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THE THERMAL CONDUCTIVITY OF DENSE FLUIDS AND THEIR MIXTURES USING THE EFFECTIVE DIAMETER REVISED ENSKOG THEORY

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A method for calculating the thermal conductivity of dense fluids and their mixtures is described. This method relies on the results of the revised Enskog theory for hard-sphere fluid mixtures, and the use of the temperature and density dependent diameters given by Mansoori and Canfield, and Rasaiah and Stell. In addition, a correction in order to take into account the internal degrees of freedom contribution was introduced. A comparison with the conformal solution model, and with accurate experimental data was made. A very good agreement was found.

1. Introduction

In recent years, there has been an increasing demand from industry for transport properties information of fluid mixtures, and in particular for thermal conductivity (λ). However, it is clear that the acquisition of reliable data for the great variety of mixtures and thermodynamic states can never be achieved in a satisfactory way by direct measurements only. There are two ways out, mainly in engineering calculations, to fulfill this gap of information. The first one uses empirical correlation schemes. These usually are limited to narrow ranges of temperatures and pressures and often mainly designed for pure fluids. A review of these methods are given in Reid et al. [1].

The second way involves the use of predictive methods more or less related to kinetic theory. In this case, the prediction of transport properties is more reliable if the method adopted is founded on a realistic physical model of the fluid mixture, and if it is combined with a suitable theory. Even when neither models nor the theories are exact, it is possible to give reasonably accurate results depending little on measurements or empirical prescriptions.

In predictive methods there are two groups of procedures for obtaining λ's in the dense regime. The first one is mainly based on the conformal solution model (CSM), which is related to the corresponding-states principle. The best suited method for the prediction of λ on non-polar fluid mixtures over the entire range of PVT states was given by Ely and Hanley [2]. They realized this method using a state equation, and a λ surface for a reference fluid (methane). Although some additional corrections are required in order to include the internal degrees of freedom contribution, and deviations from the corresponding states model, this method has good predictive features (for details see refs. [2] and [3]).

The other group of procedures mainly used for predicting λ's for dense fluids is related to the kinetic theory of hard spheres developed by Enskog [4]. Some examples can be found elsewhere [5–8]. Here, one procedure follows the so-called modified Enskog theory [5] (MET), an ad hoc modification of the Enskog theory to include attractive intermolecular forces. Until quite recently [9] MET was generalized to the binary case, although its ability to predict λ's in binary mixtures has not been reported. Another procedure relies on the revised Enskog theory [10] (RET) combined with a prescription to obtain effective state-dependent hard-sphere diameters in terms of the parameters associated with the potential chosen to model actual systems. We call this approach the effective-diameter revised Enskog theory (EDRET). We will show in this paper that this procedure can be generalized to the binary case, in the same way as we did for other transport properties [11–14]. Here, the basic assumptions are three: (1) particles in the fluid mixture can be modeled by the Lennard–Jones potential. (2) The behavior of λ in this regime is mainly determined by the repulsive part of the interaction potential. (3) The hard-sphere expression for λ coming from the RET can give confident results if some prescription to obtain state-dependent effective diameters is used in order to reflect the somewhat soft repulsive part of the model potential.

The main purpose of this paper is to show the usefulness of EDRET to predict λ's of one-component fluids and their mixtures, and to present some comparison between our approach and the CSM. The paper is organized as follows: in section 2, we present the details of our method. In section 3, the numerical results are presented and compared with the CSM, and experimental data.

2. Theory

Our starting point is the set of coupled non-linear integro-differential equations for the hard-sphere single particle distribution functions given in the

RET, first derived by van Beijeren and Ernst [10]. Here, the two hard-sphere radial distribution functions are the same functionals of the number densities as the radial distribution functions of a binary mixture in nonuniform equilibrium. The RET equations can be solved by the use of the Chapman–Enskog solution method. The molecular fluxes and the transport coefficients for dense hard-sphere binary mixtures, up to the Navier–Stokes level, can be directly obtained on the basis of the procedure used in ref. [15].

Thermal conductivity in a binary mixture, λ, is defined through the following expression [16]:

$$J_q = -\lambda \frac{\partial T}{\partial r} - \rho T D_1^{\mathrm{T}} \frac{\partial \mu_1}{\partial r} , \tag{1}$$

where J_q is the heat flux, T is the temperature, ρ is the mass density, D_1^{T} is the thermal diffusion coefficient and μ_1 is the chemical potential of component 1.

Here, we must have a comment. Diffusion and heat conduction in a fluid mixture become inextricably coupled. In a uniform mixture, as time progresses in the course of an experimental determination, concentration gradients appear in the mixture and they themselves provide driving forces for opposing fluxes. Eventually, in a steady state thermal diffusive flux is exactly balanced by this back diffusive flux, so that there is no net molecular flow. Hence, to stress this fact experimentalists define two λ coefficients. The first one is λ_0, this is the thermal conductivity of a uniform mixture (no concentration gradients), and the second one is λ_∞, the thermal conductivity corresponding to a fluid in the steady state (no mass fluxes). Since many accurate experiments actually measure λ_∞, as in the transient hot-wire technique, we decided to calculate this quantity. The formal definition of λ_∞ for a binary mixture is given by [17]

$$J_q = -\lambda_\infty \frac{\partial T}{\partial r} \qquad (J_i = 0) , \tag{2}$$

where J_i is the mass flux for component i.

The explicit expressions for the linear transport coefficients in the RET were gathered and discussed in detail by Lopez de Haro et al. [15]. These will serve to us as a point of departure for the calculations presented in this paper. So, following their notation, the explicit expression for λ_∞ is

$$\begin{aligned} \lambda = {} & \tfrac{5}{4} k_{\mathrm{B}} \sum_{i=1}^{2} \left(1 + \frac{12}{5} \sum_{j=1}^{2} \rho b_{ij} M_{ij} M_{ji} \chi_{ij}^{\mathrm{c}}\right) \frac{n_i}{n} \left(a_1^{(i)} - \sum_{k=1}^{2} (1 - \delta_{kl})(d_{i,1}^{(l)} - d_{i,1}^{(l)}) d_k^{\mathrm{th}}\right) \\ & + \tfrac{4}{3} k_{\mathrm{B}} \sum_{i=1}^{2} \sum_{j=1}^{2} \left(\frac{2\pi m_i m_j k_{\mathrm{B}} T}{m_i + m_j}\right)^{1/2} \frac{n_i n_j \sigma_{ij}^4 \chi_{ij}^{\mathrm{c}}}{m_i + m_j} . \end{aligned} \tag{3}$$

Here, k_B is Boltzmann's constant, $\rho b_{ij} = 2/3\pi\sigma_{ij}$, $M_{ij} = m_i/(m_i + m_j)$, where m_i is the mass of the hard sphere of diameter σ_i, n_i is the number density of component i, and χ_{ij}^{c} is the pair distribution function at contact. The $a_1^{(i)}$ and $d_{i,1}^{(k)}$ are the coefficients that appear in the Sonine polynomial expansion of the one particle distribution function, in the so-called Nth Enskog approximation, i.e., when the first N Sonine polynomials are taken into account in the expansion. The $a_1^{(i)}$ and $d_{i,1}^{(k)}$ are determined from a set of linear equations (for details see ref. [15]). The coefficients d_k^{th} are given by the equations

$$\sum_{j=1}^{2} (d_{i,0}^{(j)} - d_{i,0}^{(l)})(1 - \delta_{jl})\boldsymbol{d}_j^{\mathrm{th}} = a_0^{(i)} \frac{\partial}{\partial \boldsymbol{r}} \log T \qquad (i \neq 1) \tag{4}$$

and

$$\boldsymbol{d}_j^{\mathrm{th}} = d_j^{\mathrm{th}} \frac{\partial}{\partial \boldsymbol{r}} \log T . \tag{5}$$

The evaluation of λ for a given set of $\{n_i\}$, $\{\sigma_i\}$, $\{m_i\}$ and T using eqs. (3)–(5), requires knowledge of χ_{ij}^{c}. An exact, explicit equation for χ_{ij}^{c} in terms of the number densities and the set of hard-sphere diameters is not available, but several approximate expressions already exist. In particular, the so-called Carnahan–Starling approximation [18] appears to be quite accurate when compared to molecular dynamics data.

In order to use eq. (3) to obtain numerical estimates of λ for real mixtures, a prescription to obtain state-dependent hard-sphere diameters in terms of the parameters associated with the potential chosen to model the actual systems is needed. As mentioned above, we considered that each component of the binary mixture is modeled through a Lennard-Jones potential

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

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

$$\sigma_{12} = \sigma_{21} = \tfrac{1}{2}(\sigma_1 + \sigma_2) . \tag{7}$$

The effective diameters can be obtained by several schemes well established in equilibrium liquid state theory. The most widely used schemes coming from a first order perturbation theory are those given by Barker and Henderson

(BH) [19], by Weeks, Chandler and Andersen (WCA) [20], and by Verlet and Weiss (VW) [21]. From the schemes coming from a variational theory, we have those given by Mansoori–Canfield [22] and Rasaiah–Stell [23] (MC/RS). All these schemes give a hard-sphere diameter depending on both temperature and density, except that given by BH that is temperature dependent only.

In order to obtain numerical estimates of λ's for actual fluids using EDRET, a correction to include the internal degrees of freedom contribution is needed. But, until now, there is no formal theory to handle transport properties of polyatomic dense fluids, although several attempts have appeared [24, 25] with a very limited success. In this paper we will follow an heuristic approach followed by some authors [5, 26], and suggested by a previous work of Mason and Monchick [27] on the basis of the Wang Chang–Uhlenbeck–De Boer theory [28]. This theory was developed by these authors to deal with the transport properties of polyatomic gases in the dilute regime. Mason and Monchick showed that the λ can effectively be separated into two parts: a part dealing with the transfer of thermal energy by the translational motion of the molecules, and a part dealing with the transfer of energy to the internal degrees of freedom of the molecules. Hence, we will assume that λ of a dense fluid can be split into a part due to the energy transfer by molecular motion and collisional transfer (λ'), given by EDRET, and a part due to the energy transfer associated with the internal degrees of freedom of the molecules (λ''). Thus,

$$\lambda = \lambda' + \lambda'' . \tag{8}$$

In addition, we assume that λ'' for the one-component fluid can be represented by the first order approximation formula given by Mason–Monchick for quasi-elastic collisions [5]:

$$\lambda'' = \rho D C_V''/M = \lambda_0''/\chi^{c} , \tag{9}$$

where D is the self-diffusion coefficient, and λ_0'' is the internal contribution to λ for the dilute hard-sphere gas, C_V'' is the molar heat capacity at constant volume for the internal degrees of freedom, and M is the molecular weight.

For the case of the binary mixture the evaluation of λ'' has not been explored from the point of view of kinetic theory. Hence, a mixing rule is the only way out. This rule should keep a close analogy with eq. (9) in order to have a fair density dependence. Hence, we modified the empirical mixing rule given by Li [29]:

$$\lambda''_{\mathrm{mix}}(\rho, T, x_i) = \left(\sum_{i=1}^{2} \sum_{j=1}^{2} x_i x_j \lambda''_{ij}\right) \Big/ \chi^{c}_{12}(\rho, T, x_i) , \tag{10}$$

where

$$\lambda''_{ij} = \tfrac{1}{2}[(\lambda''_{0i})^{-1} + (\lambda''_{0j})^{-1}]^{-1} . \tag{11}$$

Here, λ''_{0i} is the internal contribution to thermal conductivity of component i in the dilute regime.

In order to obtain a general formula for the evaluation of λ''_0 or λ''_{0i}, given by eqs. (9) or (11), we use the modified Eucken correlation for polyatomic gases:

$$\lambda''_{0i} = f_{\text{int}}(C^0_{p,i} - \tfrac{5}{2}R)\eta_{0i}/M_i , \tag{12}$$

where η_{0i} is the dilute gas viscosity, $C^0_{p,i}$ is the ideal gas molar heat capacity, R is the gas constant, M_i is the molecular weight of component i, and f_{int} has a constant value of 1.32.

$C^0_{p,i}$ values for different systems were obtained through a temperature expansion up to 6th order, except for the noble gases where the internal contribution was not considered (actually we used the expansions that appear in the TRAPP computer program developed by Ely and Hanley [3]).

3. Numerical results and discussion

Values of λ for several one-component fluids (noble gases, N_2, O_2, CO_2, and some hydrocarbons), and some of its mixtures were calculated following the method described above, i.e., λ's were calculated through eq. (3), and the state-dependent hard-sphere diameters were determined with the MC/RS scheme. For one-component fluids we used eq. (3), but in the form given in the standard Enskog theory [4]. The Lennard-Jones parameters were obtained from ref. [1], except for the case of argon that will be mentioned below.

Our calculations were done in the dense regime mainly, i.e. at reduced densities (ρ_r, density/critical density) greater than 1.1, and at several temperatures. Figs. 1–5 are some examples of these calculations.

In a previous work, Karkheck and Stell [30] compared λ calculations for argon, xenon, and oxygen using the prescriptions to obtain the hard-sphere diameter mentioned above, except for the VW one, with experimental data along the liquid saturation line. They concluded that the MC/RS prescription is the best suited for predicting λ's. We confirmed this conclusion for noble gases and some hydrocarbons using all the above mentioned prescriptions, but not limiting our calculations to the liquid saturation line. As an example we show fig. 1. Here, λ calculations for argon using different prescriptions to obtain the diameter are presented, and compared with the accurate correlation

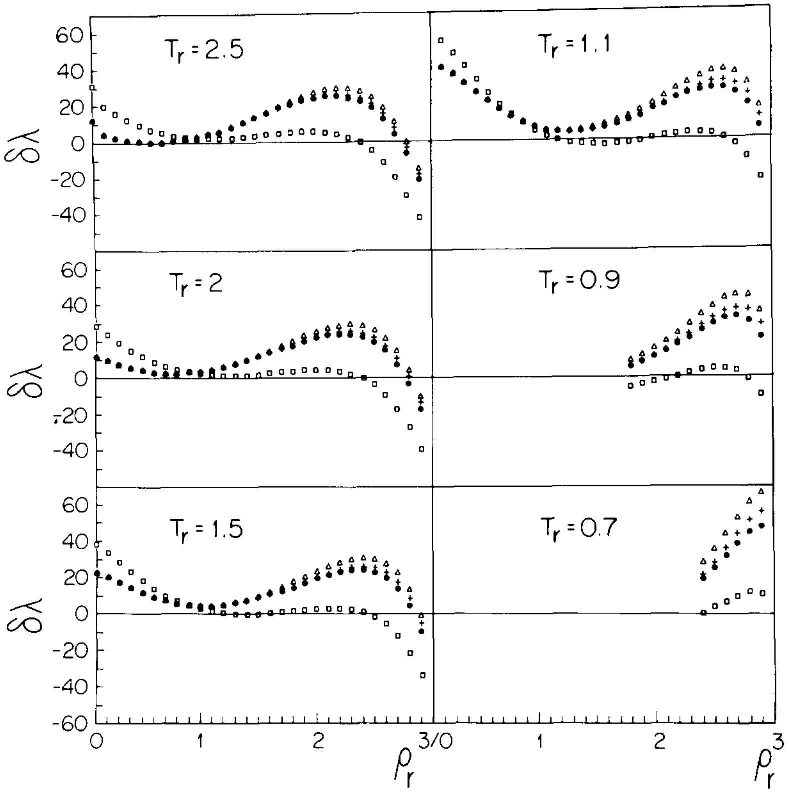

Fig. 1. Percent deviation for predicted λ's from experimental data, $\delta\lambda$, versus the reduced density, ρ_r, for six different reduced temperatures, and several prescriptions to obtain the state-dependent hard-sphere diameters. (□) MC/RS; (+) BH; (●) WCA; (△) VW.

of Younglove and Hanley [31] (Lennard-Jones parameters, $\sigma = 3.405$ Å, $\varepsilon/k = 119.8$ K), along the phase diagram. As we can see, our procedure increasingly overestimates λ as we progressively go to lower reduced densities. At lower densities (below $\rho_r \approx 0.7$) the other schemes to obtain the hard-sphere diameter (BH, WCA and VW) are better to fit the experimental data. At higher temperatures they become more accurate. This is not surprising because these schemes were built to fit the low density equilibrium properties, whereas the MC/RS scheme was directed toward the denser regimes. The important point to emphasize is that since the crossover occurs at a reduced density of about 0.7, our recommendation is that one uses the other schemes from reduced densities below 0.7 and the MC/RS scheme from 0.7 onwards. The general conclusion is: the MC/RS prescription gives better predictions in a wide range of fluid reduced densities ($\rho_r \approx 0.7$–2.7 at $T_r > 1$), and at liquid densities

($T_r < 1$). This is in close agreement with our previous work in other transport properties [8, 11–14].

When a comparison is made between our λ calculations, and accurate experimental data for nitrogen, methane, ethane, and ethylene, we found a better agreement in the denser or liquid region of the phase diagram than in the moderate or low density one, confirming the conclusions given for the case of argon.

Figs. 2 and 3 show λ for liquid nitrogen and ethylene respectively, along the saturation line. Here, we compare our procedure, the CSM, and experimental data [32, 33]. In a general way, we can say that our calculations are closer to the experimental data than CSM. On the other hand, in these figures we can see that the internal degress contribution as implemented above is less important as density increases. This agrees with previous results where the role of this contribution has been discussed [34].

Figs. 4 and 5 show λ for mixtures. Fig. 4 shows a nitrogen/oxygen mixture ($X_{N_2} = 0.78569$, $X_{O_2} = 0.21431$, $\rho = 0.6\ g/cm^3$). Here, λ calculations are compared with CSM, and with experimental data for air [35], at several temperatures. As we can see in this figure, EDRET without the internal degrees contribution gives a better fitting to the experimental data than CSM. If we include the internal degrees contribution to EDRET, we have a better fitting to the experimental data at lower temperatures, but at high temperatures our procedure overestimates λ around 15%.

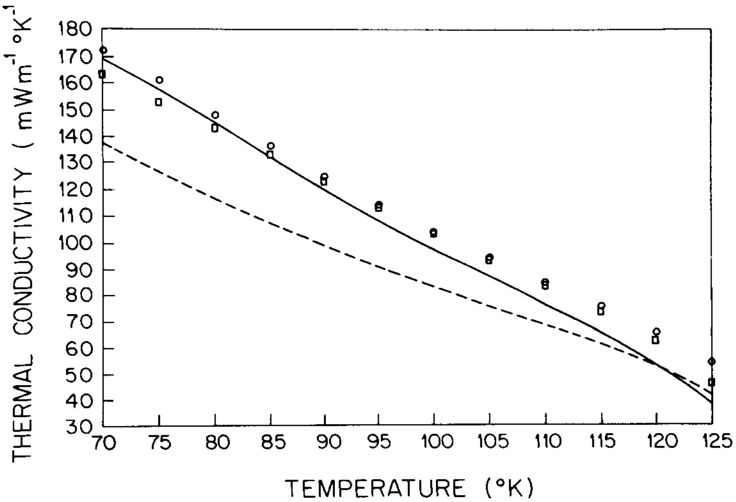

Fig. 2. Thermal conductivity, λ, of liquid nitrogen versus temperature, at the saturation line. (□) experimental; dashed line, CSM; solid line, EDRET without the internal degrees correction; (○) EDRET with the internal degrees correction.

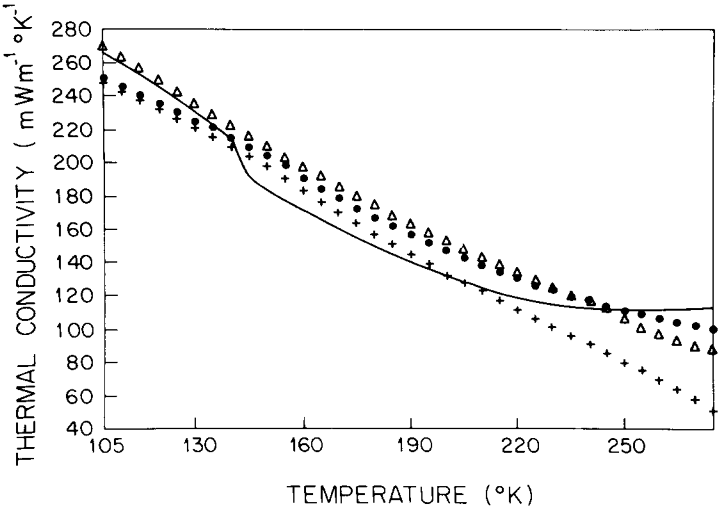

Fig. 3. Thermal conductivity, λ, of liquid ethylene versus temperature, at the saturation line. (△) experimental; solid line, CSM; (+) EDRET without the internal degrees correction; (●) EDRET with the internal degrees correction.

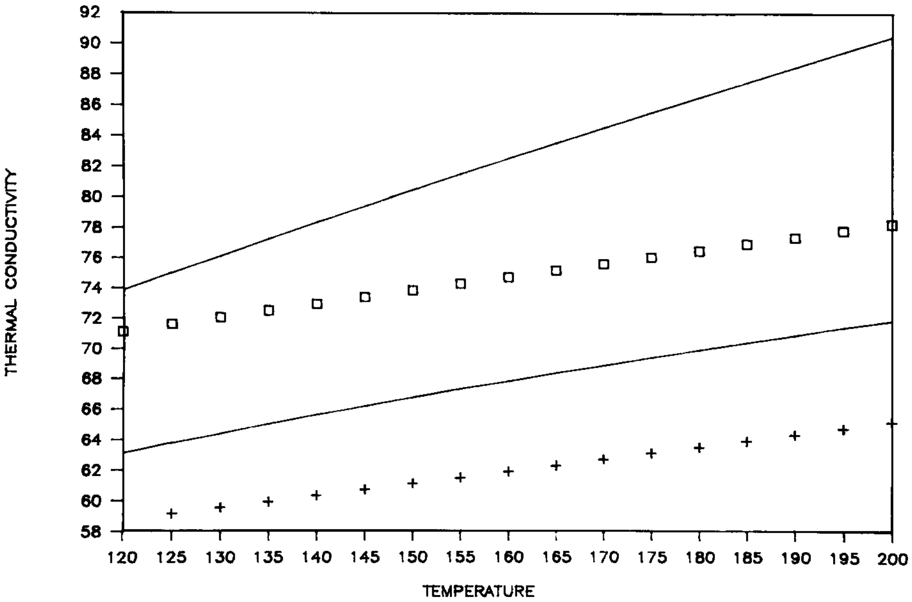

Fig. 4. Thermal conductivity of air at 0.6 g cm^{-3} versus temperature. (□) experimental; (+) CSM; lower solid line, EDRET without the internal degrees correction; upper solid line, EDRET with the internal degrees correction.

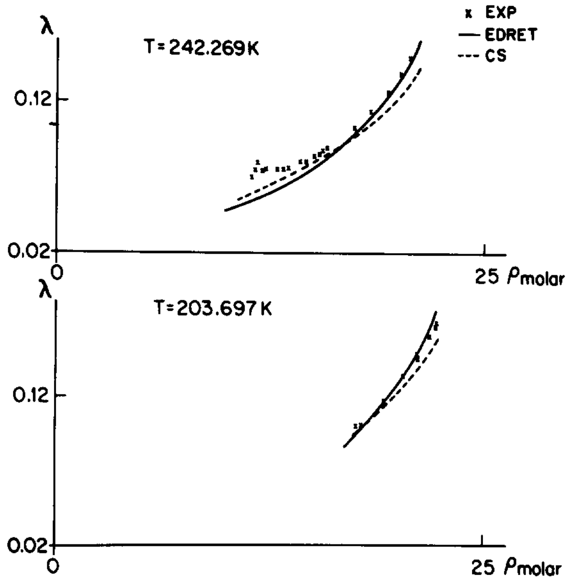

Fig. 5. Thermal conductivity in W m^{-1} K^{-1}, of a mixture of methane/ethane (X_{CH} = 0.68526) versus the molar density.

In fig. 5, we show two examples of our λ calculations for the methane/ethane mixture ($X_{\mathrm{CH_4}}$ = 0.68526). These calculations were done at two different temperatures, 242.269 and 203.697 K. The experimental data come from ref. [36]. As we can see in this figure, our procedure gives a better fitting to the experimental data than CSM. The major deviation occurs near the critical point, since our procedure at its present form cannot evaluate critical enhancement. Although, the existence of critical enhancement in mixtures is under discussion yet [36, 37]. At higher temperatures ($T > T_c$), not shown in this figure, our procedure underestimates λ's, and in the high densities is better than CSM, but not at values around the critical density. For lower densities, until experimental data let us make comparisons, both methods underestimate λ by a few per cent.

The lack of accurate experimental data for several mixtures, along wide ranges of densities and temperatures, do not permit a major test for our procedure. Although it is promising, a more stringent test is needed.

In summary, the above results are encouraging since the described procedure has quite good predictive features with very little input (the *L-J* parameters and the C_p^0's), and it is an alternative method to the CSM as implemented in the TRAPP computer program [3], that has a lot of experimental information included.

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