from its radial distribution function lead to different equations of state. The scaled particle theory,¹⁵ extended to mixtures by Lebowitz, Helfand, and Praestgaard,¹⁶ gives a result identical to the P–Y compressibility result, so comparison with it is automatically included. We do not include the perturbation theory results of Henderson and Barker,¹⁷ since no one form of their theory compared as well to the computer simulations as did our theory. We do compare our results with the best empirical equation of state, the extension of the single-component expression of Carnahan and Starling¹⁸ to mixtures by Mansoori, Carnahan, Starling, and Leland (MCSL).¹⁹ This expresses the pressure as the sum of 2/3 of the P–Y compressibility result plus 1/3 of the P–Y virial result. We include MCSL results in our tables in order to permit comparison with this excellent empiricism.

TABLE I. Compressibility factor in 50-50 mixture of hard spheres, $\gamma = 1.1$.^a

z	$p/\rho kT$				
	MC	Eq. (41)	P-Y C	P-Y V	MCSL
0.1577	1.634	1.633	1.639	1.627	1.635
0.1750	1.715	1.729	1.736	1.726	1.733
0.2188	2.018	2.001	2.016	1.994	2.008
0.2659	2.374	2.354	2.380	2.337	2.366
0.3152	2.832	2.804	2.852	2.768	2.824
0.3436	3.129	3.110	3.173	3.055	3.133
0.3668	3.412	3.391	3.471	3.316	3.419
0.4195	4.186	4.150	4.282	4.009	4.191
0.4731	5.233	5.144	5.351	4.885	5.196
0.5270	6.446	6.460	6.776	5.995	6.516
0.5305	6.567	6.559	6.881	6.075	6.612
0.5500	7.065	7.153	7.524	6.557	7.201
0.5688	7.752	7.787	8.208	7.059	7.825
0.5808	8.358	8.231	8.689	7.408	8.262
0.5866	8.500	8.458	8.930	7.581	8.480
0.6037	8.989	9.169	9.693	8.120	9.168
0.6197	9.833	9.915	10.491	8.673	9.885
0.6351	10.688	10.705	11.327	9.242	10.443
0.6496	10.725	11.525	12.194	9.821	11.403
0.6634	9.408	12.387	13.092	10.410	11.728
0.6887	10.473	14.217	14.968	11.609	13.848
0.7214	11.611	17.164	17.921	13.423	16.422
0.7784	15.570	24.777	24.980	17.472	22.477
0.7961	18.103	28.136	27.841	19.029	24.903
0.8353	26.352	38.468	35.843	23.143	31.610
0.8731	54.710	55.171	46.479	28.248	40.402

^a z is the reduced density from Eq. (42); MC is Monte Carlo data of Rotenberg (Ref. 11); P-Y C is the Percus-Yevick compressibility [also scaled particle theory (Ref. 16)] and P-Y V is the Percus-Yevick virial results (Ref. 7); MCSL is the empirical equation of Mansoori, Carnahan, Starling, and Leland (Ref. 19).

In Table I, we compare our theory with the binary equimolar Monte Carlo data of Rotenberg for diameter ratio $\gamma = 1.1$.¹¹ In Table II, we compare the results of Eq. (41) with the Monte Carlo data of Smith and Lea for the diameter ratio $\gamma = 1.667$.¹² In Table III, we compare the results of Eq. (41) with the equimolar molecular dy-

TABLE III. Compressibility factor in 50-50 mixture of hard spheres, $\gamma = 3$.^a

z	$p/\rho kT$				
	MD	Eq. (41)	P-Y C	P-Y V	MCSL
0.3151	2.373	2.374	2.386	2.332	2.368
0.3635	2.778	2.783	2.804	2.708	2.772
0.4194	3.363	3.376	3.414	3.239	3.356
0.4839	4.243	4.285	4.352	4.019	4.241
0.5143	4.761	4.828	4.912	4.467	4.764
0.5933	6.572	6.745	6.873	5.953	6.566
0.6845	9.771	10.514	10.590	8.514	9.898

^a z is the reduced density from Eq. (42); MD is molecular dynamics data of Alder (Ref. 13); P-Y C is the Percus-Yevick compressibility [also scaled particle theory (Ref. 16)] and P-Y V is the Percus-Yevick virial results (Ref. 7); MCSL is the empirical equation of Mansoori, Carnahan, Starling, and Leland (Ref. 19).

namics data of Alder for the diameter ratio $\gamma = 3$.¹³ Our theory is within the claimed range of accuracy of all the computer experiments up to well beyond the range of fluid densities.²⁰ Our results are excellent, significantly better than the P-Y result derived from either path to an equation of state, and thus are better than those offered by the scaled particle theory. Indeed, our results are almost as accurate as the MCSL empiricism. There is considerable scatter in the computer data at $\gamma = 1.1$ and $\gamma = 1.667$, but the overall trends are unmistakable.

In Fig. 2, we plot $p/\rho kT$ from Eq. (41) against z for the diameter ratios $\gamma = 1, 1.667$, and ∞ in the fluid density range. We show a few experimental points in order to give a feeling for the accuracy of the theory. The noteworthy feature of Fig. 2 is the decrease in pressure with increasing size disparity ratio γ , at constant volume fraction of the system occupied (i.e., at constant z). This phenomenon can be understood easily in light of Eq. (6). There are separate expressions of the form of Eq. (6) for both components. So long as comparison conditions involve equal volume fraction occupied, s_c will be the same for both components. How-

TABLE II. Compressibility factor in mixtures of hard spheres, $\gamma = 1.667$.^a

z	X	$p/\rho kT$				
		MC	Eq. (41)	P-Y C	P-Y V	MCSL
0.2121	0.5	1.85	1.869	1.885	1.868	1.879
0.2828	0.5	2.30	2.351	2.391	2.343	2.375
0.3536	0.5	2.92-3.01	2.997	3.078	2.965	3.040
0.4243	0.5	4.02-4.16	3.881	4.031	3.786	3.950
0.4950	0.5	4.93-5.22	5.102	5.380	4.886	5.216
0.5218	0.5	5.86	5.696	6.034	5.397	5.821
0.5657	0.5	7.11	6.872	7.331	6.376	7.013
0.6010	0.5	8.19	8.062	8.639	7.322	8.200
0.3536	0.25	3.13	3.114	3.178	3.056	3.138
0.3536	0.75	3.02	2.949	3.051	2.940	3.014
0.3536	0.875	3.09	3.005	3.111	2.995	3.072
0.4950	0.25	5.43	5.384	5.608	5.076	5.431
0.4950	0.75	4.95	4.972	5.312	4.831	5.152

^a z is the reduced density from Eq. (42); X is the mole fraction of the smaller component; MC is Monte Carlo data of Smith and Lee (Ref. 12); P-Y C is the Percus-Yevick compressibility [also scaled particle theory (Ref. 16)] and P-Y V is the Percus-Yevick virial results (Ref. 7); MCSL is the empirical equation of Mansoori, Carnahan, Starling, and Leland (Ref. 19).

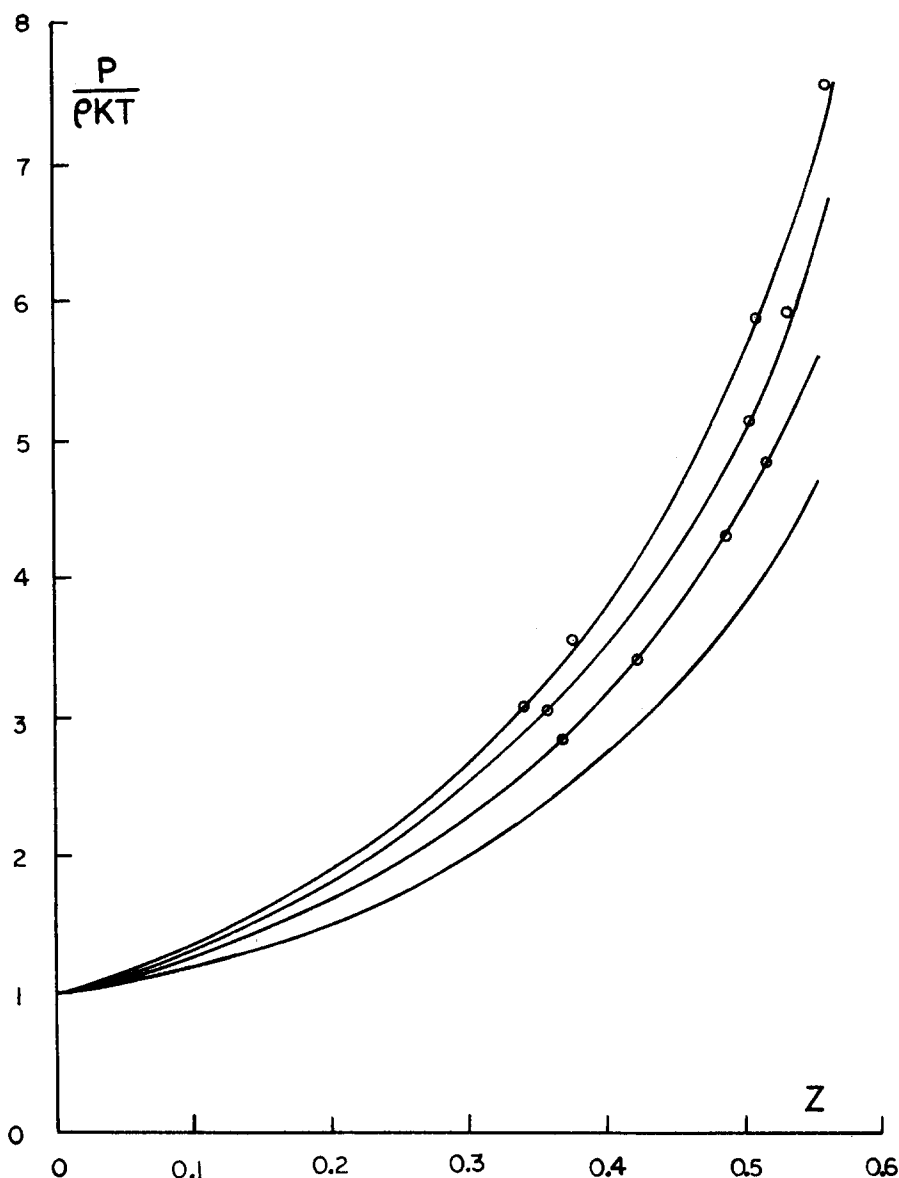


FIG. 2. Values of $p/\rho kT$ calculated as a function of reduced density z for equimolar mixtures of hard spheres of diameter ratios 1, 1.667, 3, and ∞ . A few experimental (computer) points are shown for comparison.

ever, s_a changes for each component as y increases. In the limiting case where $y=1$ and both have the same diameter σ_0 , the value of s_a for each is $\frac{7}{8}\pi\sigma_0^3$ about every one of the N particles. In the other limit where $y=\infty$, the smaller (point) particle has $s_a=0$ about each of the N particles. The larger has diameter of $2^{1/3}\sigma_0$, so s_a for it about the $\frac{1}{2}N$ small particles is $\frac{4}{3}\pi(\frac{1}{2}2^{1/3}\sigma_0)^3 = \frac{4}{3}\pi\sigma_0^3$, and s_a for it about the $\frac{1}{2}N$ large particles is $\frac{7}{8}\pi(2^{1/3}\sigma_0)^3 = \frac{7}{8}\pi\sigma_0^3$. Thus, the average annular volume decreases from $\frac{7}{8}\pi\sigma_0^3$ to $\frac{1}{4}(0 + 0 + \frac{1}{3} + \frac{7}{3})\pi\sigma_0^3 = \frac{4}{3}\pi\sigma_0^3$ as y goes from 1 to ∞ . Thus, the average a^{-1} increases, the average a decreases, and the pressure decreases. Changing y also affects ω , though the results are quite insensitive to changes in ω .

VIII. EXCESS THERMODYNAMIC FUNCTIONS

The remarkable precision offered by Eqs. (36) and (41) suggests that it would be a waste of space to tabulate various excess functions of mixing to compare with literature values, when these themselves were derived from the primary data employed in Sec. VII. The excess

functions can be calculated from Eqs. (36) and (41) and the comparable single-component equations of Ref. 1, as desired. Since the literature takes such calculations for granted, yet different definitions and choices of standard state can lead to confusion, we summarize definitions and recipes for calculating excess functions of mixing here.

Excess functions of pure components are defined as the value of the function for the component minus the value that function would have if the component were an ideal gas. The comparison may be done at constant ρ , but is more commonly done at constant p . We list the most common excess functions as they would be calculated from values of a^{-1} and $p/\rho kT$:

$$\mu_{E(\rho)} = -kT \ln a^{-1}, \quad \mu_{E(p)} = -kT \ln a^{-1} - kT \ln \left(\frac{p}{\rho kT} \right), \quad (47)$$

$$e_{E(\rho \text{ or } p)} = 0, \quad h_{E(\rho \text{ or } p)} = kT \left(\frac{p}{\rho kT} - 1 \right), \quad (48)$$

$$s_{E(\rho \text{ or } p)} = -\mu_{E(\rho \text{ or } p)}/T + k \left(\frac{p}{\rho kT} - 1 \right), \quad (49)$$

$$v_E(p) = \frac{kT}{p} \left(\frac{p}{\rho kT} - 1 \right), \quad (50)$$

$$p_E(p) = \rho kT \left(\frac{p}{\rho kT} - 1 \right). \quad (51)$$

The *thermodynamic functions of mixing* are defined as the value of the function for the mixture minus the sum of the values of the pure components: $f^m \equiv f(\text{mixture}) - \sum_k X_k f_k(\text{pure})$. The *excess thermodynamic functions of mixing* are defined as the above minus the value obtained for an ideal mixture of the same pure components (namely, $kT \sum_i X_i \ln X_i$ for the Gibbs free energy; $-k \sum_k X_k \ln X_k$ for the entropy; and zero for energy, enthalpy, volume, etc.). This comparison may be done at either constant volume fraction occupied (i.e., constant ratio of density to crystalline jam density ρ/ρ_0) or constant pressure. We list the most common excess functions of mixing, on a per particle basis, as they would be calculated from values of a_i^{-1} and $p/\rho kT$ for both the mixture and the pure components:

$$g_E^m = kT \sum_k X_k \ln \frac{\rho(\text{mixture}) a_i^{-1}(\text{pure } i)}{\rho(\text{pure } i) a_i^{-1}(\text{mixture})} \quad (\text{const. } \rho/\rho_0 \text{ or } p), \quad (52)$$

$$e_E^m = 0, \quad (53)$$

$$h_E^m = kT \left(\frac{p}{\rho kT} \right)_{\text{mixture}} - kT \sum_k X_k \left(\frac{p}{\rho kT} \right)_{\text{pure } k} \quad (\text{const. } \rho/\rho_0 \text{ or } p), \quad (54)$$

$$s_E^m = (h_E^m - g_E^m)/T \quad (\text{const. } \rho/\rho_0 \text{ or } p), \quad (55)$$

$$v_E^m = h_E^m/p. \quad (\text{const. } p). \quad (56)$$

IX. DISCUSSION

It is notoriously difficult to write an equation that describes the equilibrium properties of hard particles, either pure or in mixtures, and thus describes the repulsive cores of real molecules. There is a long history of attempts going back to before van der Waals. Some, like van der Waals' and hole and cell theories, base their work on molecular or statistical mechanical arguments. Others, like the multiparameter equations of state widely employed in the chemical industry to correlate data, make no attempt to derive the result from any molecular picture. In the last 25 years, enormous strides have been made in two major directions. First, computer experiments on various model systems have been made with enough precision to offer stringent tests to people developing theories. Second, with the solution of the hypernetted chain and Percus-Yevick integral equations and the scaled particle theory, theoreticians could offer reasonably simple, quite accurate, analytic expressions, derived by making approximations in an otherwise exact statistical mechanical theory, for the properties of hard particles.

The theory reformulated here in Sec. II must be viewed as a "competitor" with these other theories of fluids. All liquid theories involve approximations. Clearly, ours makes its in the expression for ω . However, our theory is rigorous up to this point, and we are gratified at the way in which the approximation enters at a point

where intuition can be applied and where the results are insensitive to the nature of the approximation. Whether a particular approximation means a theory is "semi-empirical" instead of "analytic," or that a theory is or is not "self-contained," depends on who is evaluating it—their goals, the climate of opinion, and on their subjective esthetics.

Perhaps a set of reasonable criteria could be agreed upon for evaluating fluid theories. Relevant features would include simplicity of results, simplicity of formulation, agreement with experiment, physical or intuitive insight, suitability for extension to more demanding related problems, rigor of derivation, unambiguity of results, and sensitivity of results to the nature of the approximations made. It is important to realize that the best current theories leave a lot to be desired in their derivations and results, however familiar we may be with them.

For example,²¹ the solutions of the Percus-Yevick and hypernetted chain (HNC) integral equations effectively represent different schemes for summing infinite subsets of Mayer-Yvon diagrams. The choice of which diagrams to sum is based solely on the ease of summing, not on any estimate of magnitude of contribution. Only after the solutions are obtained and compared with computer experiments can one say, after the fact, how good the approximation is. Worse yet, when either the P-Y or HNC results for the correlation function are substituted into the virial equation, they generate an equation of state with too low a pressure; when they are substituted into the compressibility equation, they generate another with too large a pressure. These two paths would yield identical results if the correlation function were correct. Which should one use and on what grounds should one choose? Perhaps more disconcerting is the fact that the HNC approximation includes more diagrams than the P-Y, so in principle the HNC should be a better theory. Comparison of the results with experiment shows the opposite, so one must conclude that the P-Y result is fortuitously good. One subset of the graphs that it omits because it cannot sum them just happens to cancel another subset also omitted for the same reason; adding more graphs does not necessarily improve the theory.

Simplicity of result as a criterion might give a slight preference to P-Y or scaled particle theory, so long as one was interested only in the pressure. However, most people who employ a theory of fluids are as interested in the chemical potential as they are in the pressure, and our result for the activity is far simpler than the expressions generated by these other theories.

The radial distribution function or pair correlation function is a difficult starting point for a theory of dense fluids because use of the virial or compressibility equation to go from the result to the pressure amplifies errors. Remarkably accurate correlation functions lead to disappointing thermodynamic properties. It then is taxing to use insight to improve upon the lowest order result. Henderson and Barker,¹⁷ for example, have presented a perturbation theory of hard sphere mixtures which employs P-Y results, the Padé ap-

proximant for single-component systems (an empirical approach to extend virial coefficient data to high density), and the superposition approximation. They find that different approximations are needed to fit different ranges of y and ρ .

Many people who want hard core results for grafting on attractive wells in developing a theory of realistic molecules abandon their hope for a molecular theory of the hard cores and resort to empirical expressions. The best of these is certainly that of Carnahan and Starling (C-S).^{18,19} This was originally formulated by rounding off to the nearest integer the first six virial coefficients for hard spheres, noting that those integers fit a rather simple formula, assuming that the formula worked for all coefficients, and summing the resulting series. Alternatively, the C-S pressure is arbitrarily taken to be the sum of 2/3 of the P-Y compressibility value and 1/3 of the P-Y virial value.

The theory presented here is about as good as C-S in precision, is formulated rather unambiguously from molecular considerations, and is quite insensitive to the nature of the approximation made. This relative insensitivity is attested by the work of Speedy,²² who modified our original theory for three-dimensional hard spheres by using

$$a^{-1} = \exp \left[\frac{-(s_c + s_a)\rho}{1 - \omega\rho} \right], \quad (57)$$

where we have written his equation in the notation of Sec. II of this paper. The difference between Eq. (57) and our Eq. (6) is the replacement of the factor $(1 - s_c\rho)$ in Eq. (6) by the factor $\exp[-s_c\rho/(1 - \omega\rho)]$ in Eq. (57). Since $s_c\rho$ is small at even high density, the effect of the replacement on the pressure is at most 1% or 2% when ω is chosen in a manner similar to our Eq. (31). Since Eq. (57) is slightly simpler than Eq. (6), we would be interested in using it if such use were justifiable. Its physical meaning, however, is so vague as to cause us to view it as an empiricism. It employs the form of II in Eq. (2) for the entire probability a^{-1} . This shows no recognition that, because the particles have finite size, a random point might overlap a core; and if it does not overlap one, that automatically means that no particle lies within $\frac{1}{2}\sigma$ of the point. These two sources of error come surprisingly near to cancelling each other in three dimensions where the annulus is seven times as large as the core. However, in two dimensions where $s_a/s_c=3$, and in one dimension where $s_a/s_c=1$, the error is more pronounced. Since the exact theory of one-dimensional fluids is well known, one criterion by which to judge any theory is that it treat one-dimensional hard rods correctly. In this Eq. (57) is clearly in error.

We believe that the theory presented here is, if anything, more satisfying than those theories with which it "competes." Its formulation is so simple that it could be presented in an undergraduate text, and the physics on which it is based is so pictorial as to contribute to

people's intuitive understanding of dense fluids. Equation (4), in fact, is exact, derived from rigorous probability theory. The theory's results for pressure are almost as simple as those of the other analytic theories, and its results for the activity and thus for the chemical potential are much simpler. The approach leads to a single equation of state, not to offering a choice with no criteria on which to choose except agreement with experiment. The results are quite insensitive to the nature of the approximation made, so long as it is physically reasonable. The approach immediately suggests extension to more complicated fluid problems, and we are already applying it to several such problems. Finally, our theory fits the computer data about as well as the best empirical equation, and fits decidedly better than than any other analytic theory of dense fluids.

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