

Behavior of a Nonconformal Mixture via Computer Simulation

H. J. M. Hanley^{1,2} and D. J. Evans^{1,3}

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A binary 50% mixture of soft spheres is studied via nonequilibrium molecular dynamics, and the equilibrium and nonequilibrium radial distribution functions for a nonconformal mixture with a mass ratio of 10 and a size ratio of about 2 are examined. This model system is related to the real methane/decane mixture, and it is shown that apparently anomalous properties of this mixture, especially the viscosity, could perhaps be understood in terms of the local or ambient mole fraction. In addition, the postulates of the Van der Waals one fluid conformal solution theory are discussed, and a mixing rule for the mass is derived.

KEY WORDS: conformal solution theory; local mole fraction; nonequilibrium molecular dynamics; radial distribution functions; soft spheres; Van der Waals one fluid theory.

1. INTRODUCTION

Few tools or techniques have contributed more to fluid theory than computer simulation. A model fluid can be constructed that leads to an unambiguous examination of fluid structure and an unambiguous test of theory, the results of which can then stimulate and guide further progress. Further, it is well known that many features of the real fluid can be represented qualitatively by simple approximations: an example is given in this paper by reporting computer simulation results for a binary mixture whose components differ in size and/or mass. The results are of interest in themselves, but are also used to test a corresponding states procedure we have proposed previously to calculate the viscosity of mixtures.

¹Thermophysical Properties Division, National Bureau of Standards, Boulder, Colorado 80303, USA.

²Department of Chemical Engineering, University of Colorado, Boulder, Colorado 80309, USA.

³Ion Diffusion Unit, Australian National University, Canberra, Australia.

The paper is organized as follows: first, the corresponding states procedure, which is based on the Van der Waals one fluid concept (VdW1), is reviewed briefly and the basic assumptions noted. It is pointed out that experience has shown that the properties of mixtures with molecules of substantially different size and mass are often reproduced poorly by this method and by others. For this reason, we next discuss the simulation of a mixture of this type, namely a 50/50 mixture of methane (C1) and decane (C10), by considering a mixture of soft spheres in which one species has approximately twice the radius and 10 times the mass of the other. Despite this obvious gross simplification, it is shown that the simulation can give insight into the real system by examining the radial distribution function in equilibrium and in *nonequilibrium* when the system is subjected to a steady shear. Specific results reported include a test of the Van der Waals theory and a calculation of the local number density, or mole fraction, in the simulated C1/C10-like mixture.

2. CORRESPONDING STATES FOR VISCOSITY

The basic postulate of the one fluid model is that the properties of a mixture at a pressure (p) [or density (ρ)], temperature (T), and mole fraction x_i ($i = 1, n$, where n is the number of components), can be equated to those of a hypothetical pure substance. For example [1], for the viscosity (η), one has

$$\eta_{\text{mix}}(\rho, T, x_i) = \eta_x(\rho, T) \quad (1)$$

Then, using corresponding states, one writes

$$\eta_x(\rho, T) = \eta_0 \left[\rho'_0, T'_0 \right] \left(\frac{\sigma_0}{\sigma_x} \right)^2 \left(\frac{\epsilon_x}{\epsilon_0} \right)^{1/2} \left(\frac{M_x}{M_0} \right)^{1/2} \quad (2)$$

where the subscript 0 refers to a reference substance, σ and ϵ are the characteristic length and energy parameters of the pair intermolecular potential (ϕ), and M is the molecular weight. The value η_x can thus be calculated from Eq. (2) given values of η_0 as a function of ρ_0 and T_0 ; the prime indicates that η_0 is to be evaluated at conditions equivalent to ρ and T :

$$\rho'_0 = \rho \left(\frac{\sigma_x}{\sigma_0} \right)^3 : T'_0 = T \left(\frac{\epsilon_0}{\epsilon_x} \right) \quad (3)$$

Convenient mixing rules for σ_x and ϵ_x are the one fluid Van der Waals rules, which are

$$\epsilon_x \sigma_x^3 = \sum_{ij} x_i x_j \epsilon_{ij} \sigma_{ij}^3 \quad (4)$$

$$\sigma_x^3 = \sum_{ij} x_i x_j \sigma_{ij}^3 \quad (5)$$

The equations are standard and have been discussed by several authors. However, the derivation of Henderson and Leonard [2] does point out the specific assumptions of the VdWl theory. The procedure is briefly as follows. The potential contribution to the energy of a pure fluid, E_ϕ , is written in terms of the radial distribution function and the pair potential:

$$E_\phi = 2\pi N\rho \int \phi(r) g(r) r^2 dr \quad (6)$$

and for a mixture

$$E_\phi = 2\pi N\rho \sum_{ij} x_i x_j \int \phi_{ij}(r) g_{ij}(r) r^2 dr \quad (6a)$$

where $g(r)$ is the radial distribution function dependent on the intermolecular separation, r ; ρ is the number density, i.e., $\rho = N/V$ with N the number of particles and V the volume. If, as is assumed in Eqs. (1) and (2), all species in a mixture obey the same force law $\phi = \epsilon f(r/\sigma)$, i.e., that $f(r/\sigma)$ is a universal function of r scaled appropriately, and the radial distribution functions scale as

$$g_{11}(r/\sigma_{11}) = g_{12}(r/\sigma_{12}) = g_{22}(r/\sigma_{22}) \dots \quad (7)$$

then Eq. (6a) can be written

$$E_\phi = 2\pi N\rho \sum_{ij} x_i x_j \epsilon_{ij} \sigma_{ij}^3 \int \phi^*(r_{ij}^*) g(r_{ij}^*) r_{ij}^{*2} dr_{ij}^* \quad (8)$$

where $\phi^* = \phi/\epsilon$ and $r^* = r/\sigma$. One then compares Eq. (8) with Eq. (6) written in a similar reduced form and states that the mixture behaves as a hypothetical pure fluid with parameters σ_x and ϵ_x defined by Eq. (4).

2.1. Mixing Rule for the Mass

Equation (2) requires a mixing rule for the mass, and such a rule follows quite easily if the scaling of the radial distribution in nonequilibrium is considered by an approach analogous to that of Henderson and Leonard above [3, 4].

The pressure tensor \mathbf{P} in the fluid is given formally by [4, 5]:

$$\mathbf{P} = \frac{1}{V} \left\{ \sum_i m_i [\mathbf{v}_i - \mathbf{u}(\mathbf{r}_i)][\mathbf{v}_i - \mathbf{u}(\mathbf{r}_i)] + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \mathbf{R}_{ij} \frac{\partial \phi_{ij}}{\partial \mathbf{r}_i} \right\} \quad (9)$$

where \mathbf{v}_i is the velocity of particle i , $\mathbf{u}(\mathbf{r}_i)$ is the streaming velocity at \mathbf{r}_i , $\mathbf{R}_{ij} = (\mathbf{r}_j - \mathbf{r}_i)$, and m_i is the mass of i . The summation is for all particles of all species in a mixture with the masses assigned appropriately.

The potential contribution \mathbf{P}_ϕ can be expressed by the equation of Irving and Kirkwood [6] in terms of the radial distribution function in nonequilibrium $g(\mathbf{r}; \gamma)$; in our case, for a shear or strain rate, γ ; thus

$$\mathbf{P}_\phi = - \frac{1}{2} \rho^2 \int \mathbf{r} \mathbf{r} \cdot \frac{1}{r} \frac{d\phi}{dr} g(\mathbf{r}; \gamma) d\mathbf{r} \quad (10)$$

In our work, we simulate Couette flow, for which the constitutive relation is

$$\dot{\mathbf{P}}_{xy}^s = - 2\eta \dot{\gamma}_{xy}^s \quad (11)$$

where $\dot{\mathbf{P}}_{xy}^s$ is the symmetric traceless contribution to \mathbf{P} and

$$\dot{\gamma}_{xy}^s = \frac{1}{2} [du_x/dy + du_y/dx] - \frac{1}{3} \text{div } \mathbf{u}.$$

A comparison between Eqs. (10) and (11) will give an expression for the potential contribution to the viscosity, η_ϕ , in terms of the radial distribution function. A convenient *but incorrect* next step is to follow H. S. Green [7] and expand the function $g(\mathbf{r}; \dot{\gamma}^s)$ in a Taylor series about $\dot{\gamma}^s$. For a pure fluid, therefore, one has then

$$g(\mathbf{r}; \dot{\gamma}^s) = g_0(r) + \nu(r) \mathbf{T} : \dot{\gamma}^s + \dots \quad (12)$$

where $g_0(r)$ is the equilibrium radial distribution function, and $\nu(r)$ is a scalar function of r with units of time; \mathbf{T} is a tensor given by

$$\mathbf{T} = [\mathbf{r} \mathbf{r} - \frac{1}{3} r^2 \mathbf{l}] / r^2 \quad (13)$$

where \mathbf{l} is the unit tensor.

Substitution of Eq. (12) into Eq. (10) gives, via Eq. (11):

$$\eta_\phi = \frac{2\pi}{15} \rho^2 \int r^3 \frac{d\phi}{dr} \nu(r) dr \quad (14)$$

and a similar derivation leads to the viscosity equation for a mixture:

$$\eta_\phi = \frac{2\pi}{15} \rho^2 \sum_{ij} x_i x_j \int r^3 \frac{d\phi_{ij}}{dr} \nu_{ij}(r) dr \quad (15)$$

It should be pointed out that the reason why the expansion (12) does not appear to be correct is that g is a nonanalytic function of γ , so the quadratic and higher-order terms in (12) diverge [8]. Nevertheless, Evans has derived Eq. (14), which involves only the term in $\nu(r)$ using a spherical harmonic expansion [9].

The Van der Waals idea is to assume that the terms ν_{ij} of Eq. (15) scale or conform as does $g_0(r)$ so that

$$\eta_\phi = \frac{2\pi}{15} \rho^2 \sum_{ij} x_i x_j \sigma_{ij}^4 \sqrt{\epsilon_{ij} M_{ij}} \int r^{*3} \frac{d\phi^*}{dr^*} \nu^*(r^*) dr^* \quad (16)$$

By comparing this equation with the corresponding expression for a pure substance one has a mixing rule,

$$\sigma_x^4 \sqrt{\epsilon_x M_x} = \sum_{ij} x_i x_j \sigma_{ij}^4 \sqrt{\epsilon_{ij} M_{ij}} \quad (17)$$

A choice for the mass M_{ij} would be $M_{ij} = 2m_i m_j / (m_i + m_j)$. Rule (17) with Eqs. (7) and (8) form, therefore, a set for the VdWl theory of viscosity.

2.2. Generalization of the VdWl Theory

The application of the VdWl theory has been considerably broadened [1] by the introduction of shape factors θ and ϕ' , which allows one to work with fluids that do not obey corresponding states, while keeping the format of VdWl equations. The mixing rules are then redefined in terms of the ratios $f_{ii,0}$ and $h_{ii,0}$ using that the critical temperature $T^c \sim \epsilon$ and the critical density $\rho^c \sim \sigma^{-3}$:

$$f_{ii,0} = (T_{ii}^c / T_0^c) \theta_{ii,0} : h_{ii,0} = (\rho_0^c / \rho_{ii}^c) \phi'_{ii,0} \quad (18)$$

and

$$h_{x,0} = \sum_{ij} x_i x_j h_{ij,0} \quad (19)$$

$$f_{x,0} h_{x,0} = \sum_{ij} x_i x_j f_{ij,0} h_{ij,0}$$

$$h_{x,0}^{4/3} \sqrt{f_{x,0} M_x} = \sum_{ij} x_i x_j h_{ij,0}^{4/3} \sqrt{f_{ij,0} M_{ij}} \quad (20)$$

where f and h for species i and for the cross interactions (ij) are to be evaluated with respect to values of a known or reference system, subscript 0: see Eq. (3). The shape factors θ and ϕ' are in principle functions of density and temperature to force species i to be conformal with the reference 0. However, it is usually preferable to consider equations for them in terms of a third parameter such as the Pitzer acentric factor and hence retain a predictive capability.

The cross interactions of Eq. (20) are given by the combining rules

$$\begin{aligned} f_{ij,0} &= \xi_{ij} (f_{ii,0} f_{jj,0})^{1/2} \\ h_{ij,0} &= \psi_{ij} (\frac{1}{2} h_{ii,0}^{1/3} + \frac{1}{2} h_{jj,0}^{1/3})^3 \end{aligned} \quad (21)$$

where ξ_{ij} and ψ_{ij} are parameters that can often be set to unity.

The viscosity equation (2) in this extended VdWl treatment becomes [1]

$$\eta_x(\rho, T) = \eta_0 [\rho h_{x,0}, T/f_{x,0}] (M_x/M_0)^{1/2} h_{x,0}^{-2/3} f_{x,0}^{1/2} \quad (22)$$

2.3. VdWl and the Soft Sphere

A mixture of soft spheres will be discussed in Section 4, and for soft spheres the VdWl expression becomes as follows. Consider a binary mixture of soft spheres with mass m and αm , respectively, in which all interactions follow the intermolecular potential law

$$\phi(r) = d/r^{12} \quad (23)$$

In terms of the usual σ and ϵ parameters, Eq. (23) is

$$\phi(r) = \epsilon (\sigma/r)^{12} \quad (23a)$$

although it should be noted that the intermolecular interaction is characterized by only the one parameter d . If the particles are designated 1 and 2,

respectively, the like and cross interactions can be written in terms of the 1 – 1 interaction, d_{11} , and the potential parameters β and δ :

$$\phi_{11} = d_{11}/r^{12}, \quad \phi_{12} = \beta d_{11}/r^2, \quad \phi_{22} = \delta d_{11}/r^{12} \quad (24)$$

Note that these potentials ensure that the components of the mixture obey corresponding states, since $\phi = \epsilon f(r/\sigma)$.

Since the temperature and density cannot be distinguished in a soft sphere system, we introduce a state parameter X :

$$X = \left(\frac{N}{2V} \right) (d/kT)^{1/4} \quad (25)$$

or, replacing d by $\epsilon\sigma^{12}$ as in Eq. (23a),

$$X = \rho^* / \sqrt{2} T^{*1/4} \quad (25a)$$

where $\rho^* = (N/V)\sigma^3$ and $T^* = Tk/\epsilon$, with k as Boltzmann's constant.

The mixing rules for the system are simple; Eqs. (4) and (5) become

$$d_x^{1/4} = \sum_{ij} x_i x_j d_{ij}^{1/4} \quad (26)$$

and Eq. (16) is

$$d_x^{1/3} \sqrt{M_x} = \sum_{ij} x_i x_j d_{ij}^{1/3} \sqrt{M_{ij}} \quad (27)$$

In the special case of a binary 50/50 mixture, Eqs. (26) and (27) are

$$d_x^{1/4} = \frac{d_{11}^{1/4}}{4} [1 + 2\beta^{1/4} + \gamma^{1/4}] \quad (28)$$

and

$$d_x^{1/3} \sqrt{M_x} = \frac{d_{11}}{4} [1 + 2\beta^{1/3} \sqrt{2\alpha/(1+\alpha)} + \delta^{1/3} \sqrt{\alpha}] \quad (29)$$

2.3.1. Viscosity

The VdWl viscosity of a soft sphere mixture at state point X follows from Eq. (2):

$$\eta_x(X) = \eta_0 \left[X \left(\frac{d_x}{d_0} \right)^{1/4} \right] \left(\frac{d_0}{d_x} \right)^{1/6} \left(\frac{M_x}{M_0} \right)^{1/2} \quad (30)$$

where the reference viscosity η_0 is to be evaluated at state point $X(d_x/d_0)^{1/4}$. Now, if the reference system is chosen to be the soft sphere interacting with potential $\phi = d_{11}/r^{12}$, Eq. (30) becomes

$$\eta_x(X) = \eta_0 \left[X \frac{(1 + 2\beta^{1/4} + \delta^{1/4})}{4} \right] [\alpha] \quad (31)$$

where

$$[\alpha] = 4 \frac{(1 + 2\beta^{1/3} \sqrt{2\alpha/(1 + \alpha)} + \delta^{1/3} \sqrt{\alpha})}{(1 + 2\beta^{1/4} + \delta^{1/4})^2} \quad (32)$$

3. RESULTS FOR HYDROCARBON MIXTURES

Equation (22) has been used successfully to predict the viscosity of hydrocarbon mixtures [1, 10], and a comparison with viscosity data is indicated by two selected examples in Table I. The agreement shown is, however, only typical provided the components of the mixture are not substantially different in mass, size, or polarity. In particular, the results for a mixture of methane and decane were not always satisfactory. But the viscosity of this mixture behaves in an apparently peculiar manner at high densities, as can be seen by Fig. 1. Shown is a plot of the viscosity [11] at 444 K at a constant reduced density ($\rho^+ = \rho/\rho_x^c$) of 2.3, where ρ_x^c was obtained via Eqs. (18)–(21). The viscosity is constant at the decane value for $X_{c1} \leq 0.9$, and it is obvious by inspection that any corresponding states procedure would have great difficulty predicting it in terms of the mole fraction. The prediction of Eq. (22) is given by the curve.

The results shown actually lead to this investigation because it was most probable that the basic assumptions of the VdWl model were inadequate. Hence it was felt that a computer simulation of a model mixture which approximates that of methane/decane would be instructive. Accordingly, as a first step, a mixture of soft spheres was considered. As remarked in the introduction, while it is appreciated that a soft sphere is a substantial

Table I. Viscosity of Mixtures at Saturation Compared With the VdW1 Equation (22)

| Temp (K) | x_1 | Viscosity (10^6 Pa · s) | | |
|-------------|--|----------------------------|-------|-----|
| | | Expt. | Calc. | |
| 313 | Toluene (1)- <i>n</i> -octane ^a | | | |
| | 0.2634 | 470 | 464 | |
| | 0.8282 | 485 | 507 | |
| | 0.8880 | 498 | 511 | |
| | 368 | 0.2634 | 255 | 273 |
| | | 0.8282 | 266 | 301 |
| 0.8880 | | 270 | 310 | |
| 298 | <i>n</i> -Hexadecane (1)-benzene(2)- <i>n</i> -hexane ^b | | | |
| | 0.5315 | | | |
| | $x_2 = 0.2836$ | 1,497 | 1,477 | |
| | 0.0757 | | | |
| | $x_2 = 0.4724$ | 492 | 487 | |
| | 0.1221 | | | |
| | $x_2 = 0.5406$ | 581 | 588 | |

^aT. D. Ling and M. Van Winkle, *Ind. Eng. Chem.* 3:88 (1958).

^bE. L. Heric and J. G. Brewar, *J. Chem. Eng. Data* 14:55 (1969).

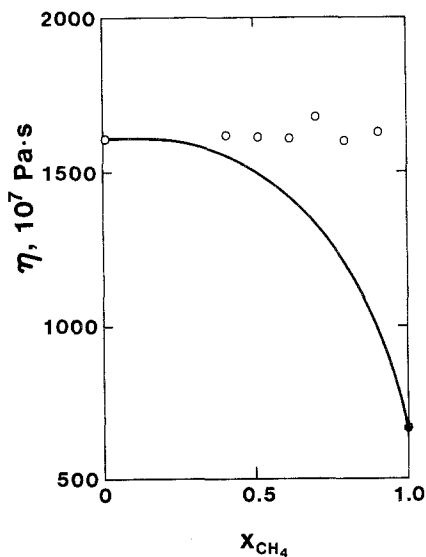


Fig. 1. Plot of the viscosity of methane-decane mixtures at $T = 444$ K at a constant reduced density of 2.3. Data from ref. [11]. This viscosity is constant until $x_{CH_4} \geq 0.9$. The curve is the calculation from Eq. (22).

simplification of a real molecule, one would hope that the qualitative features of a real mixture could be assessed with the model, especially since the transport properties of a fluid are relatively insensitive to the choice of the intermolecular pair potential.

4. COMPUTER SIMULATION

Nonequilibrium molecular dynamics has been applied to a binary soft sphere mixture under constant Couette flow; that is, the system is subjected to a constant strain rate in the $x - y$ plane. Details of the simulation technique have been reported in refs. [4] and [12]; see also ref. [13]. The essential feature of our nonequilibrium molecular dynamics is that the system is examined at equilibrium in the usual way but then is studied in a steady state after an external force, in this case a strain rate, γ , is imposed. Components of the pressure tensor are evaluated from Eq. (9), the potential energy is set to be pairwise additive, the temperature is evaluated from $T = (1/3) \langle \sum_i [v_i - u(\mathbf{r}_i)]^2 \rangle$, and the viscosity can be extracted from Eq. (11), since $\dot{\gamma}_y^z$ is given.

We found it most convenient to work at constant density and temperature: the system was therefore thermostated to compensate for the viscous heating. A discussion on the thermodynamics describing a system with these constraints is given in refs. [8] and [14].

The system consisted of 108 (N) particles with species 1 labeled by an odd particle number and species 2 by an even particle number. Thus $N_1 = N_2 = N/2$ or $x_1 = x_2 = 1/2$. The particles interacted with the potentials of Eq. (24) truncated at 2.5σ . The system was first characterized by setting α for the mass, β and δ for the potentials, and was then studied at a state point X of Eq. (25). In this work, X was equated to ρ^* of Eq. (25a), so the temperature T^* was fixed at 0.25.

4.1. Radial Distribution Functions

The radial distribution functions for the binary mixture were evaluated from the histogram

$$4\pi r^{*2} \Delta r^* \left(\frac{X}{2} \right) g_{ij}(r_{ij}^*) = \langle N_{ij} \rangle_{r^*, \Delta r^*} \quad (33)$$

where $\langle N_{ij} \rangle_{r^*, \Delta r^*}$ is the average number of particles in the shell between r^* and Δr^* of type i around particle j . $g_{ij}(r_{ij}^*)$ is scaled as $r_{ij}^* = r/\sigma_{ij}$.

An attractive feature of the nonequilibrium simulation technique is that the scalar variable $\nu(r)$ can be evaluated by a similar histogram:

$$\frac{8\pi}{15} \gamma^s r^{*2} \Delta r^* \left(\frac{X}{2} \right) \nu(r_{ij}^*) = \langle r_x r_y / r^2 \rangle_{r^*, \Delta r^*} \quad (34)$$

using that the tensor T of Eq. (12) simplifies to $(r_x r_y / r^2)$ for Couette flow. Since $\nu(r_{ij}^*)$ scales with r^* but also has units of time, the dimensionless form is defined by

$$\nu_{ij}^*(r_{ij}^*) = \nu(r_{ij}^*) \left(\frac{\epsilon_{ij}}{m_{ij}} \right)^{1/2} \sigma_{ij}^{-1} \quad (35)$$

or, alternately, by

$$\nu_{ij}^*(r_{ij}^*) = \nu(r_{ij}^*) (d/kT)^{-1/2} (m/kT)^{-1/2} \quad (35a)$$

4.2. Properties in a Mixture

Having $g(r)$ and $\nu(r)$ adds to the scope and flexibility to the treatment of a mixture. For example, the potential part of the pressure for a pure fluid is given by

$$p_\phi = \frac{2\pi}{3} \rho^2 \int g(r) \frac{d\phi}{dr} r^3 dr \quad (36)$$

and for a mixture

$$p_\phi = \sum_{ij} x_i x_j p_\phi(ij) \quad (37)$$

where

$$p_\phi(ij) \sim \int g(r_{ij}) \frac{d\phi_{ij}}{dr_{ij}} r_{ij}^3 dr_{ij}$$

Then with ϕ_{ij} defined and $g(r_{ij})$ calculated in the mixture, one can evaluate Eq. (37). Similarly, for the potential energy per particle (Eq. (6)),

$$\bar{E}_\phi = 2\pi\rho \int g(r) \phi r^2 dr \quad (38)$$

and

$$\bar{E}_\phi = \sum_{ij} x_i x_j \bar{E}_\phi(ij) \quad (39)$$

and for the viscosity from Eqs. (14) and (15),

$$\eta_\phi = \frac{2\pi}{15} \rho^2 \int r^3 \frac{d\phi}{dr} \nu(r) dr \quad (14)$$

and

$$\eta_\phi = \sum_{ij} x_i x_j \eta_\phi(ij) \quad (40)$$

5. SIMULATION OF METHANE-DECANE

Simulations were carried out with the soft sphere mixture setup to approximate the C1/C10 mixture, and the radial distribution functions in particular were obtained. Since $V_{C1}^c/V_{C10}^c \approx 1/6$ and $M_{C1}/M_{C10} \approx 10$ (with V^c the critical volume), we set the potential parameter δd of Eq. (24) to $1296.0d_{11}$ so that $(d_{C1}/d_{C10})^{1/4} = 6$, and we set the mass parameter α to 10. Thus the simulation was run for a 50% mixture whose species had masses m and αm , respectively, with

$$\phi_{11} = d_{11}/r^{12}, \quad \phi_{12} = d_{11}/r^{12}, \quad \phi_{22} = 1296.0 d_{11}/r^{12} \quad (41)$$

The potential parameter β of Eq. (24) was set at 1 which, although obviously a further simplification, is not too significant for model calculations, and one could make a separate study on the combining rules if necessary.

Since results for a pure fluid at $X = 0.6$ are available [4], the mixture study was carried out at the state point $X = 0.26667$ obtained from Eq. (31) using the parameters of Eq. (41). All results are reported for the reduced strain rate of $\omega^* = \omega(d/kT)^{-1/2} (kT/m)^{-1/2} = 0.2$.

5.1. Radial Distribution Functions for a Pure Fluid

Figures 2 and 3 show plots of $g(r)$ and $\nu(r)$ for the pure fluid at $X = 0.6$ [15] and at $X = 0.26667$, respectively, and show as expected that the more dense fluid has the more pronounced structure.

5.2. Results for the Mixture

The results for the simulated methane/decane mixture at $X = 0.26667$ are displayed in Fig. 4, where the label 1-1 refers to the interaction between the species 1. It is clear from the plots that the larger species (2) dominates

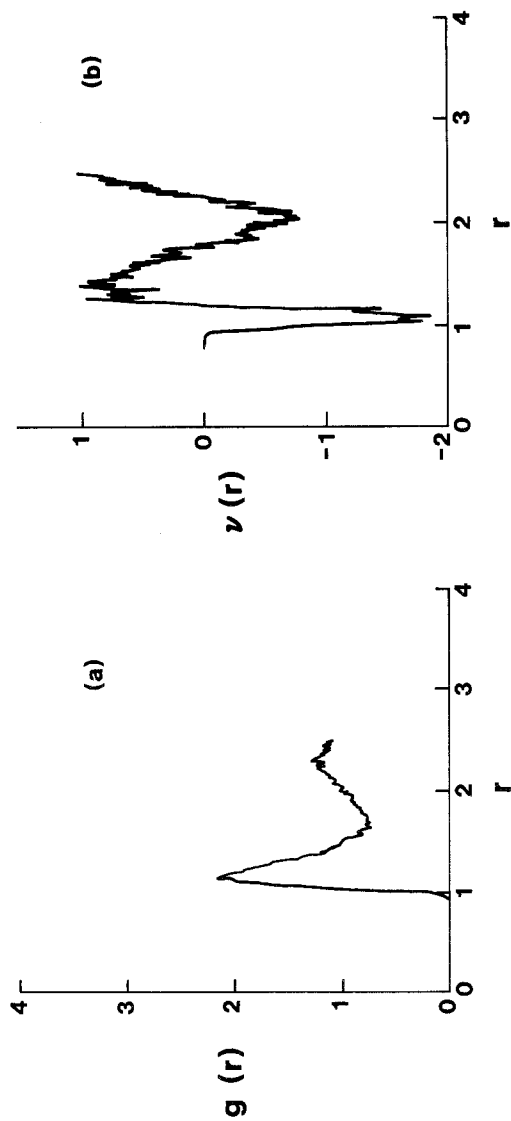


Fig. 2. (a) Plot of $g(r)$ for a soft sphere fluid at $X = 0.6$; (b) plot of $v(r)$.

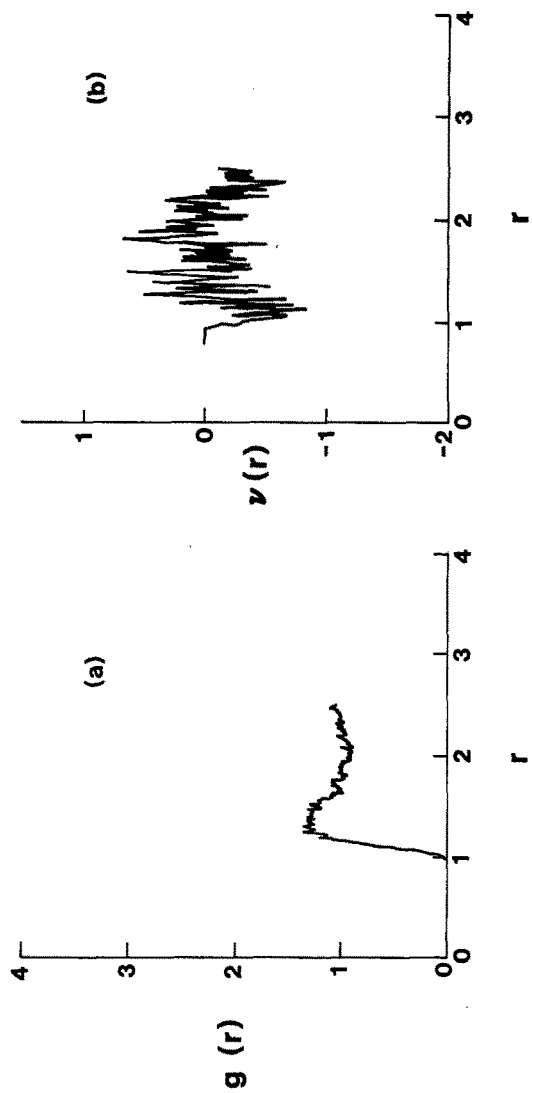


Fig. 3. (a) Plot of $g(r)$ for a soft-sphere fluid at $X = 0.2667$; (b) plot of $v(r)$.

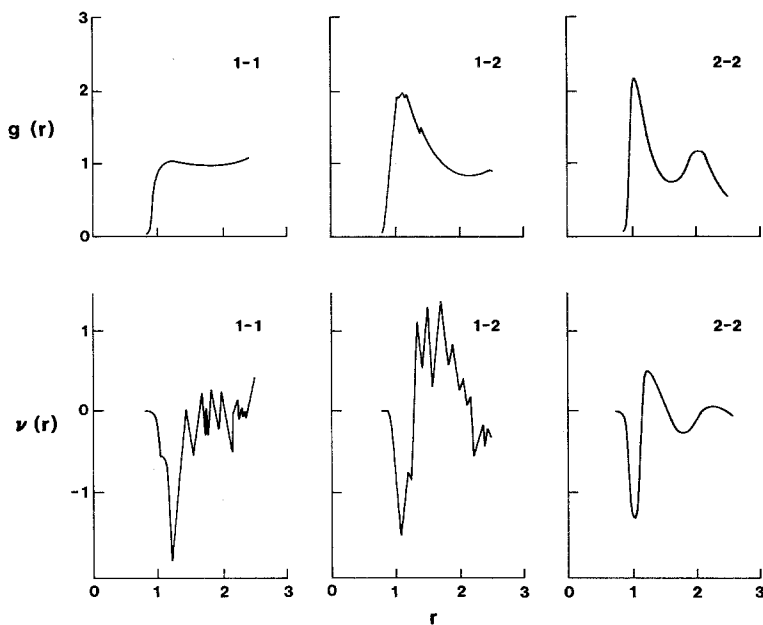


Fig. 4. Upper set: equilibrium radial distribution for an $\alpha = 10$, $\delta = 1296.0$ mixture at $X = 0.2667$; Lower set: plot of the nonequilibrium term $\nu(r)$.

the structure of the liquid, and also that the distribution functions certainly do not conform, either with respect to each other or with respect to the $X = 0.6$ values.

The exaggerated effect of a mass difference is demonstrated by the plots in Fig. 5 [15] for $\nu(r)$ corresponding to a mixture whose components are of the same size ($\beta = \delta = 1$) but with mass difference $\alpha = 100$. The plots for $g(r)$ would be the same as that of Fig. 1.

One can easily calculate the contribution to the properties of the mixture made by each species via equations such as (36)–(40), and in fact we have estimated $p_\phi(ij)$, $E_\phi(ij)$ and $\eta_\phi(ij)$ for the $\delta = 1296.0$, $\alpha = 10$ system by integrating the appropriate distribution function. Shown is the variation of these properties with intermolecular separation for the 1-1 and 2-2- contributions in Fig. 6. The scales are in reduced units and are not important: what is of interest is that the contributions have reached essentially their limiting (macroscopic) values at an intermolecular separation of $r \approx 1.8$.

5.3. Local or Ambient Mole Fraction

To return to the behavior of the real methane/decane mixture: we give a possible explanation of the apparently peculiar behavior of the viscosity shown in Fig. 1 by observing the ambient mole fraction. The concept of local

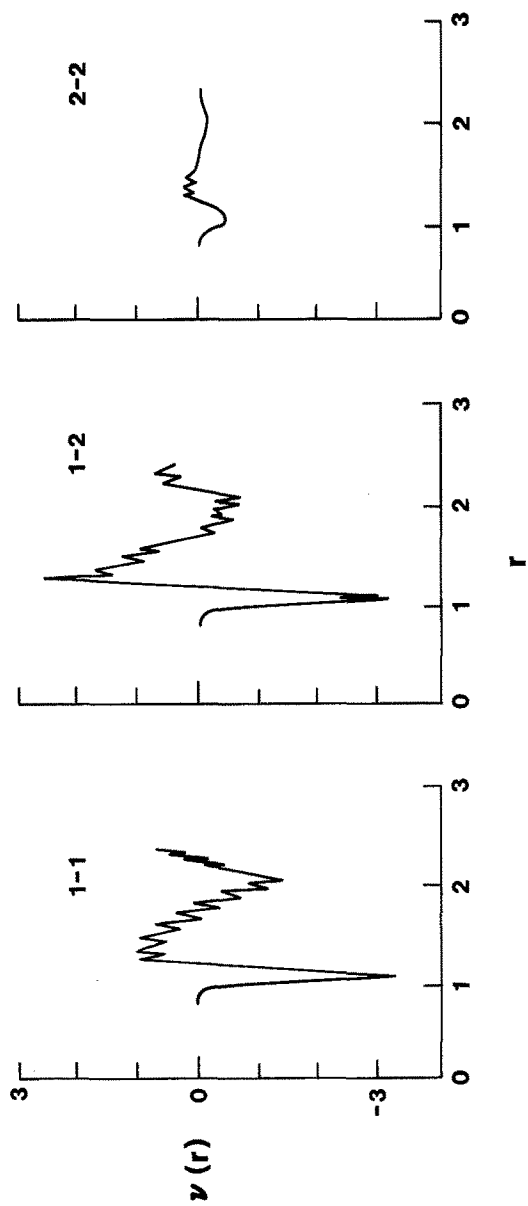


Fig. 5. Values of $\nu(r)$ for a mixture at $X = 0.6$ with $\alpha = 100$.

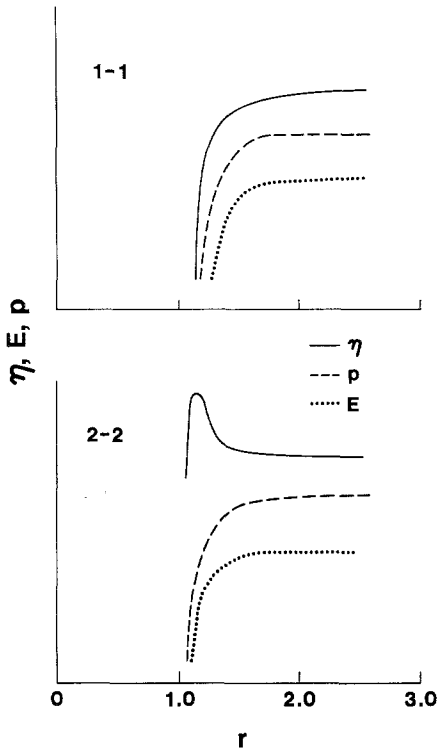


Fig. 6. Contributions of the viscosity (η), energy (E), and pressure (p) as a function of separation for the 1-1 and 2-2 interactions in the binary mixture at $X = 0.2667$ with $\alpha = 10$, $\delta = 1296.0$.

composition in a mixture is familiar, the idea being that in a mixture of diverse components, the local—or ambient—mole fraction may be different from the overall average.

Consider the fraction x_{ij} for the number of particles of type i around a central particle j normalized by all particles around j :

$$x_{ij} = \frac{n_{ij}}{n_{ij} + n_{jj}} \tag{42}$$

For the binary mixture with $N_1 = N_2 = N/2$:

$$n_{ij}(r) = 4\pi(X/2) \int_0^r R^2 g_{ij}(R) dR \tag{43}$$

Given $g_{ij}(r)$, therefore, the mole or (particle) fractions can be evaluated as a

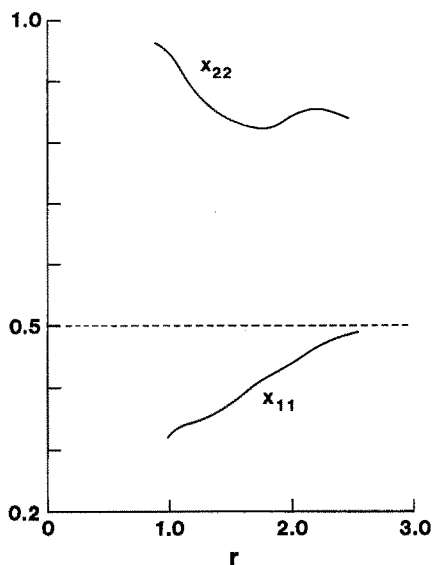


Fig. 7. The ambient mole fractions, Eqs. (42) and (43) for the $\alpha = 10$, $\delta = 1296.0$ mixture for $X = 0.2667$.

function of separation, r , and Fig. 7 illustrates the variation of x_{11} and x_{22} for the particular case of the soft sphere mixture of $\alpha = 10$ and $\delta = 1296.0$. Although $x_1 = x_2 = 0.5$ overall, one sees that $x_{22} \approx 0.85$ and $x_{11} \approx 0.35$ for $r \lesssim 2.0$. Hence, by Fig. 7, the mixture is dominated by the 2-2 interactions.

An appealing if simplistic argument is that for a real C1/C10 system, the ambient mole fraction is the key parameter since the properties of the system are determined by short range behavior. The mixture thus behaves as pure C10 until x_{C1} is close to unity. The behavior of the viscosity in Fig. 1 is consistent with this picture.

6. VdW1 THEORY AND THE SIMULATED MIXTURE

Finally, we report how the VdW1 theory predicts the viscosity (and pressure) of the soft sphere mixture with $\delta = 1296.0$ and $\alpha = 10$. The calculation uses Eq. (30) given from previous work [4] that the reference

Table II. Comparison Between the Viscosity of a Soft Sphere Mixture at $X = 0.26667$ With $\beta = 1$ and $\delta = 1296.0$ and $\alpha = 10$, Calculated by the VdW1 Equation (31) and Direct Simulation. The Hydrostatic Pressure is Included

| | VdW1 | Simulation |
|-----------|------|------------|
| Viscosity | 2.35 | 2.55 |
| Pressure | 0.64 | 0.98 |

viscosity $\eta_0 = 1.24$ at $X(d_x/d_0)^{1/4} = 0.6$. The viscosity $\eta_x(X)$ is therefore estimated from Eq. (31) with $X = 0.26667$ by Eq. (28). Table II gives the result. The agreement with the directly computed results is perhaps surprisingly good, considering the behavior of the distribution functions shown in Figs. 3 and 4.

7. CONCLUSIONS

We have demonstrated how a computer simulation of a model fluid, in our case a mixture of soft spheres, can help one to understand the behavior of a real mixture. The discussion was based on the application of the VdWI corresponding states theory to the viscosity of a mixture of methane and decane, and the computer simulation used the technique of nonequilibrium molecular dynamics. This technique is powerful; for example, we have been able to calculate the properties of a species in a mixture in equilibrium and in nonequilibrium, including the local or ambient mole fraction. We have been able to show quantitatively how the ambient mole fraction differs from the overall or macroscopic value.

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