

## Scaled Particle Theory of Fluid Mixtures

J. L. LEBOWITZ\*

*Belfer Graduate School of Science, Yeshiva University, New York*

E. HELFAND

*Bell Telephone Laboratories, Inc., Murray Hill, New Jersey*

AND

E. PRAESTGAARD\*

*Institute for Physical Chemistry, University of Copenhagen, Denmark*

(Received 25 March 1965)

An extension of a previous one-component theory of hard-sphere systems (in three, two, and one dimensions) and the surface tension of real systems is made to mixtures. The theory is based on consideration of an approximate expression for the work of adding an additional hard sphere to a mixture. Comparison between theory and molecular-dynamics calculations of the various contributions to the virial pressure (related to contact distribution functions) of such hard-sphere mixtures is excellent. Comparison of the theory with experimental surface tensions of mixtures of simple liquids is satisfactory.

### I. INTRODUCTION

IN this article there is presented an extension to fluid mixtures of a theory developed by Reiss, Frisch, and Lebowitz<sup>1</sup> (RFL) for a one-component hard-sphere fluid and generalized by Reiss, Frisch, Helfand, and Lebowitz<sup>2</sup> (RFHL) to fluids with more realistic interactions between the particles. The principal results of the one-component theory, which we here obtain also for mixtures, are simple expressions for the pressure and surface tension of a hard-sphere fluid<sup>1</sup> and for the surface tension of a real fluid.<sup>2</sup>

The hard-sphere equation of state of RFL is in very good agreement with machine computations, and coincides with that obtained later by Wertheim<sup>3</sup> and Thiele,<sup>4</sup> via the fluctuation-compressibility theorem, from the exact solution of the Percus-Yevick integral equation for the radial distribution function. The surface tension of RFHL for real fluids agrees fairly well with experiment.<sup>5</sup> The equation of state for hard-sphere mixtures which we obtain in this note again coincides (in three dimensions) with that obtained by Lebowitz,<sup>6</sup> via the fluctuation-compressibility theorem, from the exact solution of the Percus-Yevick integral equation for the radial distribution functions of mixtures, which is also in good agreement with machine computations. Our new expression for the surface tension of real fluid mixtures is in reasonable accord with extant experimental results.

In addition we obtain here new approximations for the contact values of the radial distribution functions of hard-sphere mixtures. These contact values and the corresponding ones obtained from the solution of the Percus-Yevick equation lie, respectively, slightly above and slightly below those obtained from machine computations.

Finally, our computations for hard-sphere mixtures are carried out also for one- and two-dimensional systems. As in the one-component case<sup>7</sup> our theory becomes exact in one dimension. There are at present no machine computations with which to compare our results in two dimensions.

### II. GENERAL FORMALISM

We consider an  $m$ -component fluid whose particles have hard cores of radii<sup>8</sup>  $R_i$ , i.e., the interaction potential between two fluid particles of Species  $i$  and  $j$  has the form

$$v_{ij}(r) = \begin{cases} \infty, & r < R_{ij} = (R_i + R_j), \\ \phi_{ij}(r), & R_{ij} < r. \end{cases} \quad (2.1)$$

The number densities of the fluid particles is denoted by  $\rho_i$ .

Consider the work  $W(R; \rho_1, \dots, \rho_m, R_1, \dots, R_m; \{\phi\})$  of inserting, at some fixed position in the fluid, a single solute hard-sphere particle of radius  $R$ . The radius  $R$  signifies that a fluid particle of Species  $i$  can come only as close as  $(R + R_i)$  to the center of the solute particle, i.e., the interaction potential between the single solute particle and a fluid particle of Spe-

\* Supported by the U. S. Air Force Office of Scientific Research, Grant No. 508-64.

<sup>1</sup> H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **31**, 369 (1959).

<sup>2</sup> H. Reiss, H. L. Frisch, E. Helfand, and J. L. Lebowitz, *J. Chem. Phys.* **32**, 119 (1960).

<sup>3</sup> M. Wertheim, *Phys. Rev. Letters* **8**, 321 (1963); and in *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz (W. A. Benjamin, Inc., New York, 1964), p. II-276.

<sup>4</sup> E. Thiele, *J. Chem. Phys.* **38**, 1959 (1963).

<sup>5</sup> Reference 2; and S. W. Mayer, *J. Chem. Phys.* **38**, 1803 (1963).

<sup>6</sup> J. L. Lebowitz, *Phys. Rev.* **133**, A895 (1964).

<sup>7</sup> E. Helfand, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **34**, 1037 (1961).

<sup>8</sup> The analysis in this section is similar to Ref. 1 for a one-component system; part of it is presented briefly in *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz (W. A. Benjamin, Inc., New York, 1964), p. II-299.

cies  $i$  is,

$$v_i(r) = \begin{cases} \infty, & r < R + R_i, \\ 0, & R + R_i < r. \end{cases} \quad (2.2)$$

Since  $r \geq 0$ , meaningful  $R$ 's are greater than  $-R_1$ , where  $R_1 \leq R_2 \leq \dots \leq R_m$ .  $W(R)$  is equal to the change in the configurational part of the Helmholtz free energy upon adding the solute particle to the system, i.e.,  $W(R)$  is the configurational (or nonideal gas) part of the chemical potential of a single solute particle. This change in the free energy can be readily computed for  $R \leq 0$ . Let  $Q(N_1, \dots, N_m, \Omega)$  be the configurational partition function of the system consisting of  $N_i$  particles of Species  $i$  in a large box of volume  $\Omega$ , and let  $Q(R, N_1, \dots, N_m, \Omega)$  be the same quantity when one solute particle is present. For  $R \leq 0$ , the exclusion spheres for the solute particle, of radii  $R + R_i$ , centered on each fluid particle do not overlap (since  $R + R_i \leq R_j + R_i$  for all  $i$  and  $j$ ). Hence, carrying out, in the standard definition of  $Q$ , the integration over the position of the solute particle first we find,

$$Q(R, N_1, \dots, N_m, \Omega) = \Omega^{-1} \left[ 1 - \frac{4\pi}{\Omega} \sum_{i=1}^m N_i (R + R_i)^3 \right] Q(N_1, \dots, N_m, \Omega) \quad R \leq 0, \quad (2.3)$$

which yields,

$$W(R) = -kT \ln \left[ 1 - \frac{4\pi}{\Omega} \sum \rho_i (R + R_i)^3 \right], \quad R \leq 0 \quad (2.4)$$

with  $\rho_i = N_i/\Omega$ .

An alternative means of calculating  $W(R)$  follows from the fact that the only effect of the insertion of the solute particle at some fixed position say  $\mathbf{x}$ , in the fluid, is the exclusion of the center of any molecule of radius  $R_i$  from a spherical region of radius  $(R + R_i)$  centered on  $\mathbf{x}$ . We have, as before, that  $R + R_i \geq 0$ , for all  $i$ . For  $R \geq 0$  this is equivalent to excluding *any part* of a fluid molecule from a spherical region of radius  $R$  centered on  $\mathbf{x}$ . From the relation between the probability of a configuration and the work of creating that configuration we have

$$W(R) = -kT \ln P_0(R), \quad (2.5)$$

where  $P_0(R)$  is the probability that there are no *centers* of fluid particles of radius  $R_i$  in the spherical region  $(R + R_i)$ . Now for  $R \leq 0$ , there can be at most one fluid particle in this region and this has the probability

$$P_1(R) = \frac{4\pi}{\Omega} \sum \rho_i (R + R_i)^3 = 1 - P_0(R), \quad R \leq 0, \quad (2.6)$$

leading again to Eq. (2.4) for  $W(R)$ .

Consider now the case of  $R$  very large,  $R \gg R_m$ . The leading term in the work,  $W(R)$ , of making a cavity of radius  $R$  from which all parts of the fluid particles are excluded, must be a pressure-volume term  $\frac{4\pi}{3} p R^3$  where  $p$  is the pressure of the fluid. Thermodynamic

considerations on surface tension suggest that for large  $R$ ,  $W(R)$  should also contain terms proportional to the "surface area" and "radius" of the cavity. Furthermore, for  $R$  positive but small,  $W(R)$  may be expanded in a Taylor series in  $R$  whose first three terms may be determined from the continuity of  $W(R)$  and its first two derivatives (in three dimensions) at  $R=0$ . It is now our basic approximation, patterned on that of RFL, that  $W(R)$  is given by a cubic polynomial for *all*  $R \geq 0$ , with the first three coefficients determined by  $W(R)$  near  $R=0$ . This yields

$$\begin{aligned} \beta W(R) &= \beta [W(0) + W'(0)R + \frac{1}{2}W''(0)R^2 + \frac{4\pi}{3}pR^3] \\ &= -\ln(1 - \xi_3) + [6\xi_2/(1 - \xi_3)]R \\ &\quad + [12\xi_1/(1 - \xi_3) + 18\xi_2^2/(1 - \xi_3)^2]R^2 + \frac{4\pi}{3}\beta pR^3, \end{aligned} \quad (2.7)$$

where  $\beta = 1/kT$  and

$$\xi_i = \frac{1}{\Omega} \sum_{i=1}^m \rho_i (2R_i)^i. \quad (2.8)$$

A different method for obtaining  $W(R)$  which also yields, for mixtures, some new information (approximate) about the structure of the fluid is to begin with the exact relation,

$$\beta \left[ \frac{dW(R)}{dR} \right] = 4\pi \sum_{i=1}^m (R + R_i)^2 \rho_i G_i(R + R_i), \quad (2.9)$$

where  $\rho_i G_i(R + R_i)$  is the density of fluid particles of Species  $i$  in contact with the single solute particle or cavity of radius  $R$ . Equation (2.9) follows from analysis of  $Q(R, N_1, \dots, N_m, \Omega)$ , or from the observation that the stress on the walls of the cavity is purely kinetic to which each species contributes a term  $kT\rho_i G_i(R + R_i)$ . The previous arguments show that

$$G_i(R + R_i) = \left[ 1 - \frac{4\pi}{\Omega} \sum_{j=1}^m \rho_j (R + R_j)^3 \right]^{-1}, \quad R \leq 0. \quad (2.10)$$

We can now go through an argument similar to that leading to the approximation (2.7). For very large  $R$ ,  $\rho_i G_i(R + R_i)$  must equal the density of fluid particles of Species  $i$  against a *flat* hard wall  $\rho_i^W$ . The stress against a hard wall is purely kinetic so,

$$\lim_{R \rightarrow \infty} \sum_{i=1}^m \rho_i G_i(R + R_i) = \sum \rho_i^W = \beta p = \sum \beta p_i. \quad (2.11)$$

The writing of  $p_i$  for  $\beta^{-1}\rho_i^W$  indicates that  $p_i$  is the contribution to the pressure of the  $i$ th component which may be called the  $i$ th fractional pressure. We now make the approximation that,

$$G_i(R + R_i) = \beta p_i / \rho_i + B_i / (R + R_i) + C_i / (R + R_i)^2, \quad \text{for all } R \geq 0. \quad (2.12)$$

Substituting (2.12) into (2.10) yields,

$$\beta dW(R)/dR = 4\pi\beta \sum p_i (R+R_i)^2 + 4\pi \sum \rho_i B_i (R+R_i) + 4\pi \sum \rho_i C_i \quad \text{for all } R \geq 0. \quad (2.13)$$

The coefficients  $B_i$  and  $C_i$  will be determined in our approximation from the continuity of  $G_i(R+R_i)$  and its first derivative (in three dimensions) at  $R=0$ . This gives

$$B_i = -2R_i\beta p_i/\rho_i + 2R_i/(1-\xi_3) + 6\xi_2 R_i^2/(1-\xi_3)^2, \quad (2.14)$$

$$C_i = R_i^2\beta p_i/\rho_i - R_i^2/(1-\xi_3) - 6\xi_2 R_i^3/(1-\xi_3)^2. \quad (2.15)$$

Combining (2.13), (2.14), and (2.15) and integrating with respect to  $R$  yields again (2.7). The approximation (2.12) is thus consistent with (2.7) and is indeed identical with it for a single-component fluid,  $m=1$ . For mixtures, however, (2.12) is a stronger approximation than (2.7), albeit its intuitive justification is just as good, and yields more information (approximate), which we utilize later.

### III. SURFACE TENSION OF LIQUIDS

The surface tension of a liquid in contact with its *attenuated* vapor may be expected to be qualitatively, and perhaps even quantitatively, similar to its surface tension against a hard wall. The latter may be defined in words as the negative of the coefficient of the surface area,  $S$ , term in the grand canonical potential  $\beta^{-1} \ln \Xi$  ( $\Xi$  the grand canonical partition function), for a system in a rigid container at given chemical potentials  $\mu_i$  or fugacities  $z_i$ . (To define it in terms of the densities  $\rho_i$  these have to be computed from the given fugacities in the limit of an infinite-size uniform liquid.) The difficulty with this definition is that the volume of a container  $\Omega$  specified by the external potential term in the Hamiltonian of the system,  $V(\Omega)$ , is defined unequivocally only up to terms proportional to the surface area. Different definitions of the volume will then yield different definitions of the surface tension.

Consider, for example, the system discussed in the last section enclosed in a spherical container of radius  $L$ , i.e., the center of a molecule of radius  $R_i$  can come only up to a distance  $R_i$  from the surface of the container. At extreme dilution the grand canonical potential has the form

$$\beta^{-1} \ln \Xi = \beta^{-1} \sum_{i=1}^m z_i \frac{4}{3}\pi (L-R_i)^3. \quad (3.1)$$

We could now define the volume  $V$  to be  $\frac{4}{3}\pi L^3$  and  $S = 4\pi L^2$  in which case

$$\beta^{-1} \ln \Xi = \beta^{-1} (\sum z_i) V - [(\beta^{-1} \sum R_i z_i) + O(L^{-1})] S. \quad (3.2)$$

The surface tension against a *flat* hard wall,  $\sigma_0$ , given by the coefficient of  $S$  in the limit  $L \rightarrow \infty$  is then, for

small fugacities or densities,

$$\sigma_0 = \beta^{-1} \sum R_i z_i = \beta^{-1} \sum \rho_i R_i. \quad (3.3)$$

Alternatively, we could say that each species has its own volume  $V_i = \frac{4}{3}\pi (L-R_i)^3$  and its own surface area  $S_i = 4\pi (L-R_i)^2$  in which case the surface tension vanishes at low fugacities or densities. The generalization of these definitions to higher values of the fugacities may be made in the following way: We write either,

$$\beta^{-1} \ln \Xi = p \frac{4}{3}\pi L^3 - \sigma_0 4\pi L^2 + O(L^{-1}) L^2 \quad (3.4)$$

or

$$\beta^{-1} \ln \Xi = \sum p_i \frac{4}{3}\pi (L-R_i)^3 - \sum \sigma'_i 4\pi (L-R_i)^2 + O(L^{-1}) L^2, \quad (3.5)$$

where  $p_i$  are the fractional pressures defined in (2.11). In the latter case the surface tension against a hard wall may be taken to be  $\sigma'_0$ ,

$$\sigma'_0 = \sum \sigma'_i = \sigma_0 - \sum_{i=1}^m p_i R_i = \sigma_0 - p \bar{R}, \quad (3.6)$$

where  $\bar{R}$  is of the order of a molecular radius. In terms of the work  $W(R)$  we would have,

$$\sigma_0 = \lim_{R \rightarrow \infty} \left\{ \left[ \frac{dW(R)}{dR} - 4\pi p R^2 \right] / (8\pi R) \right\}, \quad (3.7)$$

$$\sigma'_i = \lim_{R \rightarrow \infty} \left\{ [kT p_i G_i(R+R_i) - p_i] \frac{1}{2} R \right\}. \quad (3.8)$$

Equations (2.7) and (2.12) therefore yield as approximations for  $\sigma_0$  and  $\sigma'_0$

$$\sigma_0 = W''(0)/8\pi = (3kT/2\pi) \{ 2[\xi_1/(1-\xi_3)] + 3[\xi_2/(1-\xi_3)]^2 \}, \quad (3.9)$$

and

$$\begin{aligned} \sigma'_0 &= \frac{1}{2} kT \sum B_i \rho_i \\ &= \sigma_0 - \sum p_i R_i. \end{aligned} \quad (3.10)$$

It was the latter value which was used by RFL and RFHL for a one-component system. This also coincides with the definition used by Bellemans<sup>9</sup> for mixtures of hard spheres.

The important point to notice, though, is that the two different definitions of the surface tension against a hard wall,  $\sigma_0$  and  $\sigma'_0$ , only give rise to trivial differences when used for real liquids in contact with their vapor because in this case the term  $p \bar{R}$  is completely negligible: It is equal to  $10^{-2}$  dyn/cm when  $p=1$  atm and  $\bar{R}=1 \text{ \AA}$ .

### IV. COMPARISON WITH EXPERIMENT

The value of  $\sigma_0$  given by Eq. (3.7) is in fairly good agreement with the experimental surface tensions of one-component liquids, as has been shown previously.<sup>5</sup>

<sup>9</sup> A. Bellemans, *Physica* **28**, 493 (1962).

It is to be expected, and the expectation is fulfilled, that the mixture formula also yields reasonable surface tensions. Thus, it is preferable in plotting the data to perform a more sensitive test and examine the composition dependence of the excess surface tension defined by

$$\sigma^e = \sigma_0 - \sum_i x_i \sigma_i,$$

where  $x_i$  is the mole fraction and  $\sigma_i$  the surface tension of pure Species  $i$ .

The comparison is made with the experimental data of Blagoi<sup>10</sup> on the mixtures  $N_2$ -Ar,  $CH_4$ -Ar, and  $CH_4$ - $N_2$  in Figs. 1-3. For clarity in plotting, the data are extrapolated to common temperatures. The radii of the various species have been chosen in such a fashion as to give the correct surface tensions for the pure materials. This should account for the temperature dependence of the radii which Mayer<sup>5</sup> finds to be necessary to give quantitative agreement between theory and experiments on the pure materials.

The theory appears to fail to predict the asymmetry of the excess surface tension evident in the experiments. This asymmetry as well as the fact that the theoretical predictions are generally somewhat high may be due to a specific adsorption caused by the interaction potentials. For example, in the case of Ar- $N_2$ , these two molecules have approximately the same radii. The Ar potential, however, is more attractive. Therefore the Ar tends to stay in the bulk where it can take advantage of the greater number of neighbors with which it can interact, while the  $N_2$  is preferentially left at the surface.

## V. MIXTURE OF HARD SPHERES

We now apply the formalism developed in Sec. II to the special case where the fluid particles are themselves hard spheres of radius  $R_i$ . It follows that when the radius of the solute particle  $R$  is equal to some  $R_j$ , then the solute particle is identical to a fluid particle of Species  $j$ . Thus, the chemical potential of the  $i$ th

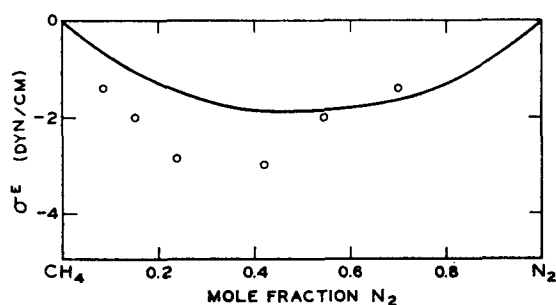


FIG. 1. Excess surface tension of  $N_2$ -Ar mixtures at 84°K. Diameter of  $N_2=3.26$  Å, diameter of Ar=3.29 Å. Solid line is theoretical and circles are experimental.

<sup>10</sup> Y. P. Blagoi, Ukr. Fiz. Zh. 5, 109 (1960).

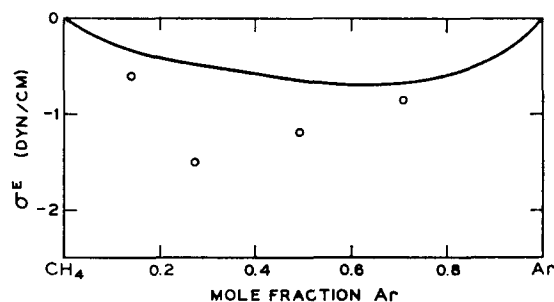


FIG. 2. Excess surface tension of  $CH_4$ -Ar mixtures at 90°K. Diameter of  $CH_4=3.77$  Å, diameter of Ar=3.21 Å. Solid line is theoretical and circles are experimental.

species is given by,

$$\begin{aligned} \mu_i(\rho_1, \dots, \rho_m, R_1, \dots, R_m) \\ \equiv kT \ln[\rho_i h^3 / (2\pi m_i kT)^{3/2}] + W(R_i). \end{aligned} \quad (5.1)$$

The thermodynamic relation,

$$\frac{\partial p}{\partial \rho_j} = \sum_{i=1}^m \rho_i \frac{\partial \mu_i}{\partial \rho_j}, \quad (5.2)$$

and the approximate  $W(R)$  given in (2.7) lead to the following expression for the pressure of a hard-sphere mixture,

$$\begin{aligned} \pi \beta p = 6[\xi_0 / (1 - \xi_3)] + 18[\xi_1 \xi_2 / (1 - \xi_3)^2] \\ + 18[\xi_2^3 / (1 - \xi_3)^3]. \end{aligned} \quad (5.3)$$

The pressure given in (5.3) is identical to that obtained from the exact solution of the Percus-Yevick equation for the radial distribution functions of a hard-sphere mixture through the use of the compressibility relation,<sup>6</sup> denoted  $p^c$ . Since the Percus-Yevick equation is itself not exact the pressure obtained from its solution via the virial theorem,

$$\beta p = \sum \rho_i + \frac{2}{3} \pi \sum_{i,j} \rho_i \rho_j R_{ij}^3 g_{ij}(R_{ij}), \quad (5.4)$$

where  $g_{ij}(R_{ij})$  is the contact value of the radial distribution function, does not coincide with  $p^c$  and is given by,<sup>6</sup>

$$\beta p^v = \beta p^c - (18\pi) \xi_3 \xi_2^3 (1 - \xi_3)^{-3}. \quad (5.5)$$

Comparison with machine computations on binary mixtures shows that  $p^c$  is slightly too high and  $p^v$  slightly too low but that both are within a few percent of the actual pressure (with  $p^c$  somewhat closer) for the whole range of fluid densities,  $\xi_3 \lesssim 0.4$ .

We now show that our approximation for the  $G_i$ 's, Eqs. (2.11)-(2.15), leads to approximate contact radial distribution functions  $g_{ij}(R_{ij})$  which then yield a virial equation of state identical to that obtained in (5.3). To accomplish this we note again that, for hard-sphere mixtures, when  $R=R_j$  the solute particle is just another fluid particle of Species  $j$ . This requires that  $G_i(R_i+R_j)$  be equal to the value of the radial

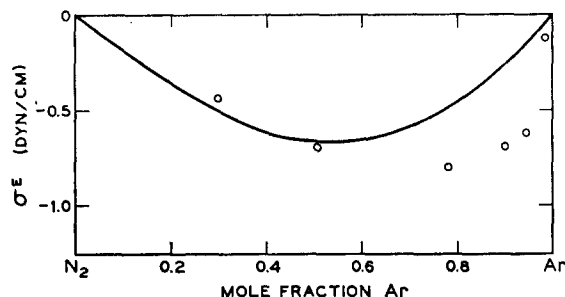


FIG. 3. Excess surface tension of  $\text{CH}_4\text{-N}_2$  mixtures at  $90^\circ\text{K}$ . Diameter of  $\text{CH}_4=3.77 \text{ \AA}$ , diameter of  $\text{N}_2=3.09 \text{ \AA}$ .

distribution function of two fluid particles with radii  $R_i$  and  $R_j$  in contact,

$$G_i(R_i+R_j) = G_j(R_j+R_i) = g_{ij}(R_i+R_j). \quad (5.6)$$

Combining (2.12), (2.14), (2.15) and the first part of (5.6) yields

$$\beta p_i = \frac{\rho_i}{(1-\xi_3)} + \left[ \left( \frac{1}{6}\pi \right) \beta p - \frac{\xi_0}{(1-\xi_3)} \right] \frac{\rho_i R_i^2}{\xi_2} \quad (5.7)$$

with  $p \equiv \sum p_i$ . This produces an expression for  $G_i(R+R_i)$ , in a hard-sphere fluid, in terms of  $p$ . We may now obtain  $p$  by combining the second equality in (5.6) with the virial theorem (5.4). Surprisingly we are led again to the pressure given in Eq. (5.3) although we have made no use at all of the relation (5.1) between  $\mu_i$  and  $W(R_i)$  which was central to our previous derivation of  $p$ . This gives us additional confidence in (5.3).

In addition to obtaining  $p$ , we now also have an approximation to the contact radial distributions  $g_{ij}(R_{ij})$ , which we denote by  $G_{ij}$

$$G_{ij} \equiv G_i(R_i+R_j) = (1-\xi_3)^{-1} + \left[ \frac{6\xi_2}{(1-\xi_3)^2} \right] \left( \frac{R_i R_j}{R_i+R_j} \right) + 12 \left[ \frac{\xi_2^2}{(1-\xi_3)^3} \right] \left( \frac{R_i R_j}{R_i+R_j} \right)^2. \quad (5.8)$$

This value for  $G_{ij}$  is compared directly with the results of machine computations<sup>11</sup> and the corresponding  $g_{ij}(R_{ij})$  obtained from the solution of the Percus-Yevick equation<sup>6</sup> in Fig. 4. The quantities plotted are

$$Y_{ij} \equiv \frac{2}{3}\pi(\rho_i \rho_j / \rho) (R_i + R_j)^3 G_{ij}$$

for an equimolar mixture of spheres of radius 1 and 3.

## VI. ONE- AND TWO-DIMENSIONAL MIXTURES OF HARD SPHERES

The analysis of Sec. II and Sec. V can be extended also to one- and two-dimensional systems of hard-sphere mixtures, in analogy to the previous analysis for pure systems.<sup>7</sup>

<sup>11</sup> B. J. Alder, J. Chem. Phys. **40**, 2724 (1964).

In one dimension the volume of the cavity for  $R>0$  is  $2R$ . Since in one dimension there are no curvature effects it is strictly true that  $dW = pdV = 2pdR$ . Furthermore  $W(R)$  is continuous at  $R=0$ , so that we have the *exact* equations,

$$\beta W(R) = -\ln[1 - 2 \sum_{i=1}^m \rho_i (R+R_i)], \quad R \leq 0, \quad (6.1)$$

$$\beta W(R) = -\ln[1 - 2 \sum \rho_i R_i] + 2\beta p R, \quad R \geq 0. \quad (6.2)$$

Combining this with (5.1) and (5.2) yields the exact equation of state,

$$\beta p = \sum \rho_i / (1 - 2 \sum \rho_i R_i). \quad (6.3)$$

The pressure may also be derived from the continuity of  $G_i(R+R_i)$  at  $R=0$  and its independence of  $R$  for  $R>0$ , since for  $R>0$  the wall of the cavity acts as a hard wall. This gives the *exact* result,

$$G_i(R+R_i) = \beta p_i / \rho_i = 1 / (1 - 2 \sum \rho_j R_j) = g_{ij}(R_{ij}). \quad (6.4)$$

In two dimensions the volume of the cavity for  $R>0$  is  $\pi R^2$ . Equations (2.4) and (2.7) now become, using the continuity of  $W(R)$  and its first derivative at  $R=0$ ,

$$\beta W(R) = -\ln[1 - \pi \sum \rho_i (R_i + R)^2], \quad R \leq 0, \quad (6.5)$$

$$\beta W(R) = -\ln[1 - \pi \sum \rho_i R_i^2] + [2\pi (\sum \rho_i R_i) R / (1 - \pi \sum \rho_i R_i^2)] + \beta \pi p R^2, \quad R \geq 0, \quad (6.6)$$

the second equation being approximate. Combining

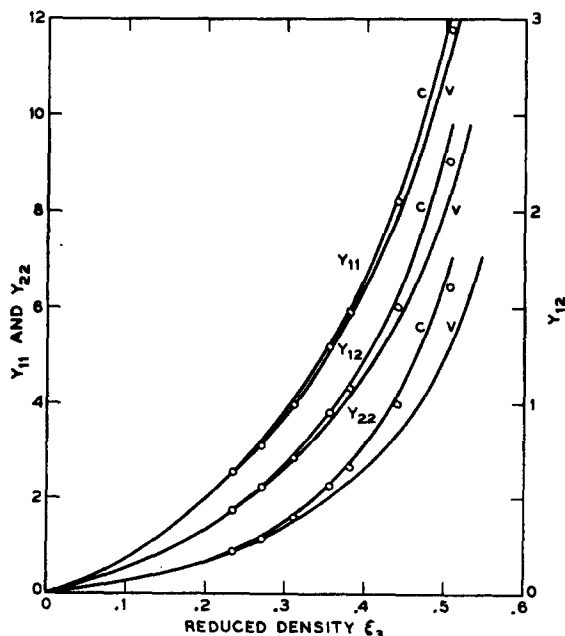


FIG. 4. Contributions to the nonideal part of the pressure,  $Y_{ij}$ , versus reduced density. Circles represent results of machine computations. Curves labeled C and V represent results of Eq. (5.8) and those obtained from the Percus-Yevick equations, respectively.

(6.6) with (5.1-5.2) yields,

$$\beta p = [\sum \rho_i / (1 - \pi \sum \rho_i R_i^2)] + [\pi (\sum \rho_j R_j)^2 / (1 - \pi \sum \rho_i R_i^2)^2], \quad (6.7)$$

for a two-dimensional system of hard disks with radii  $R_i$ .

Carrying through the analysis in terms of the  $G_i(R+R_i)$  we write, in analogy with (2.10), (2.12), and (2.14)

$$G_i(R+R_i) = [1 - \pi \sum \rho_j (R+R_j)^2]^{-1}, \quad R \leq 0, \quad (6.8)$$

$$G_i(R+R_i) = \beta p_i / \rho_i + B_i / (R+R_i), \quad R \geq 0, \quad (6.9)$$

where (6.9) is approximate and  $B_i$ , determined from the continuity of  $G_i(R+R_i)$  at  $R=0$ , is given by,

$$B_i = -\beta p_i R_i / \rho + R_i / (1 - \pi \sum \rho_j R_j^2). \quad (6.10)$$

Employing now Eq. (5.6) we find the following approximation for the contact radial distribution functions,

$$g_{ij}(R_{ij}) = (1 - \pi \sum \rho_i R_i^2)^{-1} + \pi (R_i R_j / (R_i + R_j)) (\sum \rho_i R_i^2) (1 - \pi \sum \rho_i R_i^2)^{-2}. \quad (6.11)$$

The virial theorem appropriate for hard disks in two dimensions,

$$\beta p = \sum p_i + (\pi/2) \sum \rho_i \rho_j R_{ij}^2 g_{ij}(R_{ij}), \quad (6.12)$$

again gives the equation of state (6.7).

ACKNOWLEDGMENTS

Egil Praestgaard would like to thank the Belfer Graduate School of Science and the Bell Telephone Laboratories for their hospitality during the course of a visit when the above research was performed.

Theory of Helium Dissolution in Uranium Dioxide. I. Interatomic Forces in Uranium Dioxide

DONALD R. OLANDER

*Inorganic Materials Research Division of the Lawrence Radiation Laboratory and the Department of Nuclear Engineering University of California, Berkeley, California*

(Received 30 March 1965)

Knowledge of the nature of the interatomic forces in uranium dioxide is required for theoretical treatment of phenomena such as radiation damage, adsorption, and gas solubility. The van der Waals and repulsive forces are of particular interest, for these interactions govern the behavior of neutral species in the crystal. The Kirkwood-Müller expression for the coefficients of the  $1/r^n$  dispersion forces were employed, and the form of the repulsive potentials was taken from the delta-function model of Mason and Vanderslice. The two disposable parameters in the repulsive potentials were evaluated from data on the atomic properties of the constituent ions and the lattice constant and compressibility of  $UO_2$ . The calculated cohesive energy of the  $UO_2$  lattice is in very good agreement with the value obtained from a conventional Born-Haber cycle.

**K**NOWLEDGE of the nature of the interatomic forces in uranium dioxide is required for theoretical calculation of phenomena such as radiation damage, adsorption, and gas solubility. Here we evaluate these forces using data on the atomic properties of the ions and the lattice constant and compressibility of  $UO_2$  at 0°K.

The  $UO_2$  lattice shown in Fig. 1 is of the fluorite type, and is assumed to be completely ionic in character.<sup>1</sup> The room-temperature lattice constant is  $a = 5.470 \text{ \AA}$ . Extrapolation of thermal-expansion data<sup>1</sup> to 0°K yields a value of  $a = 5.468 \text{ \AA}$ . The cation-anion distance is  $r_{O-U} = \sqrt{3}a/4 = 2.368 \text{ \AA}$ ; the oxygen-oxygen separation is  $r_{O-O} = a/2 = 2.734 \text{ \AA}$ , and the distance between uranium atoms is  $r_{U-U} = a/\sqrt{2} = 3.867 \text{ \AA}$ .

<sup>1</sup> *Uranium Dioxide: Properties and Applications*, edited by J. Belle (U.S. Government Printing Office, Washington D. C., 1961).

The cohesive energy represents the energy released when a mole of crystalline  $UO_2$  is assembled from the constituent ions initially at infinite separation. The cohesive energy consists of four components due to attractive forces and a repulsive contribution arising from the overlapping of the electron clouds of adjacent ions. The major attractive components are the Coulomb energy resulting from the interaction of the oxygen and uranium ions and the London or van der Waals forces arising from the fluctuating induced multipole moments of the ions.<sup>2-5</sup> All terms except the Coulomb

<sup>2</sup> J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, New York, 1954).

<sup>3</sup> H. Margenau, *Rev. Mod. Phys.* **11**, 1 (1939).

<sup>4</sup> R. Heller, *J. Chem. Phys.* **9**, 154 (1941).

<sup>5</sup> J. F. Hornig and J. O. Hirschfelder, *J. Chem. Phys.* **20**, 1012 (1952).