

## **Transport Coefficients of Fluid Mixtures<sup>1</sup>**

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On the basis of the successful description of the equilibrium properties of simple fluids and fluid mixtures using perturbation theory, the consequences of including density- and temperature-dependent diameters in the formulas for the transport coefficients of dense hard-sphere fluid mixtures are investigated. The advantages and limitations of this approach for the correlation of the experimental data of real mixtures, together with numerical estimates for particular mixtures, are discussed. On the other hand, recent mean field kinetic theories which include the effect of the attractive tail in the intermolecular potential are employed to derive transport coefficients for mixtures. Numerical results are presented and comparison with other theories is also made.

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**KEY WORDS:** kinetic theory; mixtures; numerical results; transport coefficients.

### **1. INTRODUCTION**

The need for accurate values of the transport properties of working fluids for industrial or scientific purposes increases every day. In particular, fluid mixtures occur in most chemical engineering applications and it is clear that the acquisition of reliable data for the enormous variety of mixtures can never be completely achieved by direct measurement only. In these circumstances, a predictive method for the transport properties of fluid mixtures that, while being reasonably accurate, depends little on measurements or empirical prescriptions is a desirable goal [1].

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Explicit theoretical expressions for the transport coefficients of real simple or multicomponent dense fluids in terms of the intermolecular forces parameters have been obtained quite recently for simple models [2–4]. The study of these models provides the major source of insight for the understanding of the transport behavior of dense fluids. Among these, the hard-sphere model has played a prominent role in kinetic studies at liquid-like densities. The first kinetic theory for a dense hard-sphere fluid is due to Enskog [5], who generalized the Boltzmann equation to describe the hard-sphere dynamics in the dense regime. This theory was later extended to deal with binary [6] and multicomponent [7] dense hard-sphere fluid mixtures, but the extensions were found to be at odds with irreversible thermodynamics [8]. The inconsistency was resolved by van Beijeren and Ernst [9], who proposed what is called the revised Enskog theory (RET). They showed that the mutual and thermal diffusion coefficients were the only linear transport coefficients which had to be corrected. As van Beijeren has pointed out recently, the RET has other attractive features [10]. In addition,  $H$  theorems have been derived from this equation [11]. van Beijeren and Ernst did not provide explicit expressions for the linear transport coefficients in terms of the masses, hard-sphere diameters, and concentrations of the components of the mixture. In addition, in Ref. 7, certain effects were ignored in the derivation of the viscosities and thermal conductivity. This situation has motivated further work on the RET. In Ref. 2, explicit and correct expressions for the linear transport coefficients of the RET were gathered and discussed in detail, and these will serve as the starting point for the calculations presented in this paper.

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 (rdf) and the hard-sphere diameters appearing in the theory to quantities associated with the real system. One possible way to achieve this connection, already suggested by Enskog, is to associate the contact value of the rdf with the thermal pressure [5]. This procedure, known as the modified Enskog theory (MET), is clear-cut only in the one-component case. An alternative approach is based on the use of statistical-mechanical techniques which have become standard in the equilibrium theory of fluids [12]. These procedures select a state-dependent hard-sphere reference potential in relation to a full potential. Such a route has been followed in Ref. 3a for a one-component Lennard-Jones fluid and the results appear to be quantitatively superior, conceptually cleaner, and technically more tractable than those of the MET. Here we extend the calculations to Lennard-Jones binary mixtures by using a state-dependent diameter  $\sigma_i$  for each separate component and adopting the hard-sphere sum rule  $\sigma_{ij} = (\sigma_i + \sigma_j)/2$  for the diameter  $\sigma_{ij}$ . We present numerical

results for the shear and bulk viscosities and the mutual diffusion coefficient using several schemes [13, 14] to model the state-dependent hard-sphere diameter.

Even if the hard-sphere model has been predominant in the study of linear transport coefficients of dense fluids, the attractive part of the intermolecular potential might appreciably contribute to the value of these coefficients in real systems. There is so far very little theoretical work and almost no systematic numerical studies on this effect.

The dense square-well fluid was investigated by Davis et al. [15] using an Enskog-like kinetic equation. More recently, Karkheck and Stell [16] have used the maximization of entropy to derive a kinetic variational theory (KVT) that includes the attractive part of the intermolecular potential in a mean field term. The pressure obtained is that which comes from approximating the full rdf by that of a hard-sphere reference system. Thus, thermodynamic quantities such as the internal energy are exact through first order in potential tail strength [3]. The KVT has been generalized to mixtures in the Kac-tail limit by Karkheck et al. [3]. As is well known the Kac potential is infinitely weak and long-ranged and it gives exactly the van der Waals equation of state. They found that only the mass diffusion, thermal diffusion, and barodiffusion coefficients show a dependence on the tail, but the shear and bulk viscosities and the thermal conductivity were the same as those of the RET [3]. Several extensions of the KVT have been derived recently either by extending the entropy analysis [4a] or by using alternative approaches [4b], but no numerical results have been obtained for mixtures. In this paper we carry out a numerical study of the mutual diffusion coefficient for binary Lennard-Jones systems in the Kac limit.

The paper is organized as follows: in Section 2 the RET formulas for the shear and bulk viscosities and the mutual diffusion coefficient are given. The KVT binary diffusion coefficient for a van der Waals mixture is also presented. In Section 3 numerical results are presented. The effect of using the Barker-Henderson (BH) [12], Rasaiah-Stell/Mansoori-Canfield (RS/MC) [13], or Weeks-Chandler-Andersen (WCA) [14] prescription in the calculation of the transport coefficients is examined. We compare our results with experimental data and discuss their use as a possible correlation scheme.

## 2. TRANSPORT COEFFICIENTS FOR A DENSE BINARY MIXTURE

In this section the formulas for the shear ( $\eta$ ) and bulk ( $\kappa$ ) viscosity and the isothermal isobaric mutual diffusion coefficient ( $D_{12}$ ) for a dense

binary mixture are given. These coefficients are defined through the usual expressions for the momentum ( $\tau$ ) and isothermal isobaric mass fluxes ( $\bar{J}_1$ ):

$$\tau = P\mathbf{I} - 2\eta \frac{\overset{\circ}{\partial}\bar{u}}{\partial\bar{r}} + \kappa \frac{\partial}{\partial\bar{r}} \cdot \bar{u}\mathbf{I} \quad (1)$$

$$\bar{J}_1 = -D_{12} \frac{\partial\rho_1}{\partial\bar{r}} \quad (2)$$

where  $P$  is the hydrostatic pressure,  $\bar{u}$  is the hydrodynamic velocity,  $\rho_i = m_i n_i$  is the mass density,  $n_i$  is the number density,  $m_i$  is the mass of species 1, and the symbol  $\overset{\circ}{\partial}$  denotes the symmetric traceless part of the corresponding tensor.

Explicit expressions for  $\eta$ ,  $\kappa$ ,  $P$ , and  $D_{12}$  using the RET have been presented in Ref. 2. Formulas for the same quantities were derived from the KVT in Ref. 3b. Both theories lead to the same viscosities but differ in the pressure and the mutual diffusion coefficient, due to the explicit appearance of the attractive tail in the latter.

Following the notation in Ref. 2 the aforementioned quantities are written as

$$\eta = \frac{1}{2} \sum_{i=1}^1 \left( 1 + \frac{4}{5} \sum_{j=1}^2 \rho b_{ij} M_{ji} \chi_{ijc} \right) \frac{n_i}{n} k_B T b_0^{(i)} + \frac{4}{15} \sum_{i=1}^2 \sum_{j=1}^2 \left( \frac{2\pi m_i m_j k_B T}{m_i + m_j} \right)^{1/2} n_i n_j \sigma_{ij}^4 \chi_{ijc} \quad (3)$$

$$\kappa = \frac{4}{9} \sum_{i=1}^2 \sum_{j=1}^2 \left( \frac{2\pi m_i m_j k_B T}{m_i + m_j} \right)^{1/2} n_i n_j \sigma_{ij}^4 \chi_{ijc} + 2 \sum_{i=1}^2 \left( \sum_{j=1}^2 \rho b_{ij} M_{ji} \chi_{ijc} \right) \frac{n_i}{n} k_B T h_i^{(i)} \quad (4)$$

$$P^{\text{RET}} = n k_B T + \sum_{i=1}^2 \sum_{j=1}^L n_i k_B T \rho b_{ij} \chi_{ijc} \quad (5a)$$

$$P^{\text{KVT}} = P^{\text{RET}} + \sum_{i=1}^2 \sum_{j=1}^2 n_i n_j a_{ij} \quad (5b)$$

$$D_{12}^{\text{RET}} = -\frac{\rho^2}{2\rho_2 m_1 n^2} d_{1,0}^{(2)} \left[ E_{11} - \frac{P_1}{P_2} E_{12} \right] \quad (6a)$$

$$D_{12}^{\text{KVT}} = -\frac{\rho^2}{2\rho_2 m_1 n^2} d_{1,0}^{(2)} \left\{ E_{11} + \frac{2a_{11}n_1}{k_B T} \right. \\ \left. - \left( E_{12} + \frac{2a_{12}n_1}{k_B T} \right) \left[ \frac{P_1 k_B T + 2(a_{11}n_1 + a_{21}n_2)}{P_2 k_B T + 2(a_{12}n_1 + a_{22}n_2)} \right] \right\} \quad (6b)$$

$$a_{ij} = \frac{1}{2} \int d\bar{r} \Phi'_{ij}(r), \quad \rho b_{ij} = \frac{2\pi}{3} n_j \sigma_{ij}^3, \quad M_{ji} = \frac{m_j}{m_i + m_j}, \quad (7) \\ \sigma_{ij} = (\sigma_i + \sigma_j)/2, \quad E_{ij} = \frac{n_i}{k_B T} \left( \frac{\partial \mu_i}{\partial n_j} \right)_{T, n_k \neq j}, \quad P_i = \sum_{j=1}^2 E_{ij}$$

Here  $\sigma_i$  is the hard-sphere diameter of species  $i$ ,  $k_B$  is the Boltzmann constant,  $T$  is the temperature,  $n = n_1 + n_2$  is the total number density,  $\rho = \rho_1 + \rho_2$  is the total mass density,  $\mu_i$  is the hard-sphere chemical potential of species  $i$ ,  $\chi_{ijc}$  is the contact value of the rdf of a hard-sphere mixture evaluated at the local density  $n$ ,  $\Phi'_{ij}$  is the attractive part of the intermolecular potential explicitly defined below, and  $b_0^{(i)}$ ,  $h_1^{(i)}$ , and  $d_{1,0}^{(2)}$  are coefficients that appear in the Sonine polynomial expansion of the one-particle distribution function [cf. Eqs. (24), (31), (33), and (37) in Ref. 2]. We consider the 10th Enskog approximation to these coefficients, which may be obtained from Eqs. (43), (45), and (47) in Ref. 2, setting  $S=2$ ,  $N=10$ , and the expressions for the bracket integrals appearing in them given in Ref. 17.

Since we are interested in obtaining numerical estimates of the transport properties for real mixtures through the RET Eqs. (3)–(6a), we need a prescription to obtain a state-dependent hard-sphere diameter in terms of the parameters associated with the potential chosen to model the actual system. Here, we chose a Lennard–Jones potential to model each component of the real system. This potential is

$$\Phi_i^{\text{LJ}}(r) = 4\epsilon_i \left[ \left( \frac{\sigma_{0i}}{r} \right)^{12} - \left( \frac{\sigma_{0i}}{r} \right)^6 \right] \quad (8)$$

where  $\epsilon_i$  is the depth of the well and  $\sigma_{0i}$  is the minimal separation of two molecules such that  $\Phi_i^{\text{LJ}}(\sigma_{0i}) = 0$ . As mentioned before we select some of the well-known criteria commonly used in liquid state theory to associate an effective  $\sigma_i$  and  $\epsilon_i$ . We refer to Refs. 12–14 for a detailed discussion of the prescriptions and to Ref. 3a for their application in this context.

On the other hand, we require an expression for  $\Phi'_i(r)$  to compute  $D_{12}^{\text{KVT}}$  [Eq. (6b)]. For each component  $\Phi'_i$  is defined by

$$\Phi'_i(r) = \infty, \quad r \leq \sigma_{0i} \\ \Phi'_i(r) = \Phi_i^{\text{LJ}}(r), \quad r > \sigma_{0i} \quad (9)$$

where  $\Phi_i$  is an infinitely repulsive potential representing the hard core and we have used part of the Lennard–Jones potential to mimic the tail. Notice that the KVT for mixtures is valid for the potential given in Eq. (9) only in the Kac limit.

### 3. NUMERICAL RESULTS AND DISCUSSION

We present preliminary numerical results for the transport coefficients discussed in Section 2. All the calculations are based on the use of the approximations given in Ref. 18 for the rdf  $\chi_{ijc}$  and the chemical potentials  $\mu_i$ . We have chosen an argon–neon mixture as a probe to test the validity of our method for the shear viscosity  $\eta$ . Such a mixture is usually modeled by Lennard–Jones potentials. Moreover, there exist experimental data for the transport properties of this system. In addition, we have also examined  $D_{12}$  for a methane–ethane mixture where, again, experimental values are available. Even if this system is definitely not composed of molecules interacting with Lennard–Jones potentials, we use this as an effective interaction.

Finally, since we were not able to find experimental results on the bulk viscosity of mixtures, we calculated it for a one-component fluid representing argon. For comparison we have included the results of the RET, taking the hard-sphere diameter  $\sigma_i$  as  $\sigma_{0i}$ . We call them RET, in contrast with the results which make use of effective diameters with a given criterion.

In our calculations the mixing rules

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2 \quad (10)$$

and

$$\varepsilon_{ij} = k \sqrt{\varepsilon_i \varepsilon_j} \quad (11)$$

were employed. Here  $k$  is a pure number. The Lorentz–Berthelot rule corresponds to  $k=1$ . A different value of  $k$  could be used to correlate experimental data, a common procedure in the literature [19].

In Fig. 1, the bulk viscosity  $\kappa$  of argon is shown as a function of the density at two temperatures. The parameters we chose are  $\varepsilon/k_B = 93.90$  K and  $\sigma_0 = 3.542$  Å [1]. At the higher temperature (dilute and moderately dense gas) we find a pair agreement between the RET and the experimental data of Hanley and Cohen [20]. This agreement is improved by using any of the criteria to select the effective diameter. The RS/MC scheme appears to be specially successful. At lower temperatures (liquid densities) the RET still does a good job, but quite surprisingly only the RS/MC improves the quantitative agreement.

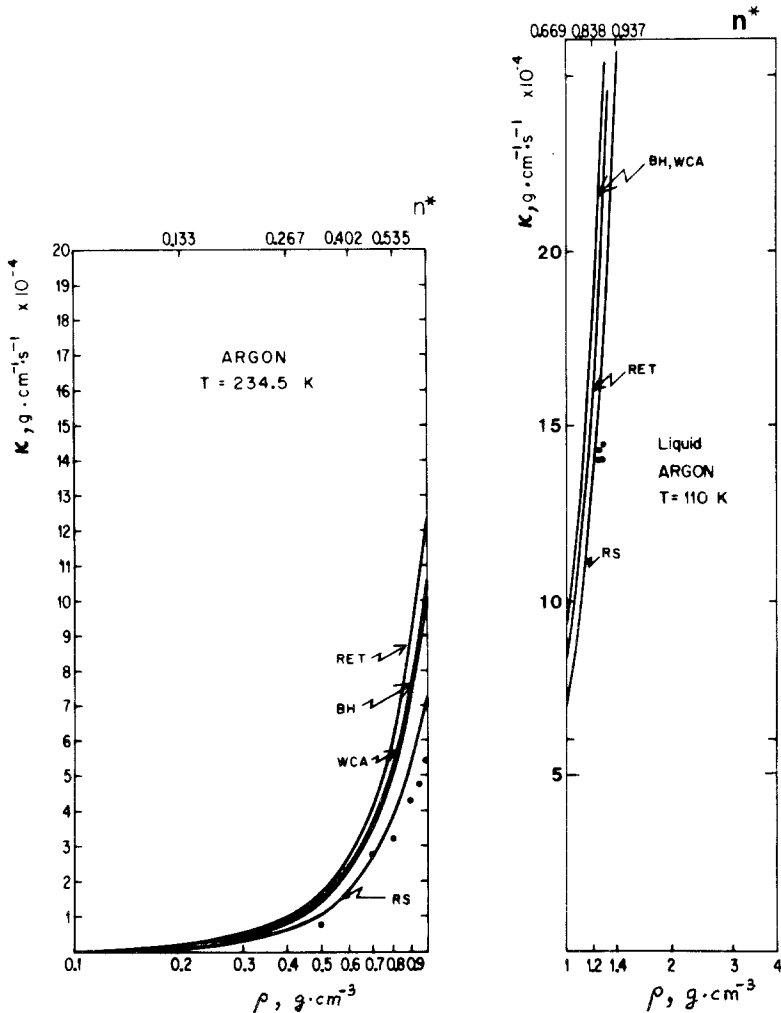


Fig. 1. Comparison of theoretical (solid lines) and experimental (filled circles) bulk viscosities as functions of mass density for dense argon at two temperatures. Here  $n^* = n_1\sigma_1^3 + n_2\sigma_2^3$  and  $\rho$  is the mass density. The RS, WCA, and BH theoretical curves reflect state-dependent diameters based upon the Lennard-Jones parameters  $\epsilon/k_B = 93.9$  K and  $\sigma_0 = 3.542$  Å.

Figure 2 shows the shear viscosity  $\eta$  of an equimolar argon-neon mixture at one temperature. The parameters employed for the neon are  $\epsilon/k_B = 32.8$  K and  $\sigma_0 = 2.82$  Å [1]. The RET is close to experiment but underestimates  $\eta$  at lower densities compared with the data of Kestin et al. [21]. We find that as in the case of a one-component fluid [3b], no

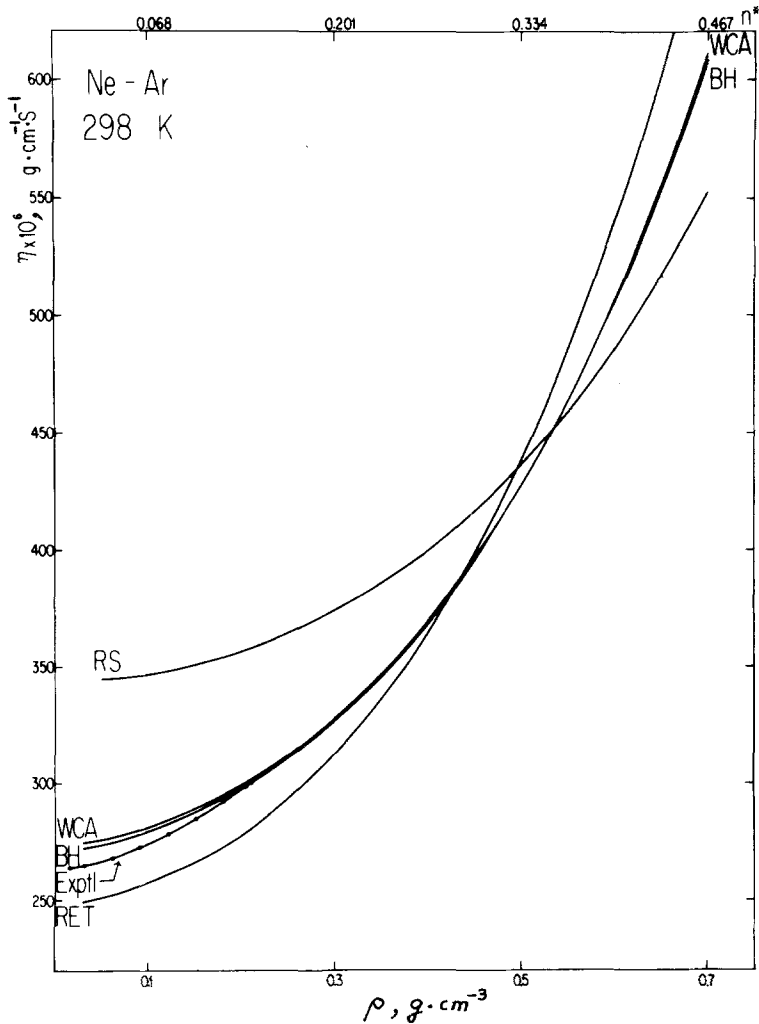
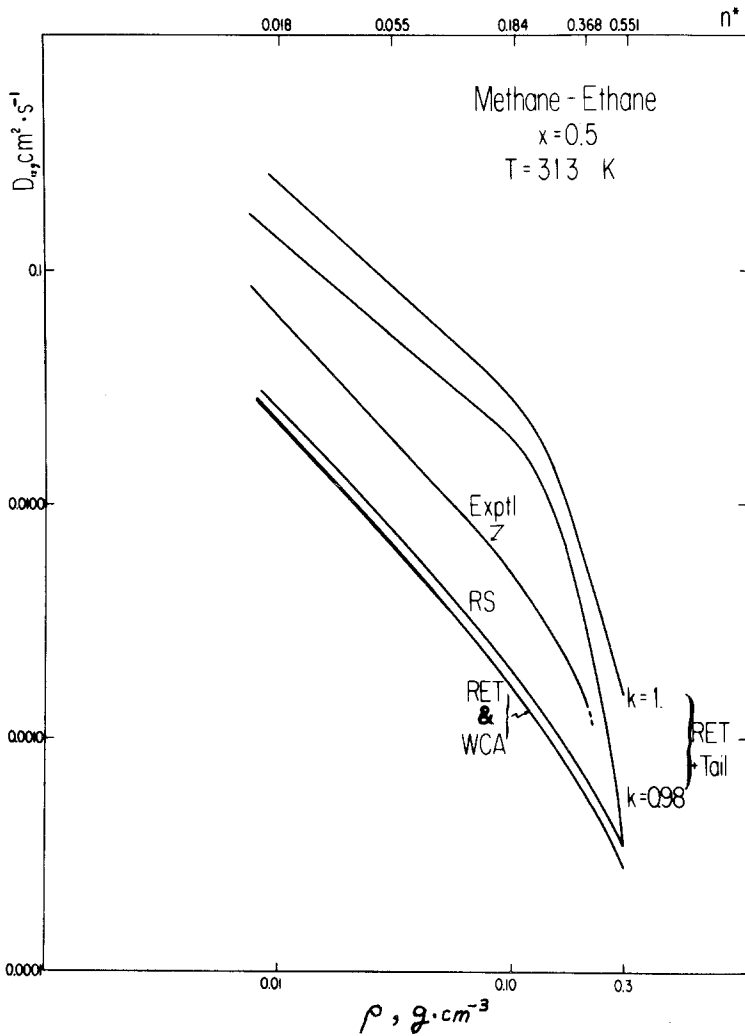


Fig. 2. Comparison of theoretical and experimental shear viscosities as functions of mass density  $\rho$  for an equimolar neon-argon mixture at  $T = 298$  K. The Lennard-Jones parameters for this system are  $\epsilon/k_B = 32.8$  K and  $\sigma_0 = 2.820$  Å for Ne and  $\epsilon/k_B = 93.9$  K and  $\sigma_0 = 3.542$  Å for Ar.

criterion for the effective diameter is to be preferred at all densities. At low densities the RS/MC seems to yield too high values, while the other criteria get closer to the data. At higher densities no definitive statement can be made due to the lack of experimental points.

In Fig. 3 the mutual diffusion coefficient  $D_{12}$  of a methane-ethane





**Fig. 3.** Comparison of theoretical and experimental mutual diffusion coefficients as functions of mass density  $\rho$  for an equimolar methane-ethane mixture at  $T=313 \text{ K}$ . The label RET + tail denotes the KVT results. The effect of the attractive tail is shown for two values of the parameter  $k$  entering into the modified Lorentz-Berthelot mixing rule. The Lennard-Jones parameters used in the calculation are  $\epsilon/k_B = 148.6 \text{ K}$  and  $\sigma_0 = 3.758 \text{ \AA}$  for Me and  $\epsilon/k_B = 215.7 \text{ K}$  and  $\sigma_0 = 4.443 \text{ \AA}$  for Et.

mixture is shown. The parameters used are  $\varepsilon/k_B = 148.6$  K and  $\sigma_0 = 3.758$  Å for methane and  $\varepsilon/k_B = 215.7$  K and  $\sigma_0 = 4.443$  Å for ethane [1]. For this mixture the RET is definitely too far below the experimental values. The effective diameter prescriptions improve the situation very little, with the RS/MC being the best one. This is not very surprising since one expects that  $D_{12}$  would depend strongly on the attractive tail. That this might be the case is suggested by our calculations with the KVT [Eq. (6b)]. We find that the inclusion of the tail substantially increases the theoretical values of  $D_{12}$ . With the Lorentz–Berthelot rule, the values obtained overestimate it with respect to the experimental data [1, 22]. If the value of  $k$  is lowered, the theoretical results come dramatically closer to the experimental ones. There is no a priori rule to set a  $k$  in Eq. (13). A change of as much as 25% in  $D_{12}$  may take place when  $k$  is varied 2% at intermediate densities. Without any basic theoretical insight about the nature of the modified mixing rule, we can say only that this point deserves further investigation.

In summary, these results, although preliminary, are encouraging and show that the procedure we have followed requires very little input while still yielding reasonably accurate predictions. Therefore, it might be worth considering as a real correlation scheme. A detailed comparison of this method with other correlation schemes, such as those of Ely and Hanley [23] and Najafi et al. [24], for real mixtures is presently under way. Extensions and refinements of the theory are also being considered.

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