A theory for the 1-1/2 fluid

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The 1-1/2 fluid is a conformal solution in which one species has a size parameter (diameter) of zero. This "point-particle" species nevertheless interacts with the other component of the mixture, as the collision diameter of a point particle and a finite particle is nonzero. A great simplifying feature of this model mixture is that the point particles do not interact with each other. For hard repulsive potentials, the properties of a 1-1/2 fluid can be obtained exactly in terms of the properties of the pure fluid obtained upon removal of all the point particles. For other potentials, the properties of the 1-1/2 fluid can be obtained only approximately. We develop two approaches to the description of the 1-1/2 fluid, both based on the methods of diagrammatic expansion and topological reduction. The first approach is an extended virial treatment, in which the free energy is expanded in the density ρ_1 of the full-sized species, keeping to all orders terms in the density ρ_2 of the point particles. A complementary approach takes the pure full-sized fluid as a reference, keeping all terms to ρ_1 while expanding in ρ_2. Monte Carlo simulation is used to show that, properly formulated, an expansion containing only terms first order in ρ_2 is capable of describing 1-1/2 fluid properties over a very broad range of conditions. © *1995 American Institute of Physics.*

I. INTRODUCTION

The structure of an engineering theory—i.e., a theory in the sense of providing an approximate description of the behavior of a complex system—comprises two elements, a reference system that is analytically tractable, and an approximate mathematical formulation that ties the reference to the target system, the system of interest. Both elements play an important role in the success of the theory, and good theories balance the contributions of the two. The reference must be fashioned to satisfy two conflicting requirements. It must be simple enough to be solvable in some sense, so that great effort is not required to establish its properties (the effort must certainly not be comparable to that required to describe the target); yet at the same time it must exhibit certain essential features of the target, so that the possibility remains to connect the two via a reasonably simple approximate treatment. Abundant examples from across the years may be cited to demonstrate the role of the reference in the success or failure of an engineering theory. In the field of chemical physics, the liquid state long eluded a satisfactory description for the want of a suitable reference. With the advent of molecular simulation it became possible to perform experiments on model liquids, and thereby to formulate reliable analytical treatments of them. Thus the well known stable of model materials—particularly the hard-sphere system and its variants—have come to serve in the role of a reference for liquid-state theory.

Many theories for mixtures fit this mold. Invariably the reference for these treatments is a pure substance, usually selected as some sort of hybrid of the components of the mixture.[1] The most prominent of these theories are the so-called *n*-fluid theories that bear the name of van der Waals.[2,3] The 1-fluid theory in particular is quite popular, although it has well known limitations.[4] We show for example in Fig. 1 application of the theory to two model mixtures. These models form true conformal solutions, so they satisfy a key ap-

proximation of the theory which real mixtures do not in general obey. The limits of the treatment, particularly relating to the volumetric properties, are apparent; the prediction of the chemical potential is expected to become worse as one departs from the limit of infinite dilution presented in the figure.[4] On the other hand, there is evidence[5] that these deficiencies do not much hamper the ability of the 1-fluid theory to predict phase equilibrium. Nevertheless, broad application of the theory to real substances must wrestle with its shortcomings a theory for truly conformal solutions, while at the same time try to compensate for the fact that real mixtures are not conformal. This makes systematic improvement of the theory difficult.

The popularity of the 1-fluid theory stems largely from its simplicity, but also from the nature of the reference upon which it is based. Pure fluids are described by relatively few parameters—just temperature and pressure—and this feature facilitates their most important characteristic; they may be rather fully characterized by experiment. The 1-fluid theory succeeds as an engineering theory where many more complex approaches fail because it does not attempt a description from first principles. Experiment has a limited but well defined role in the treatment, viz., it provides a description of the reference. However, the use of the pure fluid as a reference at the same time gives rise to the theory's shortcomings. A pure fluid cannot capture the role and influence of all the varied components of the mixture at once, nor can it properly account for the different faces that each species presents to its various neighbors; it is not very flexible. Simply put, the essential shortcoming of a pure substance as a reference material is that it is not a mixture.

In the past several years we have introduced two quite different model materials that may be suitable for use as a reference in a theory for mixtures. The *infinitely polydisperse* mixture[6] is a very curious substance that exhibits surprising simplifying features. However, it is rather far removed from
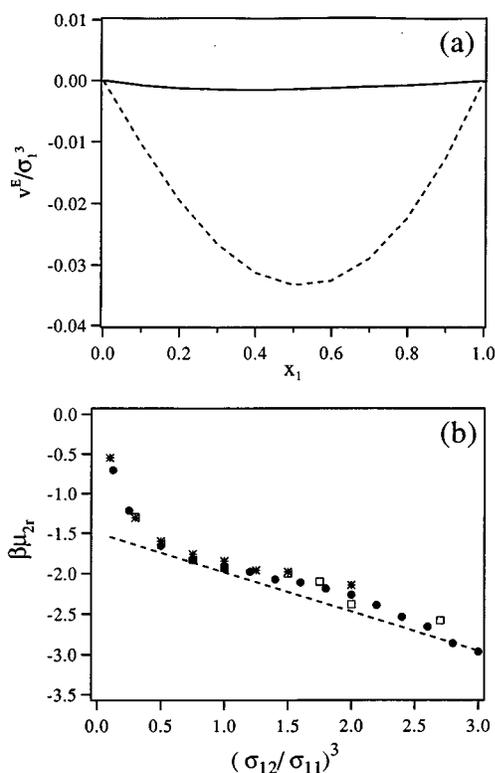
FIG. 1. Demonstration of the van der Waals 1-fluid (vdW1) theory; (a) excess volume for a mixture of hard spheres of size ratio $\sigma_2/\sigma_1 = 1/2$, at a pressure $\beta p \sigma_1^3 = 10$, presented as a function of the mixture mole fraction. The solid line is from the accurate equation of state of Mansoori *et al.* (Ref. 18) while the dashed line is the prediction of vdW1; (b) residual chemical potential of a Lennard-Jones solute of diameter σ_{22}, at infinite dilution in a solvent of diameter σ_{11}, as a function of the collision diameter $\sigma_{12} = (\sigma_{11} + \sigma_{22})/2$. $kT/\epsilon_{11} = 1.2$, and $\beta p \sigma_{11}^3 = 0.554$. Squares are the NpT Monte Carlo data of Shing *et al.* (Ref. 4), stars are molecular dynamics data of Lofti and Fisher (Ref. 19) circles are NpT Monte Carlo data taken by us, and the line is the prediction of vdW1.

a pure fluid, and so we will not consider it further in the present context. Our goal is to devise a reference that retains the possibility of experimental characterization, or at least one that holds the possibility of bridging to experiment; we deem this a vital feature of a reference for a practical theory of mixtures.

The second model substance we have introduced holds this potential. This is what we have called[7] the "1-1/2 fluid." The 1-1/2 fluid is a binary mixture in which one of the components has zero size. This of course is not to say that its presence is not felt. As the interaction between two molecules is governed by their *collision diameter* (given to a first approximation by their arithmetic mean), these "point" particles are capable of significant interplay with their "full-sized" neighbors. However, one of the main simplifying features of the model is that the point particles interact not at all with each other. The 1-1/2 fluid buys this simplicity at relatively little cost, as it retains a substantial degree of flexibility for its service as a reference substance; both the composition of the mixture and the strength of the point-particle influence can be varied independently, along with the usual state parameters of (say) the temperature and pressure. Most

important, it is not a great leap to connect the 1-1/2 fluid to an appropriate pure substance.

The goal of the present work is to develop a theory for the 1-1/2 fluid. In particular, we do attempt to present a conformal solution treatment based upon this reference. Many such approaches could be put forth, and we would rather that the inevitable concern for the merits and weaknesses of one particular formulation not distract from our study of this model substance. In the next section we review the notions of corresponding states and conformal solutions while providing a more precise definition of the 1-1/2 fluid. Then in Sec. III we present a theory for the 1-1/2 fluid that expresses its properties in terms of those of a pure fluid. We demonstrate the treatment with a 1-1/2 Lennard-Jones fluid in Sec. IV, and we conclude in Sec. V.

II. THE 1-1/2 FLUID

The 1-1/2 fluid is an example of a conformal solution. Conformal solutions[3] are composed of substances that obey corresponding states.[1] In terms of the intermolecular potential $u(r)$, a corresponding states model has the form

$$u(r) = \epsilon f(r/\sigma), \tag{2.1}$$

where r is the distance between the molecules and f is in principle any function. The potential is characterized by only two parameters, σ and ϵ, having dimensions of length and energy, respectively. As a consequence of the simple form of the intermolecular potential, the thermodynamic properties of corresponding-states materials may be mapped onto one another, so that knowledge of one substance implies knowledge about all members of the family. Mathematically, this simplification takes the form of a dimensionless equation of state that depends on only two parameters; thus we state that $P\sigma^3/\epsilon(kT/\epsilon, \rho\sigma^3)$ is an invariant (where P is the pressure, T is the absolute temperature, k is Boltzmann's constant, and ρ is the number density). An alterative, entirely macroscopic formulation, invokes the critical properties; thus $P_r(T_r, \rho_r)$ is an invariant (where the r subscript indicates a property divided by its value at the critical point). Many substances are found to obey corresponding states to a useful extent, and of course model substances such as hard spheres or that of Lennard-Jones obey the principle exactly. The approach may be extended by introducing additional characteristic lengths or energies,[8] but this is not often done.

When mixing corresponding-states materials to form conformal solutions, one must further specify the "mixing rules" that govern how unlike species interact with one another. Usually the Lorentz–Berthelot rules are applied

$$\sigma_{ij} = \tfrac{1}{2}(\sigma_i + \sigma_j),$$
$$\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2}. \tag{2.2}$$

Of the two, the energy-parameter rule is acknowledged as the weaker,[2,9] and often binary interaction parameters are introduced to correct it. These parameters produce a departure from corresponding states, so there is a cost in terms of the simplicity of the treatment when they are used.

The direct extension of corresponding states to mixtures is not a practical endeavor, as the introduction of each new

species j results in three additional dimensionless parameters in the invariant equation of state; σ_j/σ_1, ϵ_j/ϵ_1, and x_j, where x is a mole fraction and the subscripts indicate values for the particular component. A five-parameter correlation resulting from the corresponding-states treatment of a binary mixture is not very useful, and the situation gets only worse as more species are added. This circumstance is what motivates the development of conformal solutions treatments such as the n-fluid theories mentioned above.

Turning now to the topic at hand, we define a 1-1/2 fluid as a two-component conformal solution in which one of the components has a characteristic diameter σ equal to zero. Designating henceforth this species as component 2, we have $\sigma_2=0$. Thus the collision diameter $\sigma_{12}=\sigma_1/2$, while $\sigma_{22}=0$. If the function $f(r/\sigma)$ of Eq. (2.1) is of the usual form in that it approaches zero as the molecules become infinitely separated, we see that the species-2 "point" particles will not interact with one another, although they do retain some influence on the behavior of the species-1 particles. The dimensionless equation of state of the 1-1/2 fluid depends upon four parameters

$$P\sigma_1^3/\epsilon_1 = P\sigma_1^3/\epsilon_1(kT/\epsilon_1, \rho\sigma_1^3, \epsilon_2/\epsilon_1, x_2). \quad (2.3)$$

Thus we have two additional parameters, compared to a pure fluid, with which to adjust the choice of a reference in a treatment for conformal solutions.

Despite the evidently large simplification introduced by setting $\sigma_2=0$, the properties of the 1-1/2 fluid are not trivial, and in general are not even trivially related to the properties of the pure substance obtained by removing all of the point particles from the mixture. The point particles do indeed interact strongly with the full-sized particles—the major simplifications are that the point particles do not interact with one another, and they do not interact with *many* full particles. Only in the case of purely repulsive hard potentials can we write exactly the work required to insert a species-2 particle in a 1-1/2 fluid, and thereby obtain a full description of the properties of the 1-1/2 fluid in terms of a pure substance.[7,10]

III. THEORY

We shall now proceed to develop a theory for the 1-1/2 fluid, attempting two approaches. The first may be viewed as an extended virial treatment, in which we perform an expansion in the density $\rho_1(=N_1/V)$ of the full-size particles, about $\rho_1=0$, retaining to all orders terms in the density $\rho_2(=N_2/V)$ of the point particles. The second approach is the complement of the first. Here the 1-1/2 fluid properties are presented in terms of the pure substance obtained upon removal of all the species-2 point particles. Thus we consider an expansion in ρ_2, keeping terms to all orders in ρ_1. In both approaches we exploit the powerful and elegant methods of diagrammatic expansion and topological reduction.[11–13]

We begin with the diagrammatic series for the residual Helmholtz free energy density of the 1-1/2 fluid, defined in excess of the corresponding value for an ideal gas at the same temperature, composition, and density

$$\mathscr{A} \equiv -\frac{A_r}{VkT} = -\frac{(A-A^{id})}{VkT}, \quad (3.1)$$

thus[14]

$V\mathscr{A}(\rho_1,\rho_2) =$ sum of all topologically distinct, irreducible diagrams composed of black ρ_1-squares, black ρ_2-circles, and at most one f-bond between each pair of vertices, such that there are at least two black vertices and no articulation vertices,   (3.2)

where V is the volume. We use squares to represent species 1, and circles to represent species 2 (the point particle); a vertex refers generically to a ρ_1-square or a ρ_2-circle.

Because the point particles do not interact, we can eliminate from this series all diagrams having an f-bond directly connecting two ρ_2-circles, thus

$V\mathscr{A}(\rho_1,\rho_2) =$ sum of all topologically distinct, irreducible diagrams composed of black ρ_1-squares, black ρ_2-circles, and at most one f-bond between each pair of vertices, such that there are at least two black vertices, no articulation vertices, and no adjacent ρ_2-circles;

or, pictorially,

$$ (3.3) $$

A. ρ_1-expansion

We define the set of coefficients T_n such that

$$V\mathscr{A}(\rho_1,\rho_2) = \sum_{n=1}^{\infty} T_n \rho_1^n, \quad (3.4)$$

thus

$T_n =$ sum of all topologically distinct, irreducible diagrams composed of n black 1-squares, some or no black ρ_2-circles, and at most one f-bond between each pair of vertices, such that there are no articulation vertices and no adjacent ρ_2-circles.   (3.5)

The first few coefficients are

$$ (3.6) $$

$$ (3.7) $$

$$ (3.8) $$

The absence of any bonds joining ρ_2-circles permits a topological reduction of each series. In particular, the infinite sums may be expressed by just a few diagrams that are written in terms of a set of renormalized bonds. The greatest economy is achieved if effective multibody interactions are introduced, and the resulting (few) diagrams written in terms of n-body faces. This complication is of course not necessary for $n=2$, which we demonstrate first.

In the diagrams of T_2 each ρ_2-circle must be joined to both 1-squares, and to nothing else. Therefore, all diagrams are parallel, and may be decomposed into products of just

two diagrams, viz., two 1-squares joined by an f-bond

$$(\square \!-\!\!\!-\! \square),$$
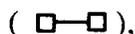
and two 1-squares bridged by a ρ_2-circle.

$$(\; \text{◭} \;).$$

We will refer to that latter diagram as $b^{(2)}$; it may appear any number of times in the product, but at least twice if the former is not present. It is convenient to define an effective f-bond,

$$f_p(\rho_2,T) = e \; e_p - 1, \tag{3.9}$$

where e_p is the sum of all products of $b^{(2)}$ diagrams, which may be summed directly

$$e_p = 1 + \text{◭} + \text{◮◭} + \cdots \cdots$$
$$= \exp[\; \text{◭} \;]. \tag{3.10}$$

Figure 2 displays the f_p function for the Lennard-Jones potential at several combinations of values of T, ρ_2, and ϵ_2. This function is of the same range as the (usual) f-bond, which is recovered when $\rho_2 = 0$. One can in fact show that, for the hard-sphere potential, $f_p = f$. In terms of this renormalized f-bond, we have

$$T_2 = (\; \overset{f_p}{\blacksquare\!\!-\!\!\blacksquare} \;) - (\; \text{◭} \;). \tag{3.11}$$

The second diagram must be subtracted because it is in f_p but does not belong in the series for T_2 (it contains an articulation circle).

The simplification of T_3 proceeds in a similar fashion. We begin by noting that the f_p bond represents all ways that two 1-squares can be joined; through a single direct f-bond, or one or more products of $b^{(2)}$, with or without a direct f-bond. Thus the f_p-bond provides a convenient building block for constructing the diagrams in T_3. A new element that must be introduced is the 3-bridge, in which a point particle is connected to all three 1-squares at once:

$$(\; \text{◮} \;);$$

we designate this $b^{(3)}$. As with $b^{(2)}$, multiple instances of this form must be in parallel, and therefore can be summed to an exponential. We represent this function as a shaded three-point diagram,

$$\text{◮} = \text{◮} + \text{◮◮} + \cdots \cdots$$
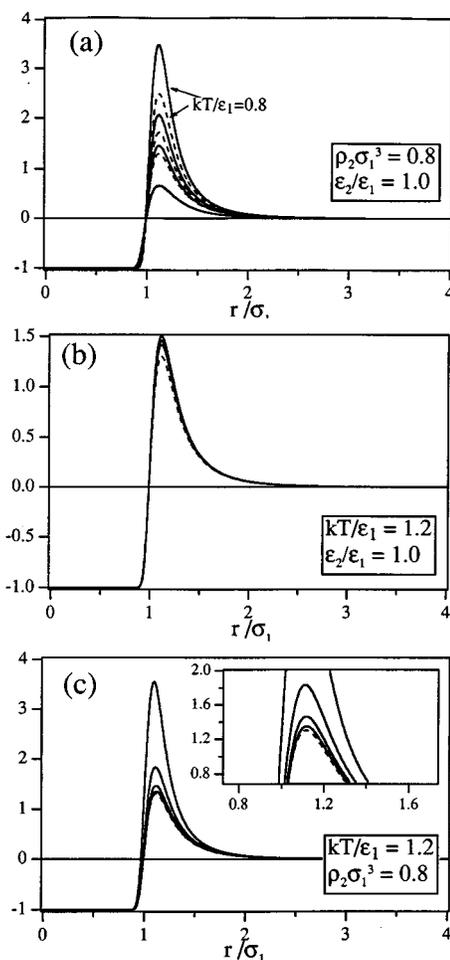$$= \exp(\; \text{◮} \;) - 1 \quad . \tag{3.12}$$

FIG. 2. The function f_p (solid line) defined by Eqs. (3.9) and (3.10), and the usual (Ref. 13) Mayer f-function (dashed line) as a function of particle separation; (a) temperature dependence: $kT/\epsilon_1 = 0.8$ (upper pair), 1.0, 1.2, and 2.0 (lower pair); (b) density dependence: $\rho_2\sigma_1^3 = 0.0$ (where $f_p = f$), 0.6, 0.8, and 1.0; (c) dependence on the well depth of the point particle, $\epsilon_2/\epsilon_1 = 0.5$ (where f_p approaches f), 1.0, 2.0, and 4.0. Other conditions are as indicated.

This diagram is plotted in Fig. 3 for two configurations of the three 1-squares; for an equilateral triangle; and for a constant separation of two, while the third recedes. It is evident that the range of this function is less than the corresponding function having two 1-squares.

Using f_p and this new three-body function, all doubly-connected diagrams having three black 1-squares, i.e., the diagrams in T_3, can be expressed in a few diagrams,

$$T_3 = \overset{f_p}{\text{◭}} + \text{◭} + \overset{f_p}{\text{◭}} + \overset{f_p}{\text{◭}} + \overset{f_p}{\text{◭}} - \text{◿} - \overset{f_p}{\text{◿}} \tag{3.13}$$

Here, all bonds between squares are f_p bonds, while those joining a square and a circle are f-bonds. Interestingly, all the diagrams containing the three-body face can be summed to a single diagram composed of three 1-squares, each joined to the other two by a $(f_p + 1)$ bond, and all mutually joined by the three-body face. As the $(f_p + 1)$-bonds disallow overlap between pairs, and the three-body face differs substantially from zero only in the presence of such an overlap (cf. Fig. 3), we surmise that the contribution from this diagram is small.
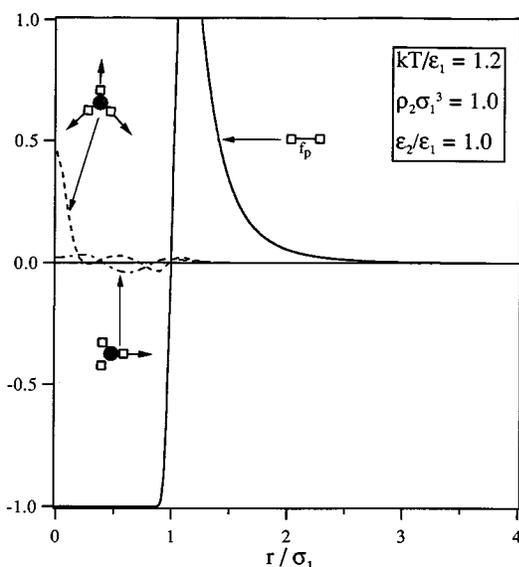
FIG. 3. The three-point diagram defined by Eq. (3.12), for two geometries of the three root points; an equilateral triangle, for which the abscissa represents the mutual separation of the three roots; an isosceles triangle, for which the separation of two roots is held as $r/\sigma_1=1$, while the abscissa represents the separation of the third root from the other two. Also presented in the plot is the f_p function defined by Eq. (3.9). Conditions are as indicated.

The only other diagrams remaining in T_3 are the single diagram having no ρ_2-circles, and the two diagrams being subtracted.

The diagrams being subtracted in Eqs. (3.11) and (3.13) are not negligible, and in fact are rather interesting. All contain a single ρ_2-circle. We suspect, but have not shown, that such terms collected from all the T_n may be partially summed to yield a form similar to the logarithm term encountered in Eq. (3.16) farther below. The subtraction terms that remain after the summation have a single ρ_2-circle connected to n 1-squares by f-bonds [forming a $b^{(n)}$-bridge], while the n 1-squares themselves are joined to one another in various ways by (f_p+1)-bonds; the "conflict" between the $b^{(n)}$ bridge and these (f_p+1)-bonds renders small the magnitude of these diagrams. Also for $n>3$, we suspect that the diagrams obtained by summing the $b^{(n)}$-bridges will tend to cancel as they do for T_3. If all these conjectures are correct (and we must emphasize the *if*), the only diagrams that contribute significantly are those containing zero or one ρ_2-circle. It is therefore reasonable to consider an expansion in ρ_2 while retaining all terms in ρ_1.

B. ρ_2-expansion

We may manipulate the diagrammatic expansion of the mixture free energy to a form that takes the pure species-1 fluid, obtained upon removal of all point particles, as a reference. All diagrams that contain only black squares are summed to the species-1 free energy, and the expansion is thus

$$
V\mathscr{A}(\rho_1,\rho_2) = V\mathscr{A}_{\text{pure}}(\rho_1) + \text{the sum of all diagrams described in Eq. (3.3), except those that contain zero black } \rho_2\text{-circles}
$$

$$
= V\mathscr{A}_{\text{pure}}(\rho_1) + \quad\blacksquare\!\!-\!\!\bullet \;+\; \triangle \;+\; \bowtie \;+\; \bowtie \;+\; \cdots\cdots,
$$
(3.14)

where $\mathscr{A}_{\text{pure}}(\rho_1)$ is the free-energy density of pure species 1 at a number density ρ_1.

An important limiting case is infinite dilution of the point particles. If we can describe this limit, we may be able to approximate finite concentrations by assuming that the point particles have no influence on the structure of the species-1 solvent (thus the work of adding a point particle is independent of the number that are already there). In this limit, all diagrams containing more than one ρ_2-circle are removed, and the result may be written in terms of total-correlation function $h^{(n)}$ bonds[12] of pure solvent

$$
V\mathscr{A} = V\mathscr{A}_{\text{pure}} + \text{sum of all topologically distinct, irreducible diagrams composed of } n>0 \text{ black } \rho_1\text{-squares, exactly one black } \rho_2\text{-circle, such that the } \rho_1\text{-squares are mutually joined by an } h^{(n)}\text{-face, and each is connected to the } \rho_2\text{-circle by a single } f\text{-bond.} \quad (3.15)
$$

In recent work,[15] we proposed a topological reduction that expresses a sum of diagrams in terms of the logarithmic of a sum of fewer diagrams. Application to Eq. (3.15) yields

$$
V\mathscr{A} = V\mathscr{A}_{\text{pure}}(\rho_1) + V\rho_2\,\ln(1+S), \tag{3.16}
$$

where S is given in terms of $g^{(n)}$-bonds,[12]

$$
VS = \text{sum of all topologically distinct, irreducible diagrams composed of one black 1-circle and } n>0 \text{ black } \rho_1\text{-squares, such that all squares are mutually joined by a } g^{(n)}\text{-face, and each square is connected to the circle by a single } f\text{-bond.}
$$

$$
VS = \bullet\!\!-\!\!\blacksquare \;+\; \langle g \;+\; \Diamond^{g^{(3)}} \;+\; \cdots\cdots\;. \tag{3.17}
$$

The residual chemical potential of point particle is simply

$$
\beta\mu_{2r} = -\ln(1+S)
$$

$$
= -\ln[\,1 + \bullet\!\!-\!\!\blacksquare \;+\; \langle g \;+\; \Diamond^{g^{(3)}} \;+\; \cdots\cdots\,]. \tag{3.18}
$$

The exact hard-sphere result may be extracted from this formulation. Consider first the $g^{(n)}$-bonds, which are zero in every configuration in which the (species-1) hard spheres overlap; now note that the f-bonds joining each species-1 hard sphere to the point particle are zero if the hard spheres do *not* overlap (a point particle can simultaneously overlap two hard spheres only if the hard spheres themselves overlap). Thus the integral over all configurations implied by the black points results in a diagram of value zero. The only diagram that survives in the sum defining VS is that composed of a single black 1-circle and a single black ρ_1-square.

●━■ .

The result corresponds to the exact expression for $\mathscr{A}$ of the hard-sphere mixture, which is easily derived independently.

The development presents us now with several possibilities for approximating the 1-1/2 fluid free energy for more complicated potentials. We have isolated five such approximations for study. The first two are merely truncation of the series for S,

(I) $V\mathscr{A}(\rho_1,\rho_2) = V\mathscr{A}_{pure}(\rho_1) + V\,\rho_2 \ln[\ 1 + ●━■\ ]$,

(II) $V\mathscr{A}(\rho_1,\rho_2) = V\mathscr{A}_{pure}(\rho_1) + V\,\rho_2 \ln[\ 1 + ●━■\ +\ ◁{}_{g}\ ]$.

The former is appealing in that it requires no structural properties of the reference for its application, and in fact the single diagram present may be given in terms of the (experimentally-obtainable) second virial coefficient of the reference. Both forms remain exact for hard spheres. The third approximation is obtained by assuming that there are no structural correlations in the solvent, i.e., all distribution functions $g^{(n)}$ are unity

(III) $V\mathscr{A}(\rho_1,\rho_2) = V\mathscr{A}_{pure}(\rho_1) + V\,\rho_2\ ●━■$.

This form, like the next one, no longer yields the exact result when applied to hard spheres. In the next form we retain pair correlations in the reference, and set $g^{(n)} = 1$ for $n \geqslant 3$,

(IV) $V\mathscr{A}(\rho_1,\rho_2) = V\mathscr{A}_{pure}(\rho_1) + V\,\rho_2 \ln[\ \exp(●━■)\ +\ ◁{}_{h}\ ]$.

We note that an h-bond now joins the black squares. The final form, like the first two, represents a simple truncation of series, but applied without first invoking the logarithmic reduction. It too is not exact for hard spheres.

(V) $V\mathscr{A}(\rho_1,\rho_2) = V\mathscr{A}_{pure}(\rho_1) + \rho_2\ (●━■\ +\ ◁{}_{h}\ )$.   (3.19)

C. Test of theories

We tested our approximations for the 1-1/2 fluid using the Lennard-Jones model, with properties evaluated by Monte Carlo simulation in the canonical ensemble. For systems at infinite dilution, the only quantity of interest is the chemical potential of the point-particle solute. To evaluate it, we conducted simulations of the pure Lennard-Jones fluids, and performed test-particle insertions of point particles; averaging over solvent configurations and test insertions yields the chemical potential in the usual manner.[16,17] Figure 4 shows the residual chemical potentials of point particles as a function of the solvent reduced density. Also presented in the plot are results from application of the various approximations to the hard-sphere model; this we examine to ensure
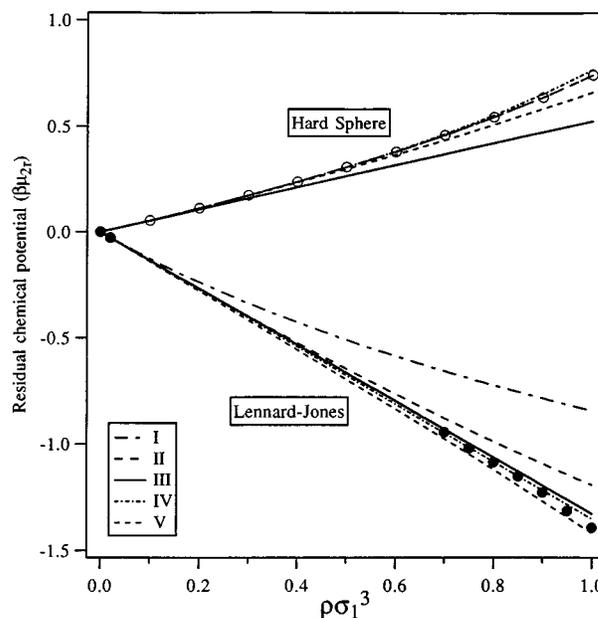

FIG. 4. Application of the various approximations discussed in the text. Plotted is the residual chemical potential of a point particle at infinite dilution. The upper curves describe a hard point particle in a hard sphere solvent, while the lower describe a Lennard-Jones points in a Lennard-Jones solvent at a temperature $kT/\epsilon_1 = 1.0$. The circles are exact results for hard spheres or, for Lennard-Jones, the results of Monte Carlo simulation.

that our approximations do not destroy the good description of hard spheres that we have been so careful to build into the treatment. Approximations (I) and (II) remain exact for hard spheres, but they do not perform well for the Lennard-Jones model. Approximation (III) works well for Lennard-Jones fluids, but at the expense of a good description of hard spheres. Approximation (IV), while not exact for hard spheres, works well for both model potentials. Approximation (V) performs well, but not as well as (IV). Based on these results, we choose approximation (IV) for further study.

It is likely that the residual chemical potential of the point particles is a weak function of their concentration. Physically, this means that the work of inserting the first point-particle has little effect on the work needed to insert subsequent ones. The reasoning is also supported by our analysis of the ρ_1-expansion of the free energy presented in Sec. III A. There we showed the diagram having two or more ρ_2-circles tended to cancel one another. It is a particularly reasonable expectation given that the point particles do not interact directly. The only way the work of insertion can be changed is through the effect of the point particles on the structure of the solvent, and even then there is only so much they can do while the overall density ρ_1 remains fixed. A very large number of point particles would likely manifest their presence by inciting a phase separation in the system. The possibility of such an effect we reserve for future study. Our interest now is to what extent can we apply the infinite dilution result to describe other mixtures; how far can we stretch the expansion of the free energy to first order in ρ_2?

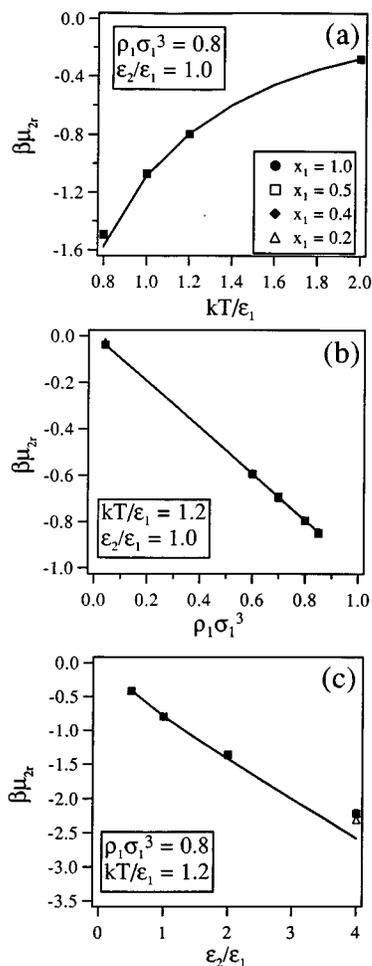We performed Monte Carlo simulations for mixtures to

FIG. 5. Residual chemical potential of Lennard-Jones point particles in Lennard-Jones 1-1/2 fluids; (a) temperature dependence; (b) dependence on number density of full-sized species; (c) dependence on well depth of point particles. Data are shown for four compositions, $x_1 = 1.0$ (point particles at infinite dilution), 0.5, 0.4, and 0.2. Composition dependence is so weak that data for different compositions cannot be distinguished. Line is the proposed theory, using approximation (IV); a single line is shown because the theory predicts no composition dependence.

FIG. 6. Internal energy of Lennard-Jones 1-1/2 fluids. Conditions and symbols are as in Fig. 5.

see if the infinite dilution approximation still provides satisfactory estimation for 1-1/2 fluids with a nonzero concentration of point particles; details of the simulations are presented in the Appendix. Figure 5 examines the residual chemical potential of point particles as a function of temperature, density of full-sized particles (ρ_1), and energy parameter (ϵ_2) (everything is in units of σ_1 and ϵ_1). Data are presented for four compositions; pure species 1 (infinite dilution of species 2), and mole fractions of 0.5, 0.4, and 0.2, respectively, of species 1. Note that systems having same reduced density of full-sized particles (ρ_1), but different mole fractions (x_1), differ in the total density (ρ_1/x_1). In this manner we compare systems that have the same number of full-sized particles in a unit volume, but which differ in the number of point particles present. Figure 5(a) considers the effect of temperature at constant $\rho_1 = 0.8$ (a dense, liquidlike value), and with $\epsilon_2 = \epsilon_1$. Figure 5(b) investigates the effect of solvent density ρ_1. The gap in the data corresponds to the two-phase region of the pure species-1 fluid. The temperature for this
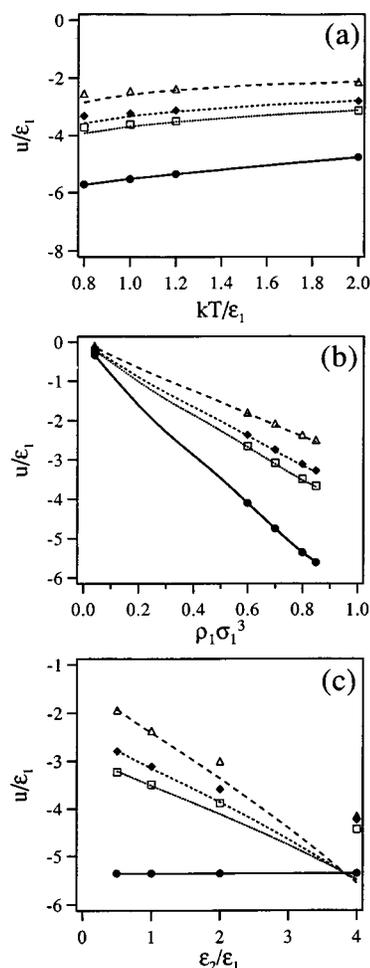
figure is 1.2, and again the energy parameter is that of the solvent. In Fig. 5(c) the effect of the energy parameter is examined. In all figures we find that the infinite-dilution approximation holds, the residual chemical potential of the point-particles is not affected by changes in composition. Moreover, the data are well described by the theory, taken as approximation (IV) above. Breakdown of that approximation is finally observed for large values of the point-particle energy parameter ϵ_2.

In Figs. 6 and 7, we apply approximation (IV) to estimate the energy and the pressure, respectively, and we compare the results to simulation data. Parts (a), (b), and (c) of each figure correspond to the same parts of Fig. 5. Data at infinite dilution, $x_1 = 1$, are again included, although they of course are not affected by ϵ_2 [part (c) of each figure]. The theory again compares well with the data, with a discrepancy arising for large ϵ_2 [consistent with Fig. 5(c)] and, to a lesser extent, at low temperature.

IV. CONCLUDING REMARKS

We have demonstrated that a good description of the 1-1/2 fluid can be obtained from knowledge of the pure fluid obtained upon removal of all the point particles. The most
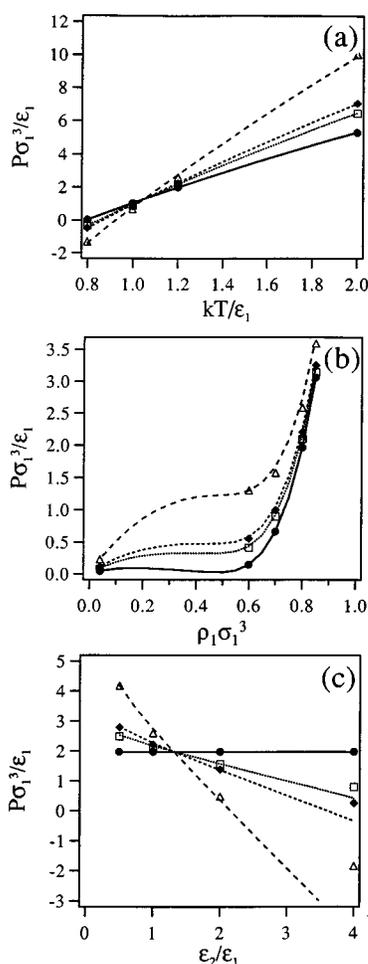
FIG. 7. Pressure of Lennard-Jones 1-1/2 fluids. Conditions and symbols are as in Fig. 5.

effective formulation of the theory requires knowledge of the pair structure of the reference, in addition to its thermodynamic properties. The limit of infinite dilution of the point particles seems sufficient for a description of the 1-1/2 fluid at much higher concentrations of the point particles, i.e., a form of Henry's law applies broadly. The good news from this result is that we can describe a wide range of 1-1/2 fluids; the bad news *might* be that the value of the 1-1/2 fluid as a useful and robust reference for other mixtures is diminished. If the point particles have little influence on the structure of the full-sized ones, there may be little gain in considering a 1-1/2 fluid over a simple pure fluid as a reference for a theory. This outcome can be concluded only by development and application of theories based on a 1-1/2 fluid reference, and subsequent comparison to more traditional conformal-solution treatments.

ACKNOWLEDGMENTS

APPENDIX

Standard Monte Carlo simulations[16] in canonical ensemble (N, V, T) were performed to measure the properties of various 1-1/2 fluids. Most simulations sampled 20 000 cycles, after an initial relaxation phase lasting 10 000 cycles; a cycle here represents one attempted translation per particle. The total number of full-sized and point particles was in most cases 500, the exception being simulations at $x_1 = 0.2$, where 864 particles were used (to ensure a sufficient number of full-size particles). Simulations were speeded substantially by the fact that the point particles do not interact with each other.

[1] The literature on this topic is vast. Some reviews or representative works include, T. W. Leland and P. S. Chappelear, Ind. Eng. Chem. **60**, 15 (1968); L. Stiel, Chem. Eng. Sci. **27**, 2109 (1972); M. R. Moldover and J. S. Gallagher, AIChE J. **24**, 267 (1978); A. J. Gunning and J. S. Rowlinson, Chem. Eng. Sci. **28**, 521 (1973); K. P. Shukla, M. Luckas, H. Marquardt, and K. Lucas, Fluid Phase Equil. **26**, 129 (1986); J. R. Fox and T. S. Storvick, Int. J. Thermophys. **11**, 49 (1990); M. L. Huber and J. F. Ely, *ibid*. **11**, 87 (1990); G. Ihm, Y. Song, and E. A. Mason, J. Chem. Phys. **94**, 3839 (1991); see also Refs. 2–5, 8, and 9.

[2] T. W. Leland, J. S. Rowlinson, and G. A. Sather, Trans. Faraday Soc. **64**, 1447 (1968).

[3] J. S. Rowlinson and F. L. Swinton, *Liquids and Liquid Mixtures*, 3rd ed. (Butterworth, London, 1982).

[4] K. S. Shing, K. E. Gubbins, and K. Lucas, J. Chem. Phys. **65**, 1235 (1988).

[5] V. I. Harismiadis, N. K. Koutras, D. P. Tassios, and A. Z. Panagiotopoulos, Fluid Phase Equil. **65**, 1 (1991).

[6] D. A. Kofke and E. D. Glandt, J. Chem. Phys. **90**, 439 (1989).

[7] D. A. Kofke, J. Chem. Phys. **95**, 7518 (1991).

[8] L. I. Stiel, Ind. Eng. Chem. **60**, 50 (1968).

[9] G. C. Maitland, R. Rigby, E. B. Smith, and W. A. Wakeham, *Intermolecular Forces: Their Origin and Determination* (Clarendon, Oxford, 1981).

[10] H. Reiss, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. **31**, 369 (1959).

[11] T. Morita and K. Hiroike, Prog. Theor. Phys. **25**, 537 (1961).

[12] G. Stell, in *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964), pp. II170–II266; G. Stell, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, London, 1976), Vol. 5B, p. 205.

[13] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, New York, 1986).

[14] H. C. Andersen, in *Statistical Mechanics. Part A: Equilibrium Techniques*, edited by B. J. Berne (Plenum, New York, 1977), Vol. 5, pp. 1–45.

[15] H.-C. Chiu and D. A. Kofke, J. Stat. Phys. **78**, 877 (1995).

[16] M. P. Allen and D. J. Tildesly, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).

[17] D. Frenkel, in *Proceedings of the NATO ASI on Computer Modeling of Fluids, Polymers and Solids*, edited by C. R. A. Catlow (Kluwer Academic, New York, 1989), pp. 83–123.

[18] G. A. Mansoori, N. F. Carnahan, K. E. Starling, and T. W. Leland, Jr., J. Chem. Phys. **54**, 1523 (1971).

[19] A. Lofti and J. Fischer, Mol. Phys. **66**, 199 (1989).