

Conformality in the Kirkwood–Buff solution theory of statistical mechanics

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The Kirkwood–Buff solution theory of statistical mechanics is examined in the light of the conformal solution approximation of the mixture radial distribution functions. By joining the mixture compressibility equation of the Kirkwood–Buff solution theory with the mixture energy and virial equations of statistical mechanics, a set of density and temperature dependent mixing rules has been developed which are used here to calculate properties of molecular fluids with varying size and interaction energy differences. It is demonstrated that the conformality approximation in the compressibility equation produces mixture results with a deviation, from the exact mixture data, on the opposite side of the predictions of the van der Waals theory of mixtures. The Kirkwood–Buff relation for the composition derivative of the chemical potential is also integrated by combining it with the conformal solution approximation and compared with the simulation data.

I. INTRODUCTION

One of the interesting problems in statistical mechanics is the prediction of mixture properties from those of the components forming the mixture. There are a number of ways to achieve this goal. The conformal solution theory^{1–3} seems to offer a practical and accurate approach. In the conformal solution theory it is assumed that there exists a hypothetical pure fluid that has the same properties as those of the mixture at the same density and temperature. This hypothetical fluid is described by the same equation of state as the pure fluids which forms the mixture. The parameters of the hypothetical fluid are related to the parameters of the pure fluids, composition, and possibly temperature and density by what are usually called the mixing rules. Many mixing rules have been suggested.^{4–6} Some are based on empirical grounds, and others are derived by making some assumptions about the mixture radial distribution functions. The latter approach will be used here to derive the mixing rules.

The Kirkwood–Buff solution theory⁷ has been studied extensively for the case of infinitely dilute solutions.^{8,9} For solutions with finite compositions this theory was employed to derive perturbation expressions with respect to composition.^{10,11} However, for effective utilization of this perturbation expansion detailed information about the pair, triplet, and higher order distribution functions is necessary. By joining the concepts of the conformal solution theory and the Kirkwood–Buff solution theory it is possible to derive mixing rules⁴ which can be then used for mixture property calculations. In the present report two sets of calculations using these mixing rules are performed. In the first set an equimolar mixture of hard spheres is studied. The deviations of the Helmholtz free energy, the compressibility factor, and the isothermal compressibility from the exact hard-sphere mix-

ture properties are calculated as a function of reduced density at three different molecular size ratios. In the second set the mixing rules are used to derive the Henry's constant for a binary mixture of Lennard-Jones fluids. The Henry's constant is calculated for the same energies of interaction ϵ_{ij} but at different size ratios, and for the same molecular sizes σ_{ij} , but at different energies of interaction. The calculations are compared with the results of the van der Waals mixing rules and the computer simulation data.¹²

II. THEORY

Total thermodynamic properties of fluids are related to the radial distribution function by the energy, virial, and compressibility equations of statistical mechanics. The statistical mechanical equation for the internal energy of pure fluids is¹³

$$U - U^0 = 1/2N\rho \int_0^\infty u(r)g(r)4\pi r^2 dr. \quad (1)$$

For mixtures the above equation takes the form¹³

$$U - U^0 = 1/2N\rho \sum_{i=1}^c \sum_{j=1}^c x_i x_j \int_0^\infty u_{ij}(r)g_{ij}(r)4\pi r^2 dr, \quad (2)$$

where U is the internal energy of the system, U^0 is the ideal gas internal energy at the same temperature and composition as the mixture, N is the total number of molecules, ρ is the molecular number density, x_i is the bulk mole fraction of component i , c is the number of components in the mixture, u_{ij} is the pair intermolecular potential energy function for molecules of type i and j , and g_{ij} is the radial distribution function of molecules of type j around a central molecule of type i .

The statistical mechanical virial equation for pure fluids is¹³

$$Z = 1 - (\rho/6kT) \int_0^\infty ru'(r)g(r)4\pi r^2 dr \quad (3)$$

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while for mixtures it becomes¹³

$$Z = 1 - (\rho/6kT) \sum_{i=1}^c \sum_{j=1}^c x_i x_j \int_0^{\infty} r u'_{ij}(r) g_{ij}(r) 4\pi r^2 dr, \quad (4)$$

where Z is the compressibility factor PV/NkT , k is the Boltzmann constant, T is the absolute temperature, and u' is the derivative of u with respect to the intermolecular distance r . Note that the assumption of pairwise additivity of the potential energy function is necessary in deriving all the above equations. This is not the case with the compressibility equation, which is independent of this assumption. The statistical mechanical compressibility equation for pure fluids is¹³

$$\rho k T \kappa_T = 1 + \rho \int_0^{\infty} [g(r) - 1] 4\pi r^2 dr, \quad (5)$$

where κ_T is the isothermal compressibility $\rho^{-1}(\partial\rho/\partial\rho)_T$. The compressibility equation for mixtures was derived in 1951 by Kirkwood and Buff.⁷ It is given by

$$\rho k T \kappa_T = \frac{|B|}{\rho \sum \sum x_i x_j |B|_{ij}}, \quad (6)$$

where $|B|_{ij}$ symbolizes the cofactor of the element B_{ij} in the $c \times c$ determinant $|B|$. The elements B_{ij} are given by

$$B_{ij} = \rho x_i [\delta_{ij} + \rho x_j G_{ij}], \quad (7)$$

where δ_{ij} is the Kronecker delta and G_{ij} is defined with respect to the radial distribution function g_{ij} as

$$G_{ij} = \int_0^{\infty} [g_{ij}(r) - 1] 4\pi r^2 dr. \quad (8)$$

To derive mixing rules⁴ we equate the internal energy (or the compressibility factor) of the mixture given by Eq. (2), to that of the hypothetical pure fluid given by Eq. (1), and we scale the resulting equation using the respective size parameters to get^{4,5}

$$\begin{aligned} \sigma_x^3 \epsilon_x \int_0^{\infty} \phi_x(r/\sigma_x) g_x(r/\sigma_x) 4\pi (r/\sigma_x)^2 d(r/\sigma_x) \\ = \sum_{i=1}^c \sum_{j=1}^c \sigma_{ij}^3 \epsilon_{ij} x_i x_j \int_0^{\infty} \phi_{ij}(r/\phi_{ij}) \\ \times g_{ij}(r/\sigma_{ij}) 4\pi (r/\sigma_{ij})^2 d(r/\sigma_{ij}), \end{aligned} \quad (9)$$

where the subscript x refers to the hypothetical fluid, and $\phi = u/\epsilon$. On the other hand, equating the virial equations, Eqs. (3) and (4), yields

$$\begin{aligned} \sigma_x^3 \epsilon_x \int_0^{\infty} \phi'_x(r/\sigma_x) g_x(r/\sigma_x) 4\pi (r/\sigma_x)^3 d(r/\sigma_x) \\ = \sum_{i=1}^c \sum_{j=1}^c \sigma_{ij}^3 \epsilon_{ij} x_i x_j \int_0^{\infty} \phi'_{ij}(r/\sigma_{ij}) \\ \times g_{ij}(r/\sigma_{ij}) 4\pi (r/\sigma_{ij})^3 d(r/\sigma_{ij}). \end{aligned} \quad (10)$$

To derive the first mixing rule we assume conformal potentials, i.e.,

$$u_{ij} = (\epsilon_{ij}/\epsilon_{00}) u_{00}(r\sigma_{ij}/\sigma_{00}), \quad (11)$$

where the subscript 00 indicates a reference fluid. This assumption implies that all the potential functions of the molecules in the mixture have the same functional form. In addition to assuming conformal potentials, we use the conformal solution approximation for the radial distribution functions g_{ij} . According to this approximation the scaled radial distribution functions in a mixture are all identical,^{4,5} i.e.,

$$g_{11}(r/\sigma_{11}) = g_{22}(r/\sigma_{22}) = \dots = g_x(r/\sigma_x). \quad (12)$$

The above two assumptions will make all the integrals in Eq. (9) equal, and hence, they will cancel from both sides. The final equation is then

$$\sigma_x^3 \epsilon_x = \sum_{i=1}^c \sum_{j=1}^c \sigma_{ij}^3 \epsilon_{ij} x_i x_j. \quad (13)$$

In this work it is assumed that the molecular interaction potential function has two parameters, ϵ and σ . Equation (13) gives one relation between the parameters of the hypothetical fluid and the parameters of the real pure fluids. To find both σ_x and ϵ_x we need a second relation. It can be obtained by using the conformal solution approximation for g_{ij} in Eq. (8), which can be written in the form

$$G_{ij} = \sigma_{ij}^3 \int_0^{\infty} [g_{ij}(r^*) - 1] 4\pi r^{*2} dr^*, \quad (14)$$

where $r^* = r/\sigma_{ij}$. Let us also scale r in Eq. (5):

$$\rho k T \kappa_{Tx} = 1 + \rho \sigma_x^3 \int_0^{\infty} [g(r/\sigma_x) - 1] 4\pi (r/\sigma_x)^2 dr/\sigma_x. \quad (15)$$

According to the conformal solution approximation the two integrals in Eqs. (14) and (15) are now equal. This leads to the relation

$$G_{ij} = \Delta_x (\sigma_{ij}/\sigma_x)^3 / \rho, \quad (16)$$

where $\Delta_x = \rho k T \kappa_{Tx} - 1$. The second mixing rule is then

$$\rho k T \kappa_{Tx} = \frac{|B|}{\rho \sum \sum x_i x_j |B|_{ij}}, \quad (17)$$

where the elements of the determinant $|B|$ are now given by

$$B_{ij} = \rho x_i [\delta_{ij} + x_j \Delta_x (\sigma_{ij}/\sigma_x)^3]. \quad (18)$$

Equation (17) is an implicit relation between σ_x and σ_{ij} which is dependent on temperature and density. Equations (13) and (17) form the necessary set of mixing rules to relate σ_x and ϵ_x to the properties of the real system. Note that Eq. (13) has the same form as the first or attractive van der Waals mixing rule.^{5,6} However Eq. (17), which is temperature and density dependent, is qualitatively different from the second (volume) mixing rule of van der Waals. The second mixing rule of van der Waals will be derived later by applying the conformal solution approximation to the virial equation for the special case of a mixture of hard spheres.

It is important to realize that since the mixing rule reported as Eq. (17) is temperature and density dependent and it is derived from the compressibility equation it should only be used to calculate the mixture isothermal compressibility κ_T . Any other thermodynamic property can then be calculated from the corresponding thermodynamic relation between that property and κ_T . Note that such limitations will not exist for mixing rules which are independent of density and temperature. Next, let us write Eq. (17) in detail for a two component mixture.⁴

For binary mixtures the determinant $|B|$ in Eq. (17) takes the form

$$|B| = \rho \begin{vmatrix} x_1 + x_1^2 \Delta_x (\sigma_{11}/\sigma_x)^3 & x_1 x_2 \Delta_x (\sigma_{12}/\sigma_x)^3 \\ x_1 x_2 \Delta_x (\sigma_{12}/\sigma_x)^3 & x_2 + x_2^2 \Delta_x (\sigma_{22}/\sigma_x)^3 \end{vmatrix} \\ = \rho x_1 x_2 [1 + x_1 \Delta_x (\sigma_{11}/\sigma_x)^3 + x_2 \Delta_x (\sigma_{22}/\sigma_x)^3 \\ + x_1 x_2 \Delta_x^2 \{ (\sigma_{11}/\sigma_x)^3 (\sigma_{22}/\sigma_x)^3 - (\sigma_{12}/\sigma_x)^6 \}]. \quad (19)$$

Substituting Eq. (17) into Eq. (19) and solving for σ_x^3 we get⁴

$$\sigma_x^3 = 1/2 \{ \sigma_{vdw}^3 - C x_1 x_2 \Delta_x \\ + [(\sigma_{vdw}^3 - C x_1 x_2 \Delta_x)^2 + 4 A x_1 x_2 \Delta_x]^{1/2} \}, \quad (20)$$

where σ_{vdw}^3 is the van der Waals mixing rule for a binary hard-sphere mixture

$$\sigma_{vdw}^3 = x_1^2 \sigma_{11}^3 + 2 x_1 x_2 \sigma_{12}^3 + x_2^2 \sigma_{22}^3 \quad (21)$$

and the coefficients A and C are defined by

$$A = \sigma_{11}^3 \sigma_{22}^3 - \sigma_{12}^6, \quad C = \sigma_{11}^3 - 2 \sigma_{12}^3 + \sigma_{22}^3.$$

Equations (13) and (20) constitute the mixing rules for binary mixtures.⁴ Next these equations will be used to calculate some properties of hard-sphere and Lennard-Jones mixtures.

III. CALCULATIONS AND RESULTS

A. Mixture of hard spheres

For a hard-sphere fluid mixture, Eq. (9), which is a result of the energy equations, will vanish. On the other hand, Eq. (10), which is a result of the virial equations, will reduce to the van der Waals mixing rule for σ as given by Eq. (21). Thus, we have two mixing rules for σ ; one is derived from the virial equation and the other is derived from the compressibility equation. For comparison both of these mixing rules will be used to calculate mixture properties. In such calculations one needs also a pure fluid equation of state which can be joined with the mixing rules. For a pure fluid of hard spheres the Carnahan–Starling equation of state will be used¹⁴:

$$\rho/kT\rho = (1 + y + y^2 - y^3)/(1 - y)^3, \quad (22)$$

where $y = \pi\rho\sigma^3/6$. The quantities $(\partial p/\partial\rho)_T$ and hence Δ appearing in Eq. (20) can be derived from the above equation:

$$\left(\frac{\partial p}{\partial\rho}\right)_T = kT(1 + 4y + 4y^2 - 4y^3 + y^4)/(1 - y)^4, \quad (23)$$

$$\Delta = (-8y + 2y^2)/(1 + 4y + 4y^2 - 4y^3 + y^4). \quad (24)$$

For a binary mixture, σ_x at a given ρ , T , and x_i can be calculated by solving Eqs. (20) and (24) simultaneously. The isothermal compressibility κ_T of the mixture, can be calculated directly from Eq. (23) after obtaining σ_x . However, the compressibility factor Z , and the Helmholtz free energy A , of the mixture have to be calculated from the following thermodynamic relations:

$$Z = p/kT\rho = 1 + 1/(kT\rho) \int_0^p \left[\left(\frac{\partial p}{\partial\rho}\right)_{\sigma=\sigma_x} - kT \right] d\rho, \quad (25)$$

$$A - A^0 = \int_0^p (p - kT\rho) d\rho/\rho^2, \quad (26)$$

where A^0 is the ideal gas Helmholtz free energy. Equations (25) and (26) can be integrated numerically to obtain A and Z . The percentage deviations of A , Z , and κ_T , as calculated from the above equations, from those predicted by the exact hard-sphere mixture equation of state,¹⁵ are plotted vs the mixture reduced density in Figs. 1–3 for equimolar binary hard-sphere mixtures. The equimolar mixture reduced density ξ is defined¹⁵ as

$$\xi = \pi\rho(\sigma_{11}^3 + \sigma_{22}^3)/12. \quad (27)$$

The above calculation was performed for three different size ratios of $\sigma_{22}/\sigma_{11} = 2, 4, 6$. It is clear from Figs. 1–3 that as the size ratio increases the deviations from the exact mixture results increase. This reflects the approximate nature of the mixing rules. For comparison the above calculations were repeated using the van der Waals mixing rule as given by Eq. (21). These results are also plotted in Figs. 1–3. From these figures one can see that the deviations based on the van der Waals mixing rule are always in the opposite direction of the deviations based on the mixing rule resulting from the Kirkwood–Buff solution theory. The reason for the opposite deviations resulting from the two mixing rules lies in the fact that at the same density the van der Waals mixing rule predicts a lower value for σ_x than the Kirkwood–Buff mixing

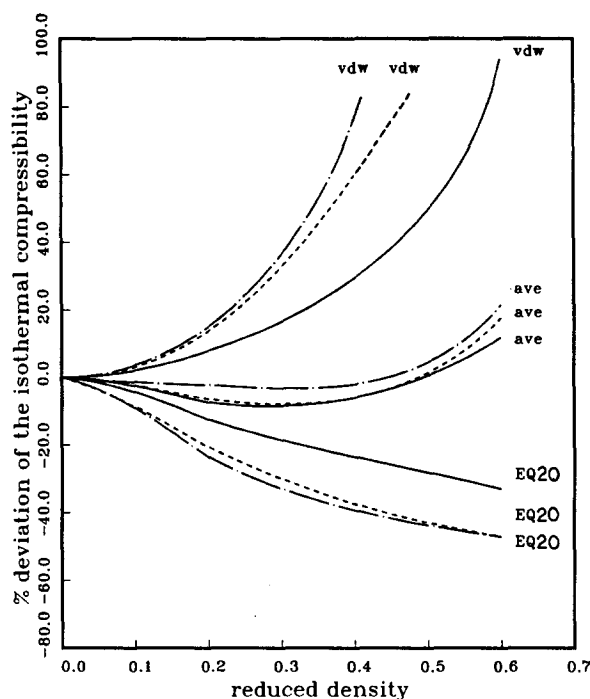


FIG. 1. The percentage deviation of the isothermal compressibility of three hard-sphere mixtures, as predicted by the van der Waals mixing rule and by Eq. (20), from the prediction of the hard-sphere mixture equation of state. The curves represent the following: — $\sigma_{22}/\sigma_{11} = 2$; - - - $\sigma_{22}/\sigma_{11} = 4$; - · - · $\sigma_{22}/\sigma_{11} = 6$.

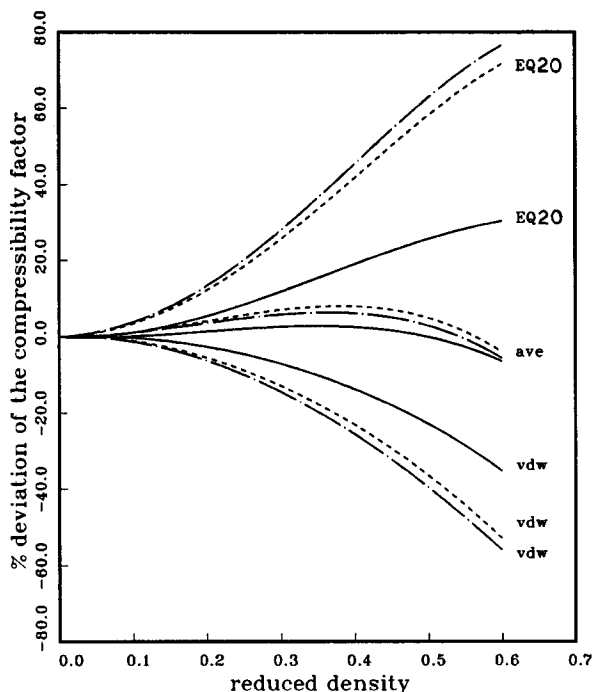


FIG. 2. The percentage deviation of the compressibility factor of three hard-sphere mixtures, as predicted by the van der Waals mixing rule and by Eq. (20), from the prediction of the hard-sphere mixture equation of state. The curves have the same interpretation as in Fig. 1.

rule, and the exact value of σ_x lies somewhere in between the two. The thermodynamic stability condition $[\partial p/\partial \rho]_T > 0$ implies that pressure is a monotonic increasing function of

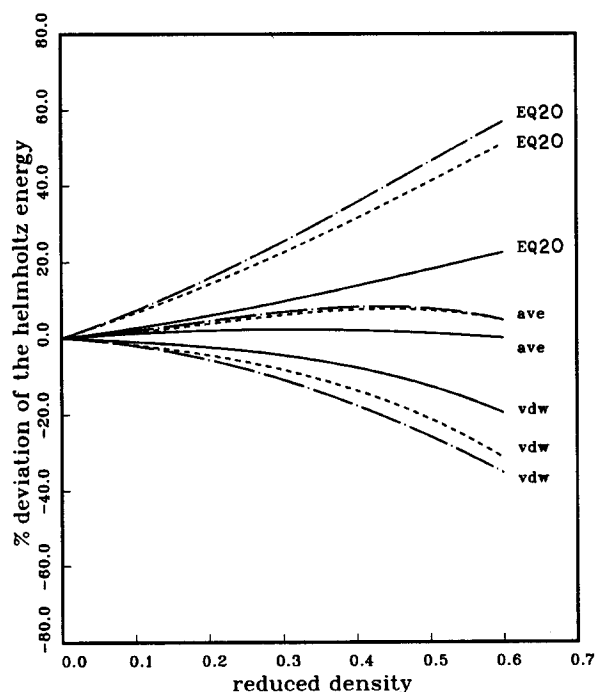


FIG. 3. The percentage deviation of the Helmholtz free energy of three hard-sphere mixtures, as predicted by the van der Waals mixing rule and by Eq. (20), from the prediction of the hard-sphere mixture equation of state. The curves have the same interpretation as in Fig. 1.

the reduced density $\rho\sigma_x^3$. Therefore, one may conclude that at higher value of σ_x the pressure will be higher. Similar conclusions can be attained for the Helmholtz free energy and the isothermal compressibility.

It is possible to show analytically that the value of σ_x calculated from Eq. (20) is larger than that calculated from the van der Waals mixing rule. From Eq. (15) it is obvious that since $\int [g-1]r^{*2}dr < 0$ then $\Delta_x < 0$. Also since $C > 0$ this implies that σ_x^3 [Eq. (20)] $> \sigma_{vdw}^3 - Cx_1x_2\Delta_x$ when $A < 0$ or, since Δ_x is negative, σ_x^3 [Eq. (20)] $> \sigma_{vdw}^3$. The latter inequality also holds when $A > 0$, but small compared to C , and since it can be shown that $C - A > 0$ then we conclude that σ_x^3 [Eq. (20)] is always greater than or equal to σ_{vdw}^3 .

The above observation suggest that if one uses an average of the two mixing rules then the result will be better than either one. For its simplicity the arithmetic average will be used. The resulting mixing rule is then

$$\sigma_x^3 = 3/4\sigma_{vdw}^3 - 1/4\{Cx_1x_2\Delta_x + [(\sigma_{vdw}^3 - Cx_1x_2\Delta_x)^2 + 4Ax_1x_2\Delta_x]^{1/2}\}. \quad (28)$$

The Helmholtz free energy, the compressibility factor, and the isothermal compressibility can be calculated using the procedure discussed above. The results for the average mixing rule are shown in Figs. 1-3. It is clear that Eq. (28) gives a better prediction than either Eq. (20) or the van der Waals mixing rule.

B. Henry's constant for mixture of Lennard-Jones fluids

Henry's constant can be calculated from Eqs. (13) and (20) and the van der Waals mixing rules for a mixture of Lennard-Jones (LJ) fluids. For the pure LJ fluid the equation of state proposed by Nicolas *et al.*¹⁶ will be used. To derive the Henry's constant we use the following relation¹²:

$$\ln(H_i/\rho kT) = \mu_{ir}^\infty/kT, \quad (29)$$

where H_i is the Henry's constant for component i and μ_{ir}^∞ is the residual chemical potential of component i in the mixture at infinite dilution. The chemical potential can be calculated from the relation

$$\mu_{ir}/kT = \int_0^\rho \left[\frac{\partial p}{\partial N_i} (N/kT) - \rho \right] d\rho/\rho^2. \quad (30)$$

To use Eqs. (13) and (20) one has to write Eq. (30) in terms of the derivative $\partial p/\partial \rho$, i.e.,

$$\mu_{ir}/kT = \int_0^\rho \left[(N/kT) \partial \left\{ \int_0^\rho \frac{\partial p}{\partial \rho} (\sigma = \sigma_x, \epsilon = \epsilon_x) d\rho \right\} / \partial N_i - \rho \right] d\rho/\rho^2, \quad (31)$$

$$\begin{aligned} \mu_{ir}/kT = (N/kT) \int_0^\rho \left[\int_0^\rho \left\{ \frac{\partial \epsilon_x}{\partial N_i} \frac{\partial p^*}{\partial \rho} + \epsilon_x \left(\rho \frac{\partial \sigma_x}{\partial N_i} + \sigma_x \rho / N \right) \frac{\partial^2 p^*}{\partial \rho^2} - T^* \frac{\partial^2 p^*}{\partial \rho \partial T^*} \frac{\partial \epsilon_x}{\partial N_i} \right\} d\rho + \rho / N \right. \\ \left. \times \epsilon_x \frac{\partial p^*}{\partial \rho} - \rho \right] d\rho/\rho^2. \quad (32) \end{aligned}$$

To derive the expression for the Henry's law constant from the above equation one needs $\partial\sigma_x^3/\partial N_i$ and $\partial\epsilon_x/\partial N_i$. For binary mixtures, in the limit as $x_1 \rightarrow 0$, $\partial\sigma_x^3/\partial N_1$ and $\partial\epsilon_x/\partial N_1$ will be in the following forms:

$$N \left[\frac{\partial\sigma_x^3}{\partial N_1} \right]_{x_1=0} = 2\sigma_{12}^3 - 2\sigma_{22}^3 + A\Delta_{22}/\sigma_{22}^3 - C\Delta_{22}, \quad (33)$$

$$N \left[\frac{\partial\epsilon_x}{\partial N_1} \right]_{x_1=0} = 2\epsilon_{12}(\sigma_{12}/\sigma_{22})^3 - 2\epsilon_{22} - (\epsilon_{22}/\sigma_{22}^3) \times N \frac{\partial\sigma_x^3}{\partial N_1}. \quad (34)$$

In addition to the above conditions one has

$$\lim_{x_1 \rightarrow 0} \epsilon_x = \epsilon_{22} \quad \text{and} \quad \lim_{x_1 \rightarrow 0} \sigma_x = \sigma_{22}.$$

Using the above relations in Eq. (32) and after a long, but straightforward, manipulation one obtains

$$\begin{aligned} \mu_{1r}^\infty/kT = & \mu_{2r}/kT \\ & + 2h(f-1)u_{2r}/kT + 2(h-1)(Z_2-1) \\ & + (h-1)^2\{Z_2-1 - u_{2r}/kT - F(T, \rho)\}, \end{aligned} \quad (35)$$

where μ_{2r} , u_{2r} , and Z_2 are the residual chemical potential, the residual internal energy, and the compressibility factor of pure component 2 at the same temperature and density of the mixture, and

$$f \equiv \epsilon_{12}/\epsilon_{22}, \quad (36)$$

$$h \equiv (\sigma_{12}/\sigma_{22})^3 \quad (37)$$

$$F(T, \rho) = \int_0^\rho \left[\int_0^\rho \left(\rho \frac{\partial^2 p}{\partial \rho^2} + T \frac{\partial^2 p}{\partial T \partial \rho} \right) / \left(\frac{\partial p}{\partial \rho} \right) d\rho - \rho \right] d\rho / \rho^2. \quad (38)$$

For the van der Waals mixing rules the expression for the residual chemical potential is given by

$$\begin{aligned} \mu_{1r}^\infty/kT \\ = & \mu_{2r}/kT + 2h(f-1)u_{2r}/kT + 2(h-1)(Z_2-1). \end{aligned} \quad (39)$$

Note that the difference between this expression and the expression from Eqs. (13) and (20) is the quadratic term in h which is missing from Eq. (39). In Figs. 4 and 5, Eqs. (35) and (39) are compared to the simulation data¹² for different values of f and h when $\rho\sigma_{22}^3 = 0.7$ and $kT/\epsilon_{22} = 1.2$. At these conditions Eqs. (35) and (39) become

$$\begin{aligned} \mu_{1r}^\infty/kT = & -1.986 - 7.946h(f-1) \\ & - 0.485(h-1) + 12.03(h-1)^2, \end{aligned} \quad (40)$$

$$\mu_{1r}^\infty/kT = -1.986 - 7.946h(f-1) - 0.485(h-1). \quad (41)$$

Figure 4 shows the simulation data and Eqs. (40) and (41) for $h = 1$, i.e., for mixture of molecules with the same size, but different energies of interaction. In this case, Eqs. (13)

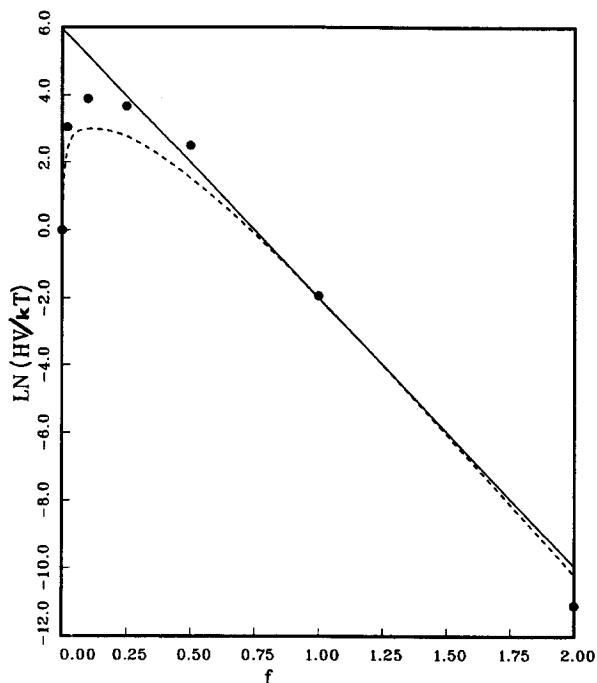


FIG. 4. Variation of μ_{1r}^∞ with $f = \epsilon_{12}/\epsilon_{22}$. The points represent the simulation data (Ref. 12) and the curves represent the following: — the van der Waals mixing rules, Eqs. (13) and (20), and the average mixing rules; - - - Eq. (49).

and (20) and the van der Waals mixing rules predict the same curve for μ_{1r}^∞ , which turns out to be a straight line. The agreement is generally good except for the small region near $f = 0$. Figure 5 shows the results for $f = 1$, i.e., the energies of

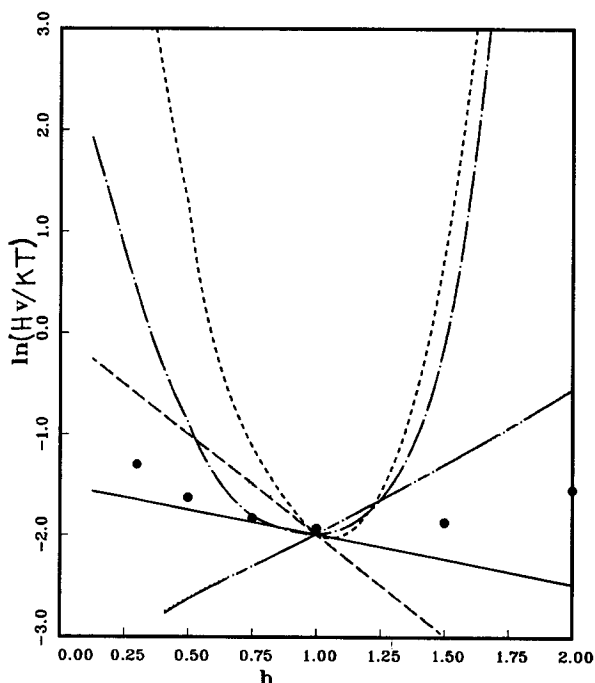


FIG. 5. Variation of μ_{1r}^∞ with $h = (\sigma_{12}/\sigma_{22})^3$. The points represent the simulation data (Ref. 12) and the curves represent the following: — the van der Waals mixing rules; - - - Eqs. (13) and (20); - · - · - the average mixing rules; · · · Eq. (49) with van der Waals mixing rule for σ_x ; - - - - Eq. (49) with σ_x from Eq. (20); - - Eq. (52).

interaction are the same for the two fluids, but the molecules have different sizes. In this case the agreement is only good in the region near $h = 1$. While the van der Waals mixing rules predict a linear behavior, Eqs. (13) and (20) predict the correct qualitative behavior of the simulation data. The curved shape is due to the quadratic term which is missing from the van der Waals expression. This term can be thought of as a correction to the van der Waals expression. However, this correction is too large, and hence making the prediction to go to the opposite side of the simulation data.

As observed in the case of hard-sphere mixture the deviations of the two mixing rules are on opposite sides. The average mixing rule, Eq. (28), gives the following expression for μ_{1r}^∞ :

$$\begin{aligned} \mu_{1r}^\infty/kT &= \mu_{2r}/kT + 2h(f - 1.25)u_{2r}/kT \\ &+ 2(1.25h - 1)(Z_2 - 1) + (h - 1)^2\{Z_2 - 1 \\ &- u_{2r}/kT - F(T, \rho)\}. \end{aligned} \quad (42)$$

This expression gives a better prediction far from $h = 1$, but it does not predict the correct behavior around $h = 1$ (ideal mixture). The reason for this can be seen from the derivative of σ with respect to N_1 for the average mixing rule. This derivative is given by

$$\begin{aligned} N \left[\frac{\partial \sigma_x^3}{\partial N_1} \right]_{x_1=0} &= 5/2\sigma_{12}^3 \\ &- 2\sigma_{22}^3 + 1/2(A/\sigma_{22}^3 - C)\Delta_{22}. \end{aligned} \quad (43)$$

This expression predicts a nonzero value of the derivative at equal sizes ($\sigma_{11} = \sigma_{22}$). This causes the incorrect behavior near $h = 1$. However, since the ideal mixtures behavior is known ($\mu_{1r}^\infty/kT = \mu_{2r}/kT$), one can subtract the additional terms which show up in Eq. (42) when we put $h = f = 1$ (the extra terms are $1/2 [Z - 1 - u_{2r}/kT]$). The resulting expression is then

$$\begin{aligned} \mu_{1r}^\infty/kT &= \mu_{2r}/kT + 2[h(f - 1.25) + 0.25]u_{2r}/kT \\ &+ 2.5(h - 1)(Z_2 - 1) \\ &+ (h - 1)^2\{Z_2 - 1 - u_{2r}/kT - F(T, \rho)\}. \end{aligned} \quad (44)$$

This equation is plotted in Figs. 4 and 5. It is clear that it is better than Eq. (35) for $h \neq 1$, but still there is a need for improvement at small and large values of h .

Henry's constant can also be calculated directly (without going through mixing rules) from the Kirkwood-Buff solution theory. The derivative of the chemical potential of component one with respect to composition is given by

$$\begin{aligned} \beta \left(\frac{\partial \mu_1}{\partial x_1} \right)_{T,p} &= 1/x_1 - \{x_2 \rho (G_{11} + G_{22} - 2G_{12})\} / \\ &\{1 + x_1 x_2 \rho (G_{11} + G_{22} - 2G_{12})\}, \end{aligned} \quad (45)$$

where $\beta = 1/kT$. For an ideal gas mixture component

$$\beta \left(\frac{\partial \mu_1^*}{\partial x_1} \right)_{T,p} = 1/x_1. \quad (46)$$

From Eqs. (45) and (46) one obtains the relation for the residual chemical potential

$$\begin{aligned} \beta \left(\frac{\partial \mu_{1r}}{\partial x_1} \right)_{T,p} &= - \{x_2 \rho (G_{11} + G_{22} - 2G_{12})\} / \\ &\{1 + x_1 x_2 \rho (G_{11} + G_{22} - 2G_{12})\}. \end{aligned} \quad (47)$$

Integrating Eq. (47) at constant T and p from $x_1 = 0$ to $x_1 = 1$ one obtains

$$\begin{aligned} \beta \mu_{1r}^\infty &= \beta \mu_{1r}^{\text{pure}} + \int_0^1 \{x_2 \rho (G_{11} + G_{22} - 2G_{12})\} / \\ &\{1 + x_1 x_2 \rho (G_{11} + G_{22} - 2G_{12})\} dx_1. \end{aligned} \quad (48)$$

The conformal solution approximation for the radial distribution function, Eq. (12), can be used to integrate the above equation. Substituting Eq. (16) in Eq. (48) one gets

$$\beta \mu_{1r}^\infty = \beta \mu_{1r}^{\text{pure}} + C \int_0^1 x_2 \Delta_x / (\sigma_x^3 + C x_1 x_2 \Delta_x) dx_1. \quad (49)$$

In the case of equal molecular sizes $C = 0$, but if the molecular sizes are different, then the integral has to be evaluated numerically by using an appropriate equation of state to calculate Δ_x . The term σ_x^3 can be calculated from either Eq. (20) or Eq. (21), which gives almost the same result as shown in Fig. 5. The curves were terminated at $h = 0.4097$ which corresponds to the saturation condition at $T^* = 1.2$. Beyond this point the Nicolas *et al.* equation of state¹⁶ predicts a vapor phase.

Equation (49) predicts the correct qualitative dependence of μ_{1r}^∞ on f as seen in Fig. 5. On the other hand, it predicts almost a linear dependence of μ_{1r}^∞ on h which is not what the simulation shows. In all cases the prediction around $h = f = 1$ is accurate, which is expected because of the ideal behavior of the mixture at these values of f and h .

Another route to the chemical potential from the Kirkwood-Buff theory is to express the derivative $\partial p / \partial N_i$ in Eq. (30) in terms of the partial molar volume as follows:

$$\left(\frac{\partial p}{\partial N_i} \right)_{T,V,N_j} = - \left(\frac{\partial p}{\partial V} \right)_{T,N} \left(\frac{\partial N_i}{\partial V} \right)_{T,p,N_j} = - V_i \left(\frac{\partial p}{\partial V} \right), \quad (50)$$

where V_i is the partial molar volume of component i . The Kirkwood-Buff solution theory gives the expressions for the compressibility and the partial molar volume. After substituting these expressions in Eq. (50) and taking the limit as x_1 approaches zero one obtains the following expression for the chemical potential at infinite dilution:

$$\mu_{1r}^\infty = - \int_0^p G_{12}^\infty / (1 + p G_{22}^\infty) dp, \quad (51)$$

where the superscript ∞ means infinite dilution. Substituting the conformal solution approximation expression for G_{ij} [Eq. (16)], in Eq. (51) one gets the chemical potential for molecules with the same energies of interaction:

$$\mu_{1r}^\infty = (\sigma_{12}/\sigma_{22})^3 \mu_{2r}. \quad (52)$$

Equation (52) is plotted in Fig. 5. The different expressions for the chemical potential results from making the conformal solution approximation in different exact equations. Apparently each of the above expressions gives a better result in a certain range of h and f .

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