

The Thermal Conductivity of Dense Fluids Using Revised Enskog Theory

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A predictive method designed to obtain the thermal conductivities of one-component dense fluids is described. This method is based on the revised Enskog theory. Here, an effective state-dependent hard-sphere diameter is used to obtain the hard-sphere diameter needed by the revised Enskog theory in order to deal with actual fluids. In addition, we introduce the contribution of the internal degrees of freedom through the Mason–Monchick procedure. Our predictions for noble gases and hydrocarbons, at high density, are compared with predictions coming from the conformal solution model, with empirical correlation schemes, and with experimental data. A very satisfactory agreement is found.

KEY WORDS: dense fluid; Enskog theory; kinetic theory; thermal conductivity.

1. INTRODUCTION

The need for accurate values of transport properties for working fluids in industrial and research problems is well established. In the same way it is clear that the acquisition of transport properties data for the great variety of compounds in all the needed thermodynamic states can never be achieved by direct measurements only. Hence, the development of predictive methods is a partial solution to this problem.

One way to obtain predictive values of thermal conductivity, λ , in the dense regime is through the use of empirical correlation schemes [1], but these are quite limited and usually designed to correlate pure fluid properties only. Another way is through the use of the conformal solution model based on an extended corresponding states principle. This method was developed by Ely and Hanley [2] with good success. In order to make this procedure applicable to actual fluids, these workers postulated that the λ

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of pure substances can be divided into two contributions. One arises from the transfer of energy from purely collisional or translational effects and is calculated through the conformal solution model (CSM). The basic assumptions of CSM are three: (1) the transport property of a fluid at some density and temperature can be equated to the transport property of a hypothetical pure fluid, (2) the transport property of the hypothetical pure fluid may be evaluated via a corresponding states principle, and (3) the reference fluid densities and temperatures may be evaluated through an extended corresponding states principle (for details see Ref. 2). The other contribution considered by Ely and Hanley [2] comes from the transfer of energy via the internal degrees of freedom. They used a modified Eucken correlation for polyatomic gases and assumed that this contribution is independent of density. The whole procedure has the additional advantage that it can be generalized to binary systems with good success.

Another way to obtain λ 's for actual dense fluids is based on the kinetic theory developed by Enskog. Here, one procedure follows the so-called modified Enskog theory (MET) [3], an ad hoc modification of Enskog theory to include attractive intermolecular forces. Until quite recently [4], 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 (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 (effective diameter revised Enskog theory, or EDRET). This procedure has been used to predict other transport properties than λ , and has been generalized to the binary case [5-8]. In this paper, we present the results of our calculations to obtain λ 's for pure fluids using this approach. In addition, a comparison with the conformal solution model and with empirical correlation schemes is presented, as well as some comparisons with accurate experimental data. In a forthcoming paper we will present the generalization of this procedure to binary systems and its associated problems.

The paper is organized as follows: in Section 2 we present the details of our procedure and in Section 3 we present our numerical results for noble gases, oxygen, carbon dioxide, and some hydrocarbons, all in the dense regime. In Section 4 we present a discussion and some concluding remarks.

2. THEORY

Until now, there has been no formal theory to handle transport properties of polyatomic dense fluids, although several attempts have

appeared [9, 10] with a very limited success. In this paper we will use an heuristic approach followed by some authors [3, 11] and suggested by a previous work of Mason and Monchick [12] on the basis of the Wang Chang-Uhlenbeck-De Boer theory [13] in order to deal with polyatomic gases in the dilute regime. Here, 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 assume that λ of a dense fluid can be split into a part (λ') due to the energy transfer by molecular motion and collisional transfer, as in the monoatomic dense fluid, and a part (λ'') due to the energy transfer associated with the internal degrees of freedom of the molecules. Thus

$$\lambda = \lambda' + \lambda''$$

In addition, we assume that λ'' can be represented by the first-order approximation formula given by Mason-Monchick for quasielastic collisions:

$$\lambda'' = \rho DC_v''/M = \lambda_0''/\chi \quad (1)$$

where D is the self-diffusion coefficient and λ_0'' is the internal contribution to λ for the dilute hard-sphere gas. χ is the hard-sphere radial distribution function at contact, ρ is the mass density, C_v'' is the molar heat capacity at constant volume for the internal degrees of freedom, and M is the molecular weight.

In order to obtain a general formula for the evaluation of λ_0'' we use the modified Eucken correlation for polyatomic gases:

$$\lambda_0'' = f_{\text{int}}(C_p^0 - 5/2R) \eta_0/M \quad (2)$$

where η_0 is the dilute gas viscosity, C_p^0 is the ideal gas molar heat capacity, R is the gas constant, and f_{int} has a constant value of 1.32.

For λ' , we assume that it can be obtained through the Enskog theory expression:

$$\lambda' = 1/\chi [1 + 1.2(2\pi n\sigma^3\chi/3) + 0.755(2\pi n\sigma^3\chi/3)^2] \lambda_0 \quad (3a)$$

where λ_0 is given by

$$\lambda_0 = \frac{75k}{64\pi\sigma^2} \left(\frac{\pi kT}{m} \right)^{1/2} \quad (3b)$$

In these expressions, n is the number density, σ is the hard-sphere diameter, T is the absolute temperature, and k is Boltzmann's constant.

We need to comment at this point that Eq. (3) can be obtained within the framework of the standard Enskog theory (SET) [14]. Although SET is an inconsistent theory, for the case of the one-component fluid the λ formulas are the same as in the corrected theory, i.e., the revised Enskog theory (RET) [15]. In addition, for the one-component fluid, these expressions for λ in the RET are the same as the equations derived with the kinetic variational theory I (KVT I) [16] for a system of particles interacting through the van der Waals potential, i.e., by a hard-core plus an infinitely long-ranged and shallow attractive potential (Kac potential).

The evaluation of Eq. (3) requires the knowledge of χ , σ , and C_p^0 . For χ , we used the approximate expression of Carnahan and Starling [17], since it appears to be quite accurate when compared to molecular dynamics data.

In order to obtain the molecular and collisional contribution for λ given by Eq. (3), we need a prescription to obtain a state-dependent hard-sphere diameter in terms of the parameters associated with the potentials chosen to model actual systems. Following our previous work, we consider that the one-component fluid is modeled through the Lennard-Jones (L-J) potential, and we determine separately the effective diameters in terms of the original L-J parameters, and the thermodynamic state of the system.

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

In a previous work, Karkheck and Stell [23] compared λ calculations for argon, xenon, and oxygen with experimental data along the liquid-vapor saturation curve, using the prescriptions pointed above, except the VW case, and they concluded that for λ calculations the MC/RS prescription is the best suited. We confirmed this conclusion for noble gases and some hydrocarbons using all the above-mentioned prescriptions, but not limiting our calculations to the liquid-vapor saturation curve. An example is Fig. 1, where λ calculations using different prescriptions to obtain the diameter are presented and compared with accurate measurements of λ in argon [24] (Lennard-Jones parameters $\sigma = 3.405 \text{ \AA}$, $\epsilon/k = 119.8 \text{ K}$). In order to do the visual comparison more easily, our

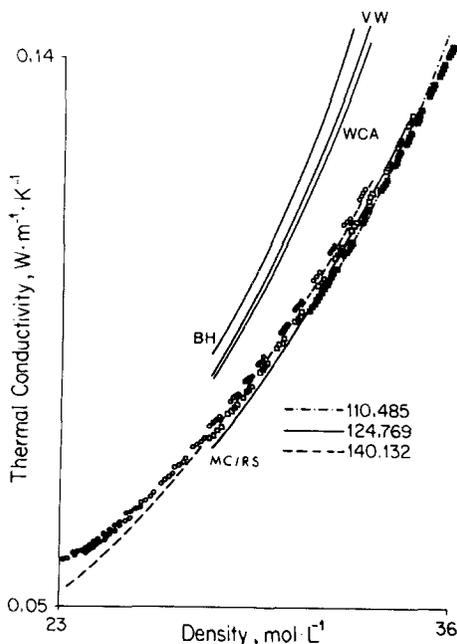


Fig. 1. Predicted values for the thermal conductivity, λ , of argon using the MC/RS prescription to obtain the state-dependent hard-sphere diameters. For comparison at 124.769 K, the predicted values using the BH, VW, and WCA prescriptions are presented. The experimental data are from Ref. 24. (■) 110.485 K; (□) 124.769 K; (●) 138.775 K; (○) 140.132 K.

numerical calculations with all the prescriptions are presented at 124.769 K only, although the trend for other temperatures follows the same behavior. The general conclusion is that the MC/RS prescription gives the best predictions, which is in close agreement with our previous work on other transport properties [5–8]. Also, we include in this figure calculations at other temperatures using the MC/RS to show its predictive abilities.

C_p^0 values for different systems were obtained through a temperature expansion up to sixth 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 [25]).

3. NUMERICAL RESULTS AND DISCUSSION

Values for the λ of several one-component fluids (noble gases, CO_2 , O_2 , and alkanes) were calculated following the method described above, i.e., λ 's were calculated through Eq. (1)–(3) with the MC/RS scheme to fix the state-dependent hard-sphere diameter. The L–J parameters were obtained from Ref. 1, except for the case of argon mentioned above.

Our calculations were in the dense regime, i.e., at reduced densities (ρ_r , density/critical density) greater than 1.1, and at several temperatures. Figures 2, 3, and 4 are examples of these calculations. In order to present some comparisons, we show in the same figures calculations using the CSM (we used the TRAPP computer program [25]). The lack of accurate experimental λ 's in wide ranges of the high-density regime and at several temperatures is a drawback. Hence, in some of the figures we use values obtained from the semiempirical correlation scheme of Stiel and Thodos [1, 26] instead of the experimental data, although an accuracy probably no better than 10 to 20% should be expected. This correlation needs values for λ at low density. We followed Bromley's formula as given in Ref. 1.

Figure 2 shows the λ of liquid methane at several temperatures and reduced densities. Here we compare our procedure and the CSM against accurate experimental data [27]. Our calculations are closer to the

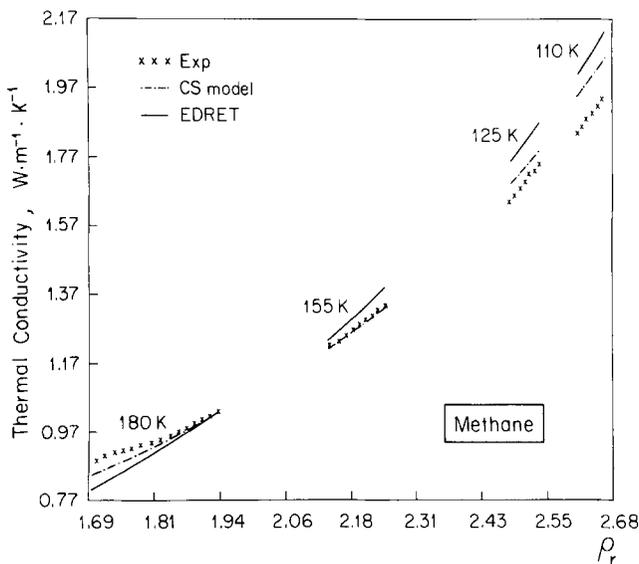


Fig. 2. Predicted values for the thermal conductivity, λ , of methane at different temperatures and reduced densities, ρ_r , using EDRET and CSM. The experimental data for comparison are from Ref. 27.

experimental data as the temperature is increased and are around 10% higher at the worst case (low temperatures). As the temperature increases, our procedure goes from overestimating to underestimating the λ for methane. The same occurs to the CSM, although its fitting is a few percent better than our method.

Figure 3 shows the λ for krypton, oxygen, and CO_2 , and Fig. 4 does the same for ethane, propane, and pentane, in the fluid state at $T = 1.1 T_c$ in all cases. For krypton we observe that our method overestimates and the CSM underestimates, with respect to the Stiel and Thodos correlation, from a few percent to more than 10% at high densities. For the other cases

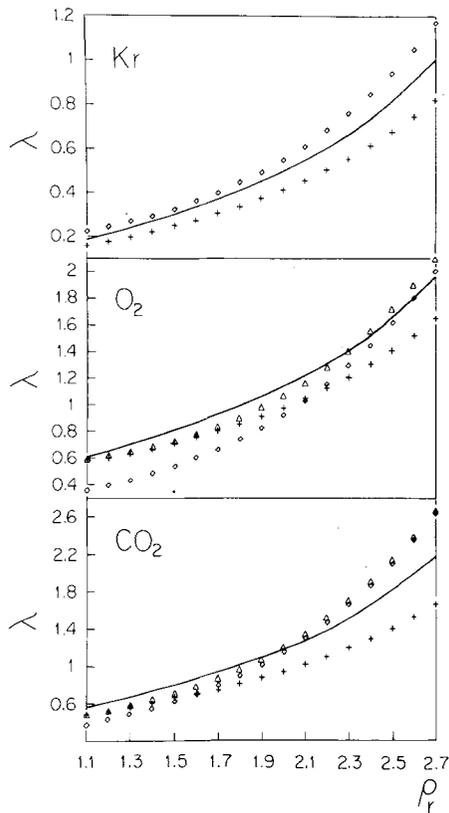


Fig. 3. Thermal conductivity, λ ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$), of Kr, O_2 , and CO_2 vs the reduced density, ρ_r . (—) Empirical correlation of Stiel and Thodos; (+) CSM. (◇) EDRET without internal degrees contribution [Eq. (3)]. (Δ) EDRET with internal degrees contribution [Eqs. (1) and (3)].

the fitting of our procedure is quite good and at some densities is better than the CSM, although this must be taken with care since the Stiel and Thodos correlation value is not obtained from experimental data and has a quite uncertain accuracy. In the worst case at very high densities the deviation of our procedure from the CSM may be of the order of 50%, and usually the semi-empirical correlation value lies between these two ends. Another thing that can be followed in these figures is the contribution of the λ associated with the internal degrees of freedom, λ'' . We can see how this contribution becomes less important as the density increases. This agrees with previous results [28].

We need to comment at this point. When a comparison was made

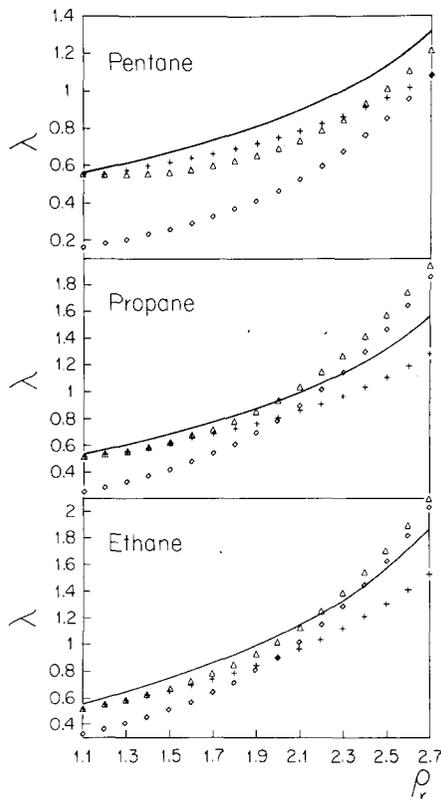


Fig. 4. Thermal conductivity, λ ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$), of pentane, propane, and ethane vs the reduced density, ρ_r . (—) Empirical correlation of Stiel and Thodos; (+) CSM. (\diamond) EDRET without internal degrees contribution [Eq. (3)]. (\triangle) EDRET with internal degrees contribution [Eqs. (1) and (3)].

between calculations for λ using EDRET with the MC/RS scheme to obtain the hard-sphere diameter, and accurate experimental data for λ in argon, 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. In particular, for argon our procedure increasingly overestimates λ as we progressively go to lower reduced densities (experimental data from Ref. 29). But at lower densities, around 0.7, the other schemes to obtain the hard-sphere diameter mentioned above (BH, WCA, and VW) better fit the experimental data. At high 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 use the other schemes for reduced densities below 0.7 and the MC/RS scheme for 0.7 and above. Another point to mention is that in the low-density limit, MET and EDRET can give different predictions for λ due to the different effective diameters actually used in both theories, since MET reduces to RET in this limit.

In summary, the above results are encouraging since the described procedure has quite good predictive properties with very little input (the L-J parameters and the C_p^0 and it is an alternative method to the CSM as implemented in the TRAPP computer program, which has a lot of experimental information included. In addition, our procedure has an additional advantage: since it preserves in some detail its kinetic theory foundation, it is able to be generalized to multicomponent mixtures. This will be discussed in a forthcoming paper [30].

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