Correlation Method for the Shear Viscosity of Fluid Mixtures at Moderate Densities

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Abstract

A method to predict the shear viscosity of fluid mixtures is described. The method relies on the results of the Revised Enskog Theory for hard-sphere fluid mixtures and the use of temperature and density dependent diameters to model each species of the real mixture. The predictions are compared against the empirical Dean and Stiel correlation scheme for twenty six binary mixtures mainly of hydrocarbons. While the overall qualitative agreement is satisfactory, quantitative results may differ substantially. Possible sources of this discrepancy are briefly discussed.

Introduction

The need for accurate values of transport properties of working fluid mixtures for industrial or scientific purposes increases every day, but it is clear that the acquisition of reliable data for the enormous variety of mixtures and thermodynamic states can never be completely achived by direct measurement only. One way out in engineering calculations is to use empirical correlation schemes quite limited to narrow ranges of temperatures and pressures, and often to pure fluids. A review of these methods is given in Reid et al [1].

Another procedure has been presented recently [2, 3] in order to estimate transport properties of dense non-polar fluid mixtures, which is based on the corresponding states principle and the one-fluid conformal solution concept, with great success.

There is another option to get transport coefficients based on more theoretical foundations [4–8]. Here explicit expressions for transport coefficients of real simple or multicomponent dense fluids in terms of the intermolecular force parameters have been obtained quite recently for simple models. Among these, the hard-sphere model has played a prominent role in kinetic studies at liquid-like

densities. Hence, in this paper we present the results of calculations for binary mixtures mainly of hydrocarbons in order to find out the usefulness of the Revised Enskog Theory (RET) [6] to predict shear viscosities of real fluid mixtures, with hard-sphere diameters modeled with the procedures developed in equilibrium liquid theory [9–12]. This paper is organized as follows: in section 1 the RET formulae are reviewed and the shear viscosity expression used is given. Our procedure to handle Lennard-Jones binary mixtures through RET is mentioned. In section 3 the results and some discussion is presented. The effect of using the Barker-Henderson (BH) [9], the Rasaiah-Stell/Mansoori-Canfield (RS/MC) [10, 11] or the Weeks-Chandler-Andersen (WCA) [12] prescriptions in the calculation of shear viscosity is examined. We compare our results with the Dean-Stiel empirical correlation scheme [13].

1. The shear viscosity of dense Lennard-Jonesian binary mixtures

As it was mentioned in the introduction there are some advances in kinetic theory that let explicit expressions for transport coefficients of real dense fluids to be derived in terms of the intermolecular force parameters of simple models. The first kinetic theory applicable for dense fluids is due to Enskog [14] who generalized the Boltzmann equation to describe the hard-sphere dynamics in the dense regime. This theory was later extended in order to deal with binary [14] and multicomponent [15] dense hard-sphere fluid mixtures, but the extensions were found to be at odds with the irreversible thermodynamics [16]. The inconsistency was resolved by van Beijeren and Ernst [17] who proposed what is called the Revised Enskog Theory (RET). H-Theorems have been derived from the RET equation [18–20] and van Beijeren pointed out that the RET has other attractive features [21]. In addition, explicit expressions for the linear transport coefficients were gathered and discussed in detail by Lopez de Haro, Cohen and Kincaid [6].

The main difficulty in applying the RET transport coefficient expressions to real fluids lies in relating the contact values of the hard-sphere radial distribution function and the hard-sphere diameters appearing in the theory to quantities associated with the real system. Our procedure to achieve this connection is presented here.

Then, our starting point is the set of coupled non-linear kinetic equations for multicomponent hard-sphere mixtures in the RET first given by van Beijeren and Enrst [17]. In the case of a binary mixture and in the absence of an outside field, this set consists of two coupled nonlinear integrodifferential equations for the two single particle distribution functions $f_i(r, V_i, t)$, $(i = 1, 2)$:

$$\left[\frac{\partial}{\partial t} + V_i \cdot \frac{\partial}{\partial r}\right] f_i(r, V_i, t) = \sum_{j=1}^{2} J_{ij}(f_i f_j) \tag{1}$$

where

$$J_{ij}(f_i f_j) = \iint \Theta \, (\hat{k} \cdot V_{ji}) \, (\hat{k} \cdot V_{ji}) \, \sigma_{ij} \, [\chi_{ij}(r, r + \sigma_{ij}\hat{k}| \{n_i\})$$

$$f_i(r, V_i', t) f_j(r + \sigma_{ij}\hat{k}, V_j', t) - \chi_{ij}(r, r - \sigma_{ij}\hat{k}| \{n_i\})$$

$$f_i(r, V_i, t) f_j(r - \sigma_{ij}\hat{k}, V_j, t)] \, d\hat{k} dV_j \, .$$

Here $f_i(r, V_i, t)$ is the average number of hard spheres of component i (with diameter σ_i and mass m_i) at the position r with velocity V_i at time t; $V_{ji} = V_j - V_i$ is the relative velocity of two spheres with velocities V_j and V_i, respectively, $\hat{k}$ is a unit vector directed along the line of centers from the sphere of component j to the sphere of component i upon collision (i. e. at contact) and Θ is the Heaviside step function. V_i' and V_j' denote the velocities of the restituting collision, which are connected to those of the direct collision V_i and V_j by the relations

$$V_i' = V_i + 2 M_{ji}(V_{ji} \cdot \hat{k})\hat{k} \, ,$$

$$V_j' = V_j - 2 M_{ij}(V_{ji} \cdot \hat{k})\hat{k} \, , \tag{2}$$

where $M_{ij} = m_i/(m_i + m_j)$. χ_{ij} is the radial distribution function of two hard spheres, one of component i and the other of component j at contact, i. e., when the distance between their centers is $\sigma_{ij} = \left(\dfrac{\sigma_i + \sigma_j}{2}\right)$. In the RET, the χ_{ij}'s are the same functionals of the local number densities $\{n_i\}$ as in a binary mixture in nonuniform equilibrium. The molecular fluxes and the transport coefficients for dense hard-sphere binary mixtures, up to the Navier-Stokes level, can be directly obtained from Eqs. (1) on the basis of the procedure used in ref. [6] and we will not repeat the derivation here. Instead we quote only the relevant results. It turns out that the momentum flux P is given by

$$P = pI - 2\eta \overline{\dfrac{\overset{\circ}{\partial U}}{\partial r}} - \kappa \left(\dfrac{\partial}{\partial r} \cdot U\right) I, \tag{3}$$

where

$$p = \sum_{i=1}^{2} n_i k_B T \left(1 + \sum_{j=1}^{2} \varrho \, b_{ij} \chi_{ijc}^{HS}\right) \tag{4}$$

is the thermostatic presure, I the unit tensor, η the coefficient of shear viscosity, κ the bulk viscosity, U the hydrodynamic velocity and the symbol $\overset{\circ}{=}$ denotes the symmetric traceless part. In Eq. (4), $\varrho \, b_{ij} = \frac{2}{3} \pi n_j \sigma_{ij}^3$, k_B is Boltzmann's constant, T the absolute temperature and χ_{ijc}^{HS} is the equilibrium value of the radial distribution function for spheres of species i and j at contact, where the equilibrium density has been replaced by the local equilibrium density $n = n_i + n_2$. Explicit expressions for η and κ for binary mixtures in terms of the molecular parameters were given in ref. [6]. The former reads [6-8]

$$\eta = \frac{1}{2} \sum_{i=1}^{2} K_i' \frac{n_i}{n} k_B T b_0^{(i)} + \frac{4}{15} \sum_{i=1}^{2} \sum_{j=1}^{2} \left(\frac{2\pi m_i m_j k_B T}{m_i + m_j} \right)^{1/2} n_i n_j \sigma_{ij}^4 \chi_{ijc}^{HS} \quad (5)$$

where

$$k_i' = 1 + \frac{4}{5} \sum_{j=1}^{2} \varrho \, b_{ij} M_{ji} \chi_{ijc}^{HS}$$

and the $b_0^{(i)}$ are coefficients that appear in the Sonine polynomial expansion of the one particle distribution functions. In the so-called $N_{||}^{Th}$ Enskog approximation, i.e. when N Sonine polynomials are taken into account in the expansion, the $b_0^{(i)}$ are determined from a set of linear equations (for details see reference [6]).

The evaluation of η for given $\{n_i\}$, $\{\sigma_i\}$, $\{m_i\}$ and T using Eqs. (5), requires knowledge of χ_{ijc}^{HS}. At this time an exact, explicit equation for χ_{ijc}^{HS} in terms of the number densities and the set of hard-sphere diameters $\{\sigma_i\}$ is not available, but several approximate expressions already exist. In particular, the so-called Carnahan-Starling [22] approximation appears to be quite accurate when compared to molecular dynamics data.

In order to use Eq. (5) to obtain numerical estimates of the shear viscosity of real mixtures, we need a prescription to get state-dependent hard-sphere diameters in terms of the parameters associated with the potentials chosen to model the actual systems. While several routes are possible, we follow the one taken in our previous work [7, 8] namely we consider that each component of the binary mixture is modeled through a Lennard-Jones potential.

$$\Phi_i^{LJ}(r) = 4\varepsilon_i \left[(\sigma_{0i}/r)^{12} - (\sigma_{0i}/r)^6 \right], \quad (6)$$

where ε_i is the well depth and σ_{0i} is the minimal separation of two molecules of species i such that $\Phi_i^{LJ}(\sigma_{0i}) = 0$, and determine separately the effective diameters in terms of σ_{0i}, ε_i, and the thermodynamic state of the system. As for the cross interaction, we assume it to be that of a hard-sphere mixture with effective diameters i.e.

$$\sigma_{12} = \sigma_{21} = \frac{1}{2}(\sigma_1 + \sigma_2).$$

The effective diameters σ_i ($i = 1, 2$), are obtained using three alternative schemes, well established in equilibrium liquid state theory. These are the variational method of Mansoori-Canfield and Rasaiah-Stell (MC/RS) and the perturbative methods of Barker and Henderson (BH) and Weeks, Chandler and Andersen (WCA).

2. Numerical Results and Discussion

In two previous papers [7, 8] we reported preliminary results for the shear viscosity of Neon-Argon mixtures obtained with the scheme presented in the previous section. Although the comparison with experimental data showed quite a good agreement, the potential of the method as a correlation prescription requires a more stringent test. In this section we present the results of extensive calculations performed for the twenty six binary mixtures shown in table 1 in the dense regime. Rather than presenting a comparison with individual experimental data, which would presumably not be available for all the densities, temperatures and mole fractions examined in this study, we compare our results with the empirical correlation method of Dean and Stiel [13] widely used to obtain shear viscosity information of fluid mixtures [1]. According to this method, the viscosity of nonpolar mixtures is calculated from the following relation.

$$\eta_m^{DS} = \eta_m^{\circ} + 10.8 \times 10^{-5} \left(e^{-1.439 \, \varrho_{rm}} - e^{-1.111 \, \varrho_{rm}^{1.858}} \right) \xi^{-1} \tag{7}$$

where

$$\xi = T_{cm}^{1/6} / M_m^{1/2} p_{cm}^{2/3}$$

with T_{cm} the critical temperature, p_{cm} the critical pressure and M_m the molecular weight of the mixture; and η_m° and ϱ_{r_m} stand for the low pressure viscosity and the reduced mass density of the mixture respectively. Equation (7) has a claimed 3.7% overall average deviation when applied to data of gases at high pressure and liquids at high temperature, but the accuracy for liquids with reduced densities greater than about 2 is expected to be poor.

In order to compare our method with this correlation, we use the following procedure:

1) η_m is obtained from equations (5), using the effective state dependent diameters as explained above. And

2) η_m^{Ds} is computed according to equation (7) with η_m° determined using the Wilke estimation method [1] for the viscosity of gas mixtures at low pressure and the pseudocritical constants T_{cm} and P_{cm} appearing in ξ calculated with the modified Prausnitz and Gunn rules [1].

In table 1 a summary of selected results obtained using the MC/RS criterion to fix the hard-sphere diameter of each component of the mixture is presented. All the data are for $T = 250\,°K$ and $X_1 = 0.75$ and the corresponding σ_{oi} and ε_i were taken from reference [1]. The MC/RS criterion was chosen because it gave the overall best estimates. For comparison, however, we show in table 2 the results obtained using either the BH or WCA criteria. As reported earlier [7, 8], for the lower reduced densities these latter criteria work better than the MC/RS scheme but as the reduced density is increased beyond 0.8, only the MC/RS criterion accurately fits the data. This is not surprising because both the BH and WCA

methods were built to fit the low density equilibrium properties, whereas the MC/RS criterion was directed towards the denser regimes. The important point to emphasize is that since the crossover occurs at a reduced density of about 0.8, our recommendation is that one uses the BH or WCA schemes from $\varrho_{r_m} \leq 0.8$ and the MC/RS criterion from $\varrho_{r_m} = 0.8$ onwards. Of course, one would not expect our method to be accurate at very small densities and the question arises whether one can determine in a similar way the reduced density at which one should switch from the exact Chapman-Enskog formula to our method with either the BH or WCA criteria. Since our main interest was the prediction of viscosities at liquid like densities we have not examined this question here.

Although not explicity shown, the features contained in the results of tables 1 and 2 remain the same when either the composition or the temperature or both are varied. This fact stresses that our method shares an important aspect of the Dean-Stiel correlation scheme namely, that the residual viscosity for most of the mixtures follows a universal curve. This is shown in figure 1. Given the different characteristics of each individual mixture, it is remarkable that a hard-sphere

Tab. 1: Deviation between the Revised Enskog Theory viscosities using RS/CM criteria to model diameters. ($T = 250\,°K$, $X_1 = 0.75$) and the Dean-Stiel empirical correlation scheme*.

Binary Mixture	ξ	$\eta°$	$\varrho_r = 0.8$ δ	$\varrho_r = 1.2$ δ	$\varrho_r = 1.6$ δ	$\varrho_r = 2.0$ δ
O_2/Ar	2.950 E-2	183.452	12.4	10.9	12.3	12.6
N_2/Ar	3.670 E-2	166.728	11.5	11.2	13.9	16.3
N_2/O_2	3.775 E-2	160.723	12.2	11.9	14.8	16.9
N_2/CO_2	3.329 E-2	146.516	13.3	13.1	17.0	20.9
N_2/CH_4	4.129 E-2	141.237	10.8	9.4	11.2	11.9
$N_2/CH_2{=}CH_2$	3.841 E-2	132.278	13.9	11.8	13.8	15.6
$N_2/CH_3{-}CH_3$	3.841 E-2	128.728	13.7	12.3	14.9	18.1
$N_2/CH_3{-}CH_2{-}CH_3$	3.772 E-2	118.998	16.5	17.3	23.9	31.3
CH_4/Ar	3.944 E-2	125.590	7.3	0.3	1.8	0.0
CH_4/O_2	4.120 E-2	117.887	9.9	5.1	4.2	2.3
CH_4/CO_2	3.657 E-2	108.783	10.0	5.7	5.8	6.3
$CH_4/CH{\equiv}CH$	4.205 E-2	92.949	14.9	9.3	8.3	8.3
$CH_4/CH_2{=}CH_2$	4.307 E-2	92.680	14.7	8.8	7.9	6.6
$CH_4/CH_3{-}CH_3$	4.297 E-2	90.406	14.1	9.4	9.2	9.4
$CH_4/CH_3{-}CH_2{-}CH_3$	4.137 E-2	85.782	14.9	12.2	15.6	20.7
$CH_4/CH_3{-}CH_2{-}CH_2{-}CH_3$	4.017 E-2	81.902	17.2	1.6	—8.1	—15.8
CH_4/n-pentane	3.938 E-2	78.336	17.4	13.1	16.6	22.8
$CH{\equiv}CH/N_2$	3.376 E-2	99.741	16.4	12.9	15.5	18.8
$CH{\equiv}CH/CH_3{-}CH_3$	3.376 E-2	84.452	17.2	12.7	16.0	21.2
$CH_2{=}CH_2/CH_3{-}CH_3$	3.582 E-2	83.834	17.0	11.6	12.9	16.3
$CH_3{-}CH_3/O_2$	3.452 E-2	96.249	14.5	11.8	15.7	19.3
$CH_3{-}CH_3/CO_2$	3.193 E-2	91.138	13.6	11.5	16.5	22.7
$CH_3{-}CH_3/CH_3{-}CH_2{-}CH_3$	3.502 E-2	76.257	15.4	13.6	19.9	28.8
$CH_3{-}CH_3/n$-pentane	3.418 E-2	71.215	16.2	13.0	19.0	28.8
Kr/Ar	2.422 E-2	205.585	11.8	9.1	10.0	10.5
Ar/Xe	2.177 E-2	201.764	11.0	7.2	7.8	8.8

* δ = Percent deviation

Tab. 2: Comparison summary of absolute average deviation between theoretical results using any criteria to select effective diameter and Dean-Stiel correlation-scheme.*

	$\varrho_r = 0.8$		$\varrho_r = 1.2$		$\varrho_r = 1.6$		$\varrho_r = 2.0$	
	$\bar{\delta}$	σ	$\bar{\delta}$	σ	$\bar{\delta}$	σ	$\bar{\delta}$	σ
MC/RS	13.7	2.6	10.3	3.8	12.8	5.1	15.8	8.0
B/H	12.7	3.5	18.9	5.2	30.3	9.5	42.4	14.5
WCA	12.8	3.6	20.0	5.4	32.9	10.0	46.9	15.5

* $\bar{\delta}$ = Average absolute percent deviation   * σ = Standard deviation

theory with state dependent diameters is able to predict qualitatively this feature without involving any corresponding states principle.

The sources of discrepancy may be of two types. One, due to the fact that we are comparing our results with an empirical correlation scheme with its own deviation from the experimental values. The other source comes from the use of a hard-sphere theory to model real fluids (not spherical and with internal degrees of freedom). This can be seen in a rough way in figure 2. Here a graph of the average of internal degrees of freedom vs the average Pitzer acentric factor, both for the binary mixtures, easily shows that as the binary mixtures have more degrees of freedom and a lesser spherical shape there is a larger deviation from the Dean-Stiel correlation scheme.
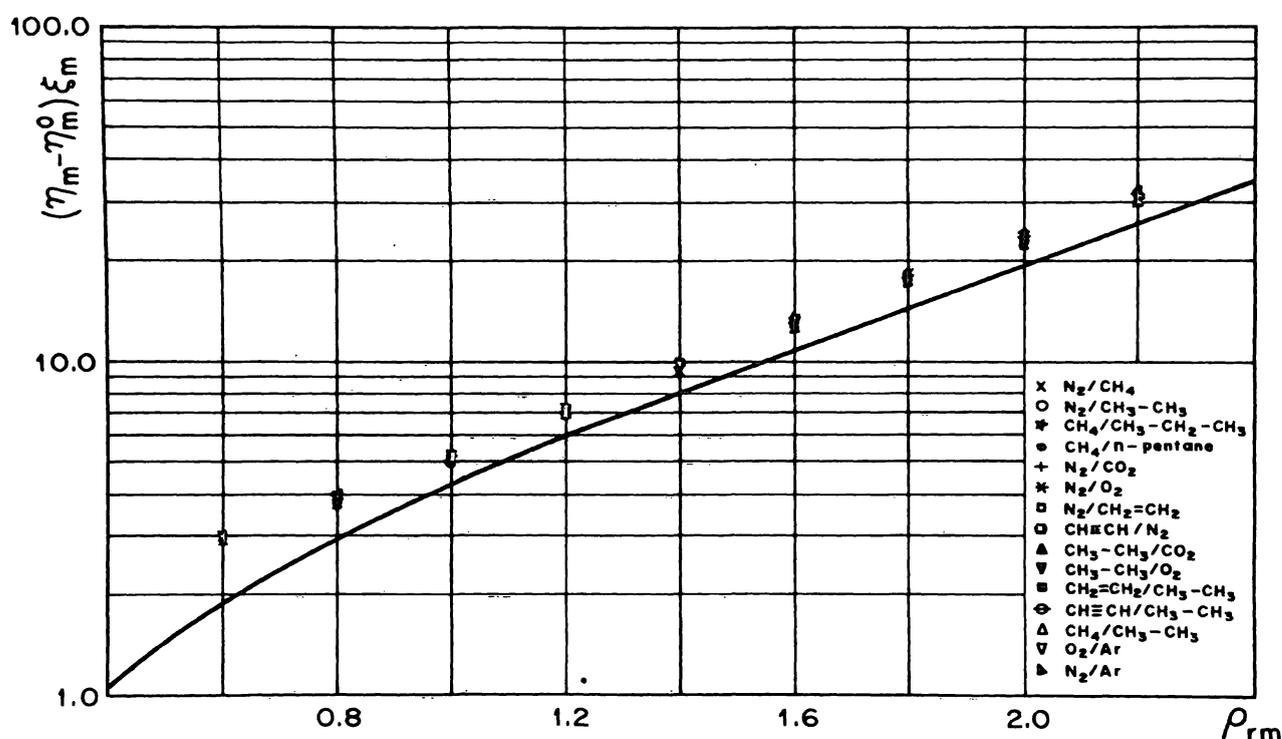

Fig. 1: Calculated values of $(\eta - \eta^\circ)\xi$ vs the reduced density of the mixture for different binary systems (η calculated by equation (5) and η° estimated by the Wilke method as given in the text). The Dean-Stiel empirical correlation scheme is the solid line.

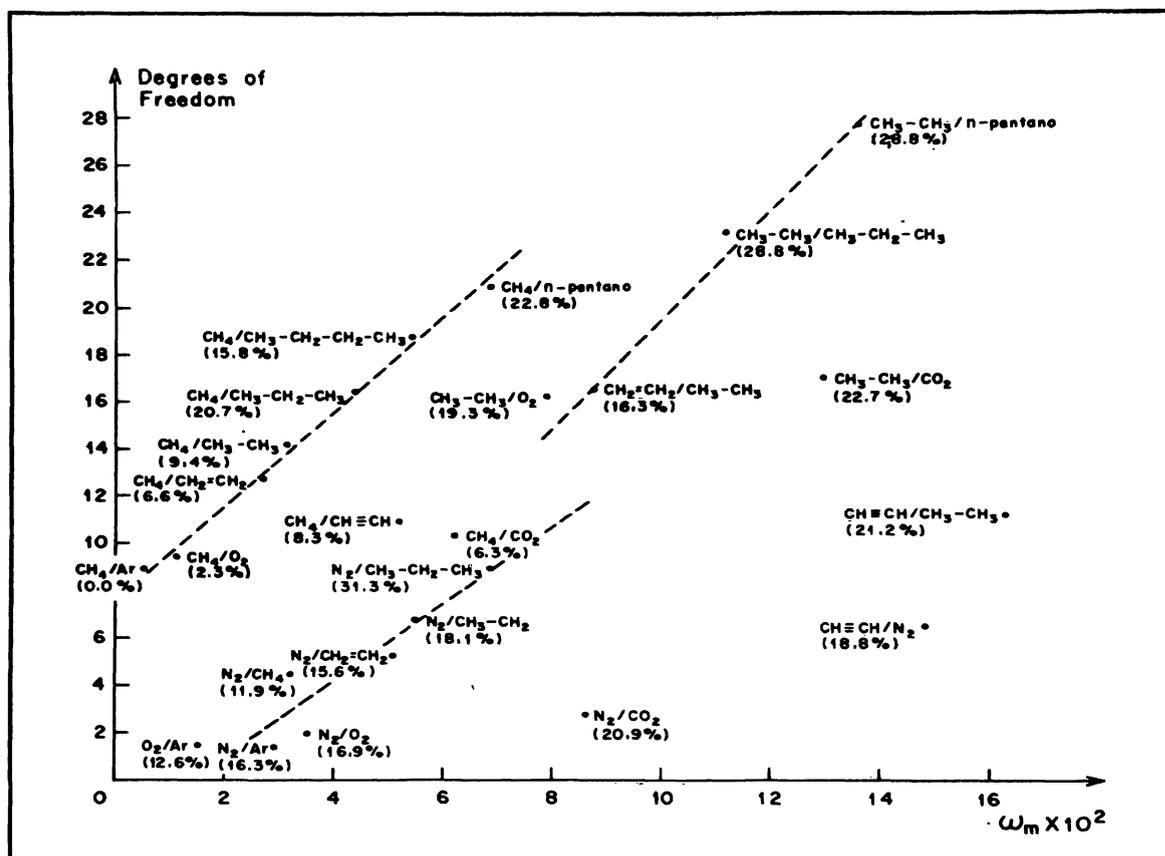Fig. 2: Graph of the average of internal degrees of freedom (3 N-3 non-linear molecules and 3 N-4 linear molecules) vs the average of Pitzer's acentric factor for different binary mixtures. In parenthesis appears the absolute percent deviation from Dean-Stiel scheme at $\varrho_{rm} = 2$. This figure shows in a rough way that as the binary mixtures have more degrees of freedom and lesser spherical shape there is a larger deviation from the Dean-Stiel correlation scheme.

In summary, these results are encouraging and show that the procedure we followed requires very little input while still yielding reasonably accurate predictions. A detailed comparison of this method with other correlation schemes like that of Ely and Hanley [2] at higher reduced densities will be published shortly [23].

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