PHYSICAL REVIEW A VOLUME 38, NUMBER 7 OCTOBER 1, 1988

# Modified Enskog theory for fluid mixtures

J. M. Kincaid and S. Pérez
*Department of Mechanical Engineering, State University of New York at Stony Brook, Stony Brook, New York 11794*

E. G. D. Cohen
*The Rockefeller University, New York, New York 10021*

(Received 25 May 1988)

We show how the modified Enskog theory for single-component fluids may be extended to the case of mixtures. The extended theory uses the Enskog kinetic theory for hard-sphere mixtures and equilibrium virial coefficient data to provide predictions of the transport coefficients of real mixtures. We show that the extended theory provides reasonable predictions of the ratio $\eta/\eta_0$ in the case of He-Ar and Ne-Ar mixtures, where $\eta$ is the shear viscosity and $\eta_0$ is the shear viscosity in the low-density limit.

The modified Enskog theory[1,2] (MET) provides a useful method for predicting the transport coefficients of pure fluids. The method uses the transport-coefficient expressions obtained by solving the Enskog kinetic equation for the hard-sphere fluid. When the hard-sphere diameter $\sigma$ and the radial distribution function at contact $\chi$ that appear in those expressions are replaced by quantities that depend on the real-fluid virial coefficients, one obtains good estimates of the real fluid's transport coefficients. In this paper we show how the MET can be extended to treat the case of multicomponent mixtures.

The MET, and the extension that we describe herein, is an *ad hoc* method in the sense that it has not been derived in any rigorous way from kinetic theory. However, the recent series of papers by Kestin *et al.*,[3] Sandler and Fiszdon,[4] and Di Pippo *et al.*[5] demonstrate that transport coefficients obtained from the Enskog equation have a functional form that is similar to those of real fluids at a fixed temperature; they showed that it is possible to correlate the shear viscosity of simple binary mixtures using the shear viscosity of the Enskog kinetic theory of hard-sphere mixtures. The Enskog shear viscosity $\eta^{\text{HS}}$, of a mixture depends on the hard-sphere diameters $\sigma_{ij}$, and the equilibrium radial distribution functions at contact, $\chi_{ij}$, as well as the molecular masses $m_i$, the temperature $T$, the mole fractions $x_i$, and the number density $n$.[6] (Here subscripts $i$ and $j$ refer to species $i$ and $j$, respectively.) They found that $\eta^{\text{HS}}$ closely matched the experimental shear viscosity data for He-Ne, Ne-Ar, and $H_2$-$CH_4$ mixtures if the $\sigma_{ij}$ and $\chi_{ij}$ were made functions of state such that the $\eta^{\text{HS}}$ exactly fit pure component viscosity data, as well as the dilute gas mixture viscosity data.

Since the values of $\sigma_{ij}$ and $\chi_{ij}$ used in the correlations described above lie within physically realistic ranges, we conclude that the functional form of the transport coefficients of the Enskog theory of hard-sphere mixtures is not too different from that of real systems. For this reason we feel that an extension of the MET to the case of mixtures might prove to be as useful as the MET has been for pure fluids. Our initial application of the extended theory at a fixed temperature, which we give here, is consistent with this expectation.

Our extension of the MET is not the first attempt to predict the shear viscosity of dense fluid mixtures. The very successful TRAPP program of Ely and Hanley[7] has been used for hydrocarbon mixtures. The TRAPP program is based on a one-fluid correlation of equilibrium properties and the one-component Enskog theory. Wakeham *et al.*[8] have used the Enskog theory of mixtures to predict the shear viscosity for several moderately dense binary mixtures by setting the $\chi_{ij}=1$ and determining the remaining parameters from dilute gas viscosity measurements. Although each of these methods has been quite successful, each has limitations that the extended MET avoids. The TRAPP program cannot be used to calculate mutual and thermal diffusion coefficients, and the method of Wakeham *et al.* is limited to low densities by setting $\chi_{ij}=1$. A third approach, the mean-field kinetic theory of Karkheck *et al.*,[9] has been used by Castillo *et al.*[10] to calculate the shear viscosity of Ne-Ar mixtures. These calculations are the only attempt we know of to calculate the shear viscosity without using much experimental data. Although their results are encouraging, the method does not (presently) work well at low densities.

The method developed in this paper is a direct extension to mixtures of the MET used by Hanley, McCarty, and Cohen[1] for one-component systems. The extended MET may be used to predict coefficients of viscosity, bulk viscosity, thermal conductivity, diffusion, and thermal diffusion. Using the extended MET, we show that it is possible to predict the shear viscosity ratio $\eta/\eta_0$ of He-Ar and Ne-Ar mixtures to within a few percent, where $\eta_0$ is the dilute gas shear viscosity. Only equilibrium virial coefficient data are needed to make these predictions. We view our results as providing further confirmation that the transport coefficients of the Enskog theory are closely related to those of simple real fluids, and that it may be possible to devise a predictive theory of transport coefficients of fluid mixtures that does not require extensive transport-coefficient data.

We begin a detailed description of our results in Sec. I by introducing the MET for single-component fluids and its extension to multicomponent mixtures. Implementation of the MET requires knowledge of the virial coefficients of the mixture, as well as their temperature derivatives. In Sec. II we show how we obtained these quantities for He-Ar and Ne-Ar mixtures. Finally, in Sec. III we combine the experimental information with the MET equations, showing how the generalized MET predictions compare with the experimental data of Iwasaki and Kestin[11] and Kestin *et al.*[3] We conclude that the MET can produce useful predictions of the shear viscosity of these simple mixtures.

## I. MODIFIED ENSKOG THEORY

The MET, as first suggested by Enskog, provides an *ad hoc* method for determining the transport coefficients of simple, dense fluids. Since there is, at present, no fully developed kinetic theory of such systems, the MET has been used often as the only available substitute.[1,2]

Enskog was probably one of the first to recognize that at fixed temperature the hard-sphere fluid was not radically different from real fluids, exhibiting much the same local structure as real fluids. By taking advantage of the simple dynamics of hard-sphere systems he was able to improve upon the Boltzmann equation in ways that extended the usefulness of that equation to moderate and even higher densities. He showed, by solving the Enskog kinetic equation, that the transport coefficients of a dense fluid of hard spheres depend on the corresponding dilute-gas transport coefficients (obtained by solving the Boltzmann equation) as well as on $B^{\mathrm{HS}}$ and $\chi^{\mathrm{HS}}$. Here $B^{\mathrm{HS}}$ is the hard-sphere second virial coefficient and $\chi^{\mathrm{HS}}$ is the hard-sphere radial distribution function for a particle separation of $\sigma$, where $\sigma$ is the hard-sphere diameter. For instance, the first Enskog approximation to the shear viscosity $\eta^{\mathrm{HS}}$ may be written

$$\eta^{\mathrm{HS}}/\eta_0^{\mathrm{HS}} = nB^{\mathrm{HS}}\left[\frac{1}{nB^{\mathrm{HS}}\chi^{\mathrm{HS}}} + \frac{4}{5} + 4\left[1+\frac{12}{\pi}\right] nB^{\mathrm{HS}}\chi^{\mathrm{HS}}/25\right], \qquad (1)$$

where $n$ is the number density and $\eta_0^{\mathrm{HS}}$ is the (Boltzmann) dilute-gas shear viscosity.[12]

Enskog's MET is based on the assumption that the transport coefficient of a simple real fluid will have the same functional form as the hard-sphere transport coefficient. In the case of the shear viscosity, an estimate for $\eta^r$ (we use a superscript $r$ to denote properties of the real fluid) is obtained by using the analytically obtained solution of the Enskog equation, replacing $\eta^{\mathrm{HS}}$ by $\eta^r$, $\eta_0^{\mathrm{HS}}$ by $\eta_0^r$ (the dilute-gas shear viscosity), and $B^{\mathrm{HS}}$ and $\chi^{\mathrm{HS}}$ by the corresponding real-fluid properties obtained from equilibrium experimental data. Since $B^{\mathrm{HS}}$ is proportional to $\sigma^3$, this makes $\sigma$ depend on $T$. An obvious way to make that correspondence is to force agreement at low densities and thus replace $B^{\mathrm{HS}}$ by $B^r$ and $nB^{\mathrm{HS}}\chi^{\mathrm{HS}}$ by $[p/(nk_BT)-1]^r$, but this is not very satisfactory because then $nB^{\mathrm{HS}}\chi^{\mathrm{HS}}=[p/(nk_BT)-1]^{\mathrm{HS}}$ is independent of the temperature [see Fig. 1(a)], so that at temperatures for which $B^r$ is negative, this requires that $\chi^{\mathrm{HS}}$ be replaced

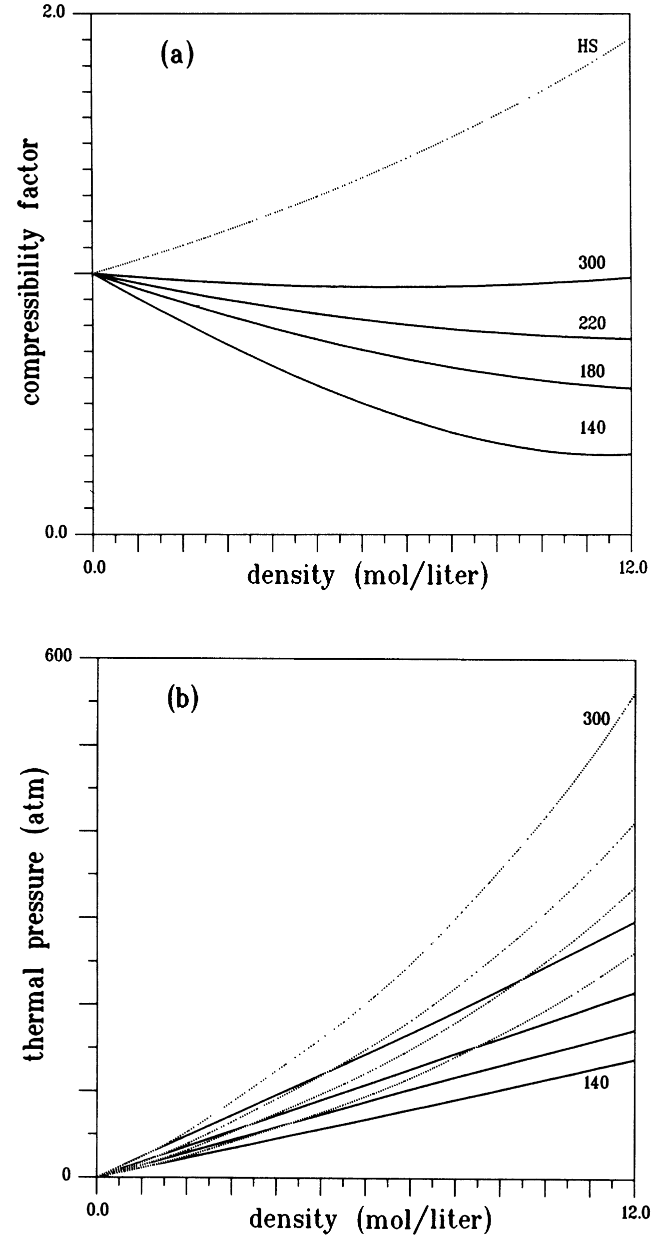

FIG. 1. (a) Compressibility factor $pV/(Nk_BT)$ vs density for Ar and the hard-sphere fluid (HS). The curves for Ar (solid curves) are labeled by the temperature in degrees Kelvin. The hard-sphere compressibility factor (dotted curve) uses a hard-sphere diameter of 3.41 Å. (b) The thermal pressure $T(\partial p/\partial T)_{V,N}$ for Ar (solid curves) and hard spheres (dotted curves) vs density for four temperatures ($T=140$, 180, 220, and 300 K). For both Ar and hard spheres at a given density, the thermal pressure decreases as $T$ decreases. The hard-sphere diameter was taken to be 3.41 Å.

by a negative number. (Here $p$ is the pressure, $k_B$ is Boltzmann's constant, and $T$ is the temperature.)

Instead, Enskog determined replacements for $B^{\mathrm{HS}}$ and $\chi^{\mathrm{HS}}$ by requiring that the "thermal pressure" $T(\partial p/\partial T)_{V,N}$ of the real fluid equal that of the hard-sphere fluid:

$$T\left(\frac{\partial p}{\partial T}\right)_{V,N}^{r}=T\left(\frac{\partial p}{\partial T}\right)_{V,N}^{\mathrm{HS}} . \tag{2}$$

As shown in Fig. 1(b), the thermal pressures of Ar and the hard-sphere fluid are much more similar than the compressibility factors. Since the thermal pressure is positive for most fluids[13] the hard-sphere thermal pressure $[=k_BT(n+n^2B^{\mathrm{HS}}\chi^{\mathrm{HS}})]$ can be forced to match the thermal pressure of the real system at low densities by changing $B^{\mathrm{HS}}$ slightly and at high densities by adjusting the magnitude of $\chi^{\mathrm{HS}}$—*without changing its sign.*

Since

$$p^r=k_BT[n+B^r(T)n^2+C^r(T)n^3+D^r(T)n^4+\cdots] ,$$

where $B^r(T)$, $C^r(T),\ldots,$ are the second, third, etc., virial coefficients of the real fluid, respectively, and $p^{\mathrm{HS}}=k_BT(n+n^2B^{\mathrm{HS}}\chi^{\mathrm{HS}})$, Eq. (2) requires that

$$\left[B^r+T\frac{dB^r}{dT}\right]n^2+\left[C^r+T\frac{dC^r}{dT}\right]n^3+\cdots=n^2B^{\mathrm{HS}}\chi^{\mathrm{HS}} . \tag{3}$$

For the hard-sphere fluid,

$$B^{\mathrm{HS}}\chi^{\mathrm{HS}}=B^{\mathrm{HS}}+C^{\mathrm{HS}}n+D^{\mathrm{HS}}n^2+\cdots , \tag{4}$$

and thus substituting Eq. (4) into Eq. (3), we obtain

$$\left[B^r+T\frac{dB^r}{dT}\right]n^2+\left[C^r+T\frac{dC^r}{dT}\right]n^3+\cdots=B^{\mathrm{HS}}n^2+C^{\mathrm{HS}}n^3+\cdots . \tag{5}$$

Therefore, Enskog's requirement, Eq. (2), leads to

$$\begin{aligned}B^{\mathrm{HS}}&=B^r+T\frac{dB^r}{dT} ,\\ C^{\mathrm{HS}}&=C^r+T\frac{dC^r}{dT} ,\\ &\vdots\end{aligned} \tag{6}$$

which, using Eq. (3), implies

$$B^{\mathrm{HS}}\chi^{\mathrm{HS}}=\left[B^r+T\frac{dB^r}{dT}\right]+\left[C^r+T\frac{dC^r}{dT}\right]n+\cdots . \tag{7}$$

In the first Enskog approximation, the MET expression for the shear viscosity is, therefore,

$$\eta^r/\eta_0^r=n\left[B^r+T\frac{dB^r}{dT}\right]\left\{\left[\left[B^r+T\frac{dB^r}{dT}\right]n+\left[C^r+T\frac{dC^r}{dT}\right]n^2+\cdots\right]^{-1}+\frac{4}{5}+4\left[1+\frac{12}{\pi}\right]\left[\left[B^r+T\frac{dB^r}{dT}\right]n+\left[C^r+T\frac{dC^r}{dT}\right]n^2+\cdots\right]\Big/25\right\} . \tag{8}$$

Hanley *et al.*[1] have shown that Eq. (8) represents the shear viscosity of simple fluids to within 10–15 % for densities up to twice the critical density.

The generalization of the MET to mixtures is straightforward. The pressure of an $s$-component mixture of hard spheres with diameters $\sigma_i$ $(i=1,\ldots,s)$ is given by

$$p^{\mathrm{HS}}=k_BT\left[\sum_{i=1}^{s}n_i+\sum_{i,j}B_{ij}^{\mathrm{HS}}\chi_{ij}^{\mathrm{HS}}n_in_j\right] , \tag{9}$$

where

$$B_{ij}^{\mathrm{HS}}\chi_{ij}^{\mathrm{HS}}=B_{ij}^{\mathrm{HS}}+\sum_{k=1}^{s}C_{ijk}^{\mathrm{HS}}n_k+\cdots , \tag{10}$$

and that of the real fluid by

$$p^r=k_BT\left[\sum_{i=1}^{s}n_i+\sum_{i,j}B_{ij}^rn_in_j+\sum_{i,j,k}C_{ijk}^rn_in_jn_k+\cdots\right] . \tag{11}$$

Equating the "thermal pressures" of the real and hard-sphere fluids leads to

$$\sum_{i,j}\left[B_{ij}^r(T)+T\frac{dB_{ij}^r}{dT}\right]n_in_j+\sum_{i,j,k}^{s}\left[C_{ijk}^r(T)+T\frac{dC_{ijk}^r}{dT}\right]n_in_jn_k+\cdots=\sum_{i,j}B_{ij}^{\mathrm{HS}}n_in_j+\sum_{i,j,k}^{s}C_{ijk}^{\mathrm{HS}}n_in_jn_k+\cdots \tag{12}$$

and thus we require

$$\begin{aligned}B_{ij}^{\mathrm{HS}}&=B_{ij}^r(T)+T\frac{dB_{ij}^r}{dT} ,\\ C_{ijk}^{\mathrm{HS}}&=C_{ijk}^r(T)+T\frac{dC_{ijk}^r}{dT} ,\\ &\vdots\end{aligned} \tag{13}$$

or, using Eq. (10),

$$B_{ij}^{\mathrm{HS}}=B_{ij}^{r}(T)+T\frac{dB_{ij}^{r}}{dT}\ , \tag{14a}$$

$$\begin{aligned} B_{ij}^{\mathrm{HS}}\chi_{ij}^{\mathrm{HS}}= &\left[B_{ij}^{r}(T)+T\frac{dB_{ij}^{r}}{dT}\right] \\ &+\sum_{k=1}^{s}\left[C_{ijk}^{r}(T)+T\frac{dC_{ijk}^{r}}{dT}\right]n_k+\cdots\ . \end{aligned} \tag{14b}$$

The extended MET is based upon Eqs. (14), which provide the means for mapping the equilibrium properties of the real fluid into those of the hard-sphere fluid. We note that if the total density $n=\sum_{i=1}^{s}n_i$ had been used as the power-series expansion variable, we would have obtained the MET result, Eq. (6), where $B,C,\ldots$ are the total virial coefficients of the mixture. Such a result would not have been too useful because the Enskog theory depends on $\{B_{ij},\chi_{ij}\}$, not $B$ and $\chi$.

Equations (14) may be obtained by an alternative method, which compares temperature derivatives of the chemical potentials. To see how this comes about, note that the chemical potential of a mixture may be expressed as

$$\begin{aligned} \mu_i(T,n_1,\ldots,n_s)=&k_BT\ln n_i+\zeta_i(T) \\ &+\hat{\mu}_i(T,n_1,\ldots,n_s)\ , \end{aligned}$$

where the term $\zeta_i(T)$ contains the thermal de Broglie wavelength and the intramolecular contributions to the partition function, and $\hat{\mu}$ contains the intermolecular contributions to the partition function. (We assume that the internal degrees of freedom of a molecule do not affect the intermolecular potential energy.) If we define the "thermal chemical potential" of species $i$ to be $T(\partial\mu_i/\partial T)_{\{n_j\}}-Td\zeta_i/dT$, then Eqs. (14) are obtained by setting the thermal chemical potentials of the hard-sphere fluid equal to those of the real fluid for each $i$. In fact, this is how we first obtained Eqs. (14).

## II. ANALYSIS OF EXPERIMENTAL VIRIAL COEFFICIENT DATA

The most difficult aspect of using the MET is the collection of equilibrium data to determine the pure and interaction virial coefficients of the mixture. We chose to test our extension of the MET on He-Ar and Ne-Ar mixtures because (i) the shear viscosity measurements reported in Refs. 3 and 11 for these systems were taken at moderate densities so that only second and third virial coefficients would be needed, and (ii) there appeared to be adequate virial coefficient data available for these systems. Below we summarize how the virial coefficient data for He-Ar (Sec. II A) and Ne-Ar (Sec. II B) were obtained.

### A. He-Ar mixtures

We determined the second and third virial coefficients, and their temperature derivatives, for He-Ar mixtures using the measurements reported by Blancett *et al.*[14] Those measurements were taken at temperatures of −50, 0, and 50 °C, at He mole fractions of 0, 0.2199, 0.4105, 0.5935, 0.8, and 1.00. They reported total virial coefficients $B$ and $C$, where

$$B=B_{11}(T)x_1^2+2B_{12}(T)x_1(1-x_1)+B_{22}(T)(1-x_1)^2 \tag{15}$$

and

$$\begin{aligned} C=&C_{111}(T)x_1^3+3C_{112}(T)x_1^2(1-x_1) \\ &+3C_{122}(T)x_1(1-x_1)^2+C_{222}(1-x_1)^3\ , \end{aligned} \tag{16}$$

where $x_1$ is the He mole fraction. Since the extended MET requires values of $dB_{ij}/dT$ and $dC_{ijk}/dT$, and the shear viscosity data were taken at $T=293.15$ K, we chose to model the temperature dependence of the virial coefficients using a power-series expansion about $T=293.15$ K. Thus we set

TABLE I. The virial coefficients of He-Ar mixtures. (These coefficients were obtained by a least-squares fit of the data of Blancett *et al.* (Ref. 14) their use should be restricted to the interval [−50,50] °C. Species 1 is He and species 2 is Ar.)

Second virial coefficients (liter/mol)

$$B_{11}=1.1902\times10^{-2}-3.0909\times10^{-5}(T-293.15)-4.080\times10^{-9}(T-293.15)^2$$

$$B_{12}=1.7924\times10^{-2}+1.7850\times10^{-5}(T-293.15)-5.911\times10^{-8}(T-293.15)^2$$

$$B_{22}=-1.6165\times10^{-2}+2.1464\times10^{-4}(T-293.15)-1.232\times10^{-6}(T-293.15)^2$$

Third virial coefficients (liter/mol)$^2$

$$C_{111}=1.0905\times10^{-4}-2.1344\times10^{-7}(T-293.15)-1.2038\times10^{-9}(T-293.15)^2$$

$$C_{112}=2.0786\times10^{-4}-9.0921\times10^{-7}(T-293.15)+3.3122\times10^{-8}(T-293.15)^2$$

$$C_{122}=6.4835\times10^{-4}-2.0539\times10^{-7}(T-293.15)-5.6259\times10^{-8}(T-293.15)^2$$

$$C_{222}=9.6911\times10^{-4}-1.7466\times10^{-6}(T-293.15)+6.3088\times10^{-8}(T-293.15)^2$$

$$B_{ij}(T)=B_{ij}^{(0)}+B_{ij}^{(1)}(T-293.15)+B_{ij}^{(2)}(T-293.15)^2$$

and (17)

$$C_{ijk}(T)=C_{ijk}^{(0)}+C_{ijk}^{(1)}(T-293.15)+C_{ijk}^{(2)}(T-293.15)^2 \ .$$

The coefficients $B_{ij}(T)$ and $C_{ijk}(T)$ were first determined using an unweighted least-squares fit to the data at $T=-50$, 0, and 50 °C; then the coefficients $B_{ij}^{(\alpha)}$ and $C_{ijk}^{(\alpha)}$ were determined by solving Eqs. (17) using the $B_{ij}(T)$ and $C_{ijk}(T)$ at the three temperatures $(\alpha=0,1,2)$. The coefficients so obtained are listed in Table I. With this representation we have $dB_{ij}/dT=B_{ij}^{(1)}$ and $dC_{ijk}/dT=C_{ijk}^{(1)}$ when $T=293.15$ K.

### B. Ne-Ar mixtures

We found fewer experimental data for these mixtures and therefore we used a combination of corresponding states and curve fitting to obtain the necessary coefficients. The pure Ar virial coefficients, $B_{22}(T)$ and $C_{222}(T)$ were taken from Gosman *et al.*[15] Those expressions can be put in reduced form by introducing an excluded volume parameter $b_{22}=2\pi N_A\sigma_{22}^3/3=0.0502$ liter/mol and a temperature-scale parameter $\epsilon_{22}/k_B=119$ K, where $N_A$ is Avogadro's number.[16] By assuming that the law of corresponding states holds for Ne and Ar, the pure Ne virial coefficients, $B_{11}(T)$ and $C_{111}(T)$, were obtained using the reduced virial coefficient expressions by selecting $b_{11}=2\pi N_A\sigma_{11}^3/3=0.0269$ liter/mol and $\epsilon_{11}/k_B=31.7$ K. [These values for $b_{11}$ and $\epsilon_{11}/k_B$ were selected by requiring that our $B_{11}(T)$ agree well with the second virial coefficient obtained from the pure neon equation of state data of Michels *et al.*[17]] To obtain the necessary "cross" parameters $b_{12}$ and $\epsilon_{12}/k_B$, we used the second virial coefficients for Ar-Ne mixtures reported by Kestin *et al.*:[3] we set $b_{12}=2\pi N_A\sigma_{12}^3/3=(b_{11}+b_{22})/2=0.0385$ liter/mol; $\epsilon_{12}/k_B$ was then obtained by setting the reduced second virial coefficient equation (of Gosman *et al.*) equal to the $B_{12}$ value from Kestin *et al.*[3] We found $\epsilon_{12}/k_B=51.21$ K. We could not obtain $C_{112}(T)$ and $C_{122}(T)$ from the experimental data, so we used the mixing rules suggested by Brewer and Vaughn:[18]

$$C_{112}(T)=[C_{111}^2(T)C_{222}(T)]^{1/3} \tag{18}$$

and

$$C_{122}(T)=[C_{111}(T)C_{222}^2(T)]^{1/3} \ . \tag{19}$$

## III. RESULTS AND DISCUSSION

The equations for the shear viscosity of the multicomponent Enskog Theory are described in numerous publications.[3-6] Our calculations were made using a subroutine library developed by López de Haro *et al.*[6] for computing the transport coefficients of the Enskog Theory. By replacing $B_{ij}^{\rm HS}$ and $B_{ij}^{\rm HS}\chi_{ij}^{\rm HS}$ in these codes with the values assigned to them by the Eqs. (14), it is a simple

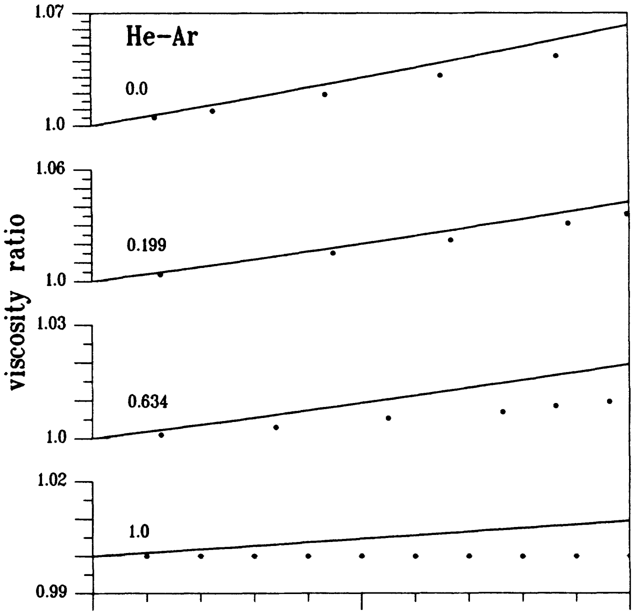

FIG. 2. Viscosity ratio $\eta/\eta_0$ vs density, where $\eta_0$ is the shear viscosity in the dilute-gas limit, for He-Ar mixtures at $T=293.15$ K. The extended MET predictions are represented by the solid curves; the experimental results (dots) are taken from Ref. 11. The curves are labeled by the mole fraction of He.

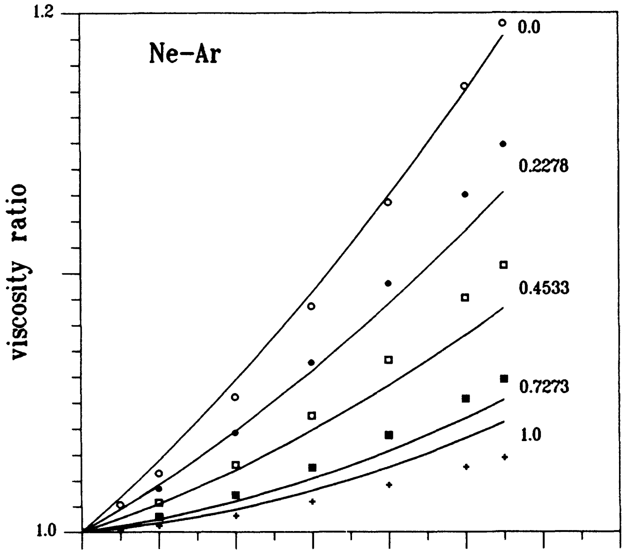

FIG. 3. Viscosity ratio $\eta/\eta_0$ vs density, where $\eta_0$ is the shear viscosity in the dilute-gas limit, for Ne-Ar mixtures at $T=298.15$ K. The extended MET predictions are represented by the solid curves; the experimental results (○,●,□,■,+) are taken from Ref. 3. The curves are labeled by the mole fraction of Ne.

matter to calculate $\eta/\eta_0$. We used the third Enskog approximation, although the first approximation (which is normally used) is almost as accurate.

In Fig. 2 we compare the MET results to the data of Iwasaki and Kestin for He-Ar mixtures ($T=293.15$ K). The MET calculations displayed in Fig. 2 were made using the virial coefficients given in Table I. For the He-Ar mixture, $\eta/\eta_0$ is very close to 1 for densities up to 2 mol/liter and the MET results lie consistently above the experimental data. Although it is true that the MET results lie within 2% of the experimental measurements, $\eta^r$ is so close to $\eta_0^r$ that the approximation $\eta/\eta_0=1$ is almost as good as the MET.

The MET results for Ne-Ar mixtures ($T=298.15$ K) are compared to the measurements of Kestin *et al.*[3] in Fig. 3 for densities up to 6 mol/liter. In this case $\eta^r/\eta_0^r$ significantly deviates from unity at the high end of the density range, providing a more stringent test of the MET. The MET values of $\eta/\eta_0$ for the mixture are always within about 2% of the experimental data.

The predictions described above, although far from conclusive, suggest that our extension of the MET to mixtures may prove to be as useful as the MET. These initial results certainly suggest that more extensive tests of the extended MET, such as calculations of the thermal conductivity and mutual and thermal diffusion coefficients, are worth pursuing. In order to use the extended MET at higher densities, where there are fewer experimental data and where higher-order virial coefficients are needed, other methods must be developed for determining the virial coefficients of the fluid mixtures. As mentioned earlier, one possible method is to determine the virial coefficients from an intermolecular potential whose parameters are chosen such that an accurate fit of equation of state data is obtained. Another possible approach would be to use one of the many varieties of thermodynamic perturbation theories[19] to model the equilibrium equation of state and then extract from that model the appropriate combination of virial coefficients.[20]

## ACKNOWLEDGMENTS

The authors gratefully acknowledge the many useful discussions they have had with Professor G. Stell, Professor J. Karkheck, and Professor M. López de Haro on this subject, as well as the financial support provided by the Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy, under Contract Nos. DE-FG02-87ER13648 and DE-AC02-881ER10807.

---

[1] H. J. M. Hanley, R. D. McCarty, and E. G. D. Cohen, Physica **60**, 322 (1972); H. J. M. Hanley and E. G. D. Cohen, *ibid.* **83A**, 215 (1976).

[2] A. Michels and R. O. Gibson, Proc. R. Soc. London, Ser. A **134**, 288 (1931); J. V. Sengers, Int. J. Heat Mass Transfer **8**, 1103 (1965); J. V. Sengers, in *Recent Advances in Engineering Science,* edited by A. C. Eringen (Gordon and Breach, New York, 1968), p. 153.

[3] J. Kestin, O. Korfali, J. V. Sengers, and B. Kamgar-Parsi, Physica **106A**, 415 (1981).

[4] S. I. Sandler and J. Fiszdon, Physica **95A**, 602 (1979).

[5] R. DiPippo, J. R. Dorfman, J. Kestin, H. E. Khalifa, and E. A. Mason, Physica **86A**, 205 (1977). See also N. Jhunjhunwala, J. P. Boon, H. L. Frisch, and J. L. Lebowitz, *ibid.* **41**, 536 (1969).

[6] M. López de Haro, E. G. D. Cohen, and J. M. Kincaid, J. Chem. Phys. **78**, 2746 (1983).

[7] J. F. Ely and H. J. M. Hanley, *A Computer Program for the Prediction of Viscosity and Thermal Conductivity in Hydrocarbon Mixtures,* Natl. Bur. Stand. (U.S.) Tech. Note No. 1039 (U.S. GPO, Washington, D.C., 1981); Ind. Eng. Chem. Fundam. **20**, 323 (1981).

[8] W. A. Wakeham, J. Kestin, and E. A. Mason, J. Chem. Phys. **57**, 295 (1972).

[9] J. Karkheck, E. Martina, and G. Stell, Phys. Rev. A **25**, 3328 (1982).

[10] R. Castillo, M. López de Haro, and E. Martina, Int. J. Thermophys. **7**, 851 (1986).

[11] H. Iwaski and J. Kestin, Physica **29**, 1345 (1963).

[12] The coefficient of $nB^{\mathrm{HS}}\chi^{\mathrm{HS}}$ in the last term of Eq. (1), $4(1+12/\pi)/25$, often appears in the literature as 0.761—which is the correct value if the fourth Enskog approximation is used. For arbitrary $N$ we have

$$\frac{\eta^{\mathrm{HS}}}{\eta_0^{\mathrm{HS}}}[N]=nB^{\mathrm{HS}}\left[\frac{1}{nB^{\mathrm{HS}}\chi^{\mathrm{HS}}}+\frac{4}{5}+\frac{4}{25}\left[1+\frac{12\eta_0^{\mathrm{HS}}[N]}{\pi\eta_0^{\mathrm{HS}}[1]}\right]nB^{\mathrm{HS}}\chi^{\mathrm{HS}}\right],$$

where $[N]$ denotes the $N$th Enskog approximation.

[13] Water is, of course, a notable exception, as well as some fluid mixtures very close to the critical point. See, for instance, J. C. Wheeler, G. Morrison, and R. F. Chang, J. Chem. Phys. **83**, 5837 (1985).

[14] A. L. Blancett, K. R. Hall, F. B. Canfield, Physica **47**, 75 (1970).

[15] A. L. Gosman, R. D. McCarty, and J. G. Hust, *Thermodynamic Properties of Argon From the Triple Point to 300 K at Pressures to 1000 Atmospheres,* Natl. Bur. Stand. Ref. Data Ser., Natl. Bur. Stand. (U.S.) Circ. No. NSRDS-NBS27 (U.S. GPO, Washington, D.C., 1969).

[16] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).

[17] A. Michels, T. Wassenaar, and P. Louwerse, Physica **26**, 539 (1969).

[18] J. Brewer and G. W. Vaughn, J. Chem. Phys. **50**, 2960 (1969).

[19] J. A. Barker and D. Henderson, Rev. Mod. Phys. **48**, 587 (1976).

[20] J. F. Ely and D. A. McQuarrie, J. Chem. Phys. **60**, 4105 (1974).