Calculation of dense fluid transport properties via equilibrium statistical mechanical perturbation theory*

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The viscosity and thermal conductivity coefficients of dense fluid argon have been calculated using the modified Enskog theory and the equilibrium statistical mechanical perturbation theory of Barker and Henderson. Agreement with experimental transport data is shown to be, in general, quite good. The results of these calculations are also compared to those obtained using the modified Enskog theory and an experimental equation of state. In this case, the results are seen to be excellent, which indicates that this approach provides us with a method of predicting transport properties of simple dense fluids from fundamental molecular theory.

I. INTRODUCTION

In the derivation of the Boltzmann equation, there are two primary assumptions made: (1) Only binary collisions are important, and (2) the molecular diameter of the molecules, σ, is small compared to the mean free path of the gas. Both of these assumptions are applicable to a dilute gas but not to a dense system. As the density of the system is increased, two effects become important because the molecules have a nonzero size. The first of these two effects can be associated with a positional correlation, which will appear in the form of the radial distribution function, $g(r)$. Since $g(r)$ is greater than unity when the molecules are close together, i.e., when $r \approx \sigma$, there is an increase in the rate of collisions. Secondly, collisional transfer of flux becomes important. In a dilute gas, the most important mechanism for the transport of flux is the movement of a molecule through a plane. In a dense system, on the other hand, it is possible for a molecule on one side of a plane to collide with a molecule on the other side of the plane and transfer some momentum or energy even though neither molecule actually crosses through the plane. This manner of flux transport is called collisional transfer. Of course, this mechanism is also present in dilute gases, but it does not become important until the density becomes large. In liquids, in fact, collisional transfer of flux is more important than molecular transfer.

Enskog has modified the Boltzmann equation in an approximate manner to include the above effects.[1,5] The two main factors that distinguish the Enskog theory from the Boltzmann equation are that the frequency of collisions in a dense system is greater than in a dilute gas, and that collisional transfer of flux is accounted for.

II. THEORY

The results of the Enskog theory that we shall use here are that[1,5]

$$\eta/\eta_0 b_0 \rho = 1/Y + 0.800 + 0.761 Y \tag{1}$$

and

$$\lambda/\lambda_0 b_0 \rho = 1/Y + 1.200 + 0.755 Y . \tag{2}$$

In the first of the two equations, η represents the viscosity of the hard sphere fluid, η_0 the viscosity of a dilute hard sphere gas, $b_0 = 2\pi\sigma^3/3$, where σ is the hard sphere diameter, and $Y = b_0 \rho g(\sigma)$, where ρ is the number density and $g(\sigma)$ is the two-body hard sphere radial distribution function at contact. This last quantity is related to the hard sphere equation of state by[2]

$$p/\rho k T = 1 + b_0 \rho g(\sigma) . \tag{3}$$

In addition, the first approximation of the Chapman–Enskog theory gives[5]

$$\eta_0 = \frac{5}{16} \frac{(\pi m k T)^{1/2}}{\pi\sigma^2 \Omega^{(2,2)*}} , \tag{4}$$

where $\Omega^{(2,2)*}$ is the reduced viscosity collision integral which is unity for hard spheres.

In Eq. (2), λ and λ_0 are the thermal conductivity of the dense hard sphere fluid and the dilute gas, respectively. In this case[5]

$$\lambda_0 = \frac{25}{32} \frac{(\pi m k T)^{1/2}}{\pi\sigma^2 \Omega^{(2,2)*}} \left(\frac{C_v}{m}\right) , \tag{5}$$

where C_v is the constant volume specific heat for the translational degrees of freedom and $\Omega^{(2,2)*}$ is unity.

The molecular dynamics rigid sphere transport coefficients have recently been calculated by Alder, Gass, and Wainwright.[3] They identify the first terms in Eqs. (1) and (2) with the kinetic contribution, the third term with the potential contribution, and the middle terms with a cross term contribution. These are all presented separately in their paper, and one can see from there that the agreement with molecular dynamics results is quite good except for densities approaching the solid phase $(v/v_0 \approx 1.5)$.

In spite of the fact that the Enskog theory is strictly a rigid sphere theory, Enskog showed how the results could be applied to real systems.[1,5] He suggested that instead of relating Y to the actual pressure of the system through Eq. (3), i.e.,

$$Y = p/\rho k T - 1 , \tag{6}$$

one should introduce the so-called "thermal pressure," $T(\partial p/\partial T)_V$. The justification for this is that the pressure

experienced by a single molecule is made up of two parts, the external pressure, p, due to the walls of the container, and the "internal pressure," $(\partial E/\partial V)_T$, which represents the force of cohesion of the molecules. The sum of these is related to the thermal pressure by the thermodynamic relation

$$T(\partial p/\partial T)_V = (\partial E/\partial V)_T + p . \tag{7}$$

Therefore, we write for Y:

$$1 + Y = \frac{1}{\rho k T}\left[T\left(\frac{\partial p}{\partial T}\right)_V \right]$$

$$= \left(\frac{p}{\rho k T}\right) + T\frac{\partial}{\partial T}\left(\frac{p}{\rho k T}\right)_V = Z + T\left(\frac{\partial Z}{\partial T}\right)_V , \tag{8}$$

where we have introduced the compressibility factor Z. Hanley et al.[4] call this the modified Enskog theory (MET). Furthermore, since $Y/\rho \to b_0$ as $\rho \to 0$, we must have

$$b_0 = B(T) + T\, dB/dT , \tag{9}$$

where $B(T)$ is the second virial coefficient.

Equations (8) and (9), along with Eqs. (1) and (2) and the dilute gas expressions for η_0 and λ_0 completely specify the modified Enskog theory. One can calculate the transport coefficients of a dense real system from equation of state data alone. Tables 9.3-2 and 9.3-3 in Hirschfelder, Curtiss, and Bird[5] and the article by Hanley et al.[4] compare the modified Enskog theory to experiment. One can see from the results that in spite of the ad hoc nature of the theory, the agreement with experiment is quite good, especially when one compares the density variation of the transport coefficients at a fixed temperature.

In a series of papers, Dymond and Alder[6] have presented an alternate extension of the Enskog theory to real fluids. They argue on physical grounds that an effective hard core diameter can be found by plotting pv/kT vs $1/T$ at constant volume. Recall that the van der Waals equation can be written in the form

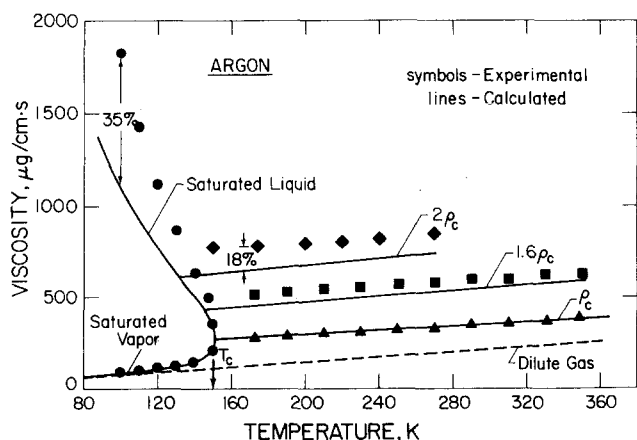$$\frac{pv}{kT} = \frac{v}{v-b} - \frac{a_1}{kTv} + \frac{a_2(v)}{T^2} + \cdots . \tag{10}$$

FIG. 1. Isochoric and saturated argon viscosity. The solid lines were calculated using Eqs. (8) and (9) and the statistical mechanical perturbation theory equation of state. The symbols represent smoothed experimental data taken from Ref. 12.
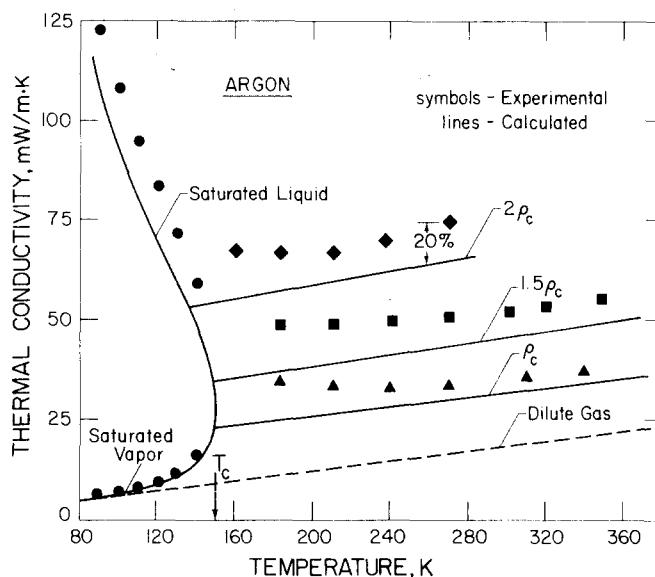

FIG. 2. Isochoric and saturated argon thermal conductivities in units of milliwatts per meter-°K. The lines were calculated using the same method as was used for the viscosity and the symbols represent smoothed experimental results taken from Ref. 12.

Equation (10) predicts that the intercept of a plot of pv/kT vs $1/T$ should lead to a straight line with an intercept at the hard sphere value of pv/kT. Knowing the molar volume v one can then determine an effective b_0, or hard sphere diameter, since $b_0 = 2\pi\sigma^3/3$. The value for σ should be independent of the density or v. This in fact turns out to be so. In practice, experimental data lie on a slight curve and the value of the intercept depends on the temperature at which the tangent to the curve is drawn. This means that the effective diameter σ is temperature dependent, but still density independent. In this way, one can obtain an effective hard core diameter as a function of temperature. The result of using this empirically determined quantity directly in the Enskog theory yields good agreement with experiment at high temperatures.

We present here a simple extension of the ideas of Dymond and Alder and use one of the statistical mechanical perturbation theory equations of state directly in place of using the van der Waals equation to analyze experimental pvT data. We arbitrarily choose the Barker-Henderson perturbation theory which under the macroscopic compressibility approximation[7] gives the following expression for the Helmholtz free energy:

$$\frac{A}{NkT} = \frac{A_0}{NkT} + 2\pi\rho\beta \int_\sigma^\infty g_d(y, r)u(r)r^2\, dr$$

$$- \pi\rho\beta\left(\frac{\partial\rho}{\partial p}\right)_0 \int_\sigma^\infty g_d(y, r)u^2(r)r^2\, dr . \tag{11}$$

In this equation A_0 is the Helmholtz free energy of a system of hard spheres with diameter d, $g_d(y, r)$ is the radial distribution function of the hard sphere system, $y = \pi\rho d^3/6$ and d is defined by the relation

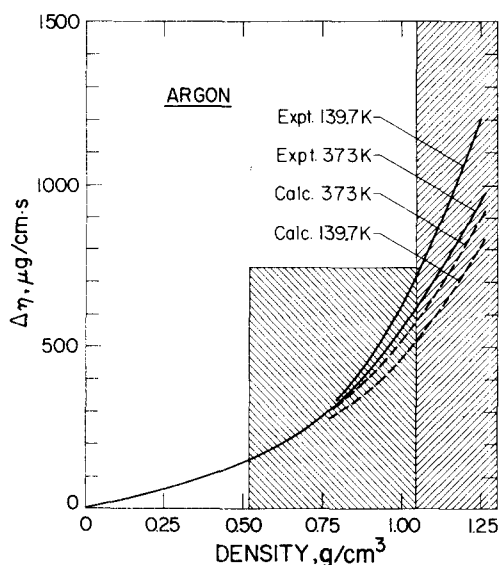$$d(T) = -\int_0^\sigma \left[e^{-u(r)/kT} - 1 \right] dr , \tag{12}$$

FIG. 3. Excess argon viscosity, $\Delta\eta = \eta - \eta_0$. The solid lines represent experimental results and the dashed lines show the corresponding calculations. The shaded regions denote the ranges $\rho_c - 2\rho_c$ and $2\rho_c$ and above.

where $u(r)$ is the intermolecular potential function. We find the compressibility factor Z from the thermodynamic relation

$$Z = \frac{p}{\rho kT} = \rho \left(\frac{\partial (A/NkT)}{\partial \rho} \right)_{N,T} = Y \left(\frac{\partial (A/NkT)}{\partial Y} \right)_{N,T} . \quad (13)$$

After defining the reduced quantities $d^* = d/\sigma$, $T^* = kT/\epsilon$, and $u^* = 4(x^{-12} - x^{-6})$, and going through some amount of algebra, we find the following theoretical expressions for $1 + Y$ and b_0 [cf. Eqs. (8) and (9)]:

$$1 + Y = Z_0(y) - \frac{Z_2(y, d^*)}{T^{*2}} - \frac{3yJ^*(T^*)}{T^*}$$

$$\times \left\{ D_0(y) + \frac{1}{T^*} \frac{\partial}{\partial y}(Z_1 - W_1) + \frac{1}{T^{*2}} \frac{\partial}{\partial y}(Z_2 - W_2) \right\}$$

$$(14)$$

and

$$b_0 = \frac{2\pi d^3}{3} \left[1 + \frac{64}{105 d^{*3} T^{*2}} - \frac{3J^*(T^*)}{T^*} \right] . \quad (15)$$

$Z_0(y)$ is the compressibility factor for the hard sphere reference system and $D_0(y) \equiv \partial Z_0(y)/\partial y$. The quantities J^*, Z_i, and W_i are defined by

$$Z_2(y, d^*) = -6y \frac{\partial}{\partial y} \left[yC_0(y) \int_{1/d^*}^{\infty} g_d(y, x) u^{*2}(d^*x) x^2 dx \right],$$

$$C_0(y) \equiv \left(\frac{\partial}{\partial y} [yZ_0(y)] \right)^{-1} ,$$

$$J^*(T^*) = \frac{1}{d^*} \int_0^1 u^*(x) e^{-u^*(x)/T^*} dx ,$$

$$Z_1(y, d^*) = 12y \frac{\partial}{\partial y} y \int_{1/d^*}^{\infty} g_d(y, x) u^*(d^*x) x^2 dx ,$$

$$W_1 = 96y \int_{1/d^*}^{\infty} g_d(y, x) \{ 2(d^*x)^{-1/2} - (d^*x)^{-6} \} x^2 dx ,$$

and

$$W_2 = -96yC_0(y) \int_{1/d^*}^{\infty} g_d(y, x) u^*(d^*x)$$

$$\times \{ 2(d^*x)^{-12} - (d^*x)^{-6} \} x^2 dx .$$

Substitution of Eqs. (14) and (15) into Eqs. (1) and (2) yields the desired results, modified Enskog theory expressions for the viscosity and thermal conductivity of a dense fluid in terms of the intermolecular potential, which in this case is taken to be a Lennard–Jones 6–12 potential, $u(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$. Note that if the small terms of order $1/T^*$ and less are neglected, Eqs. (14) and (15) simply specify that one use the Barker–Henderson value of $d(T)$ in the hard sphere equation of state.

III. RESULTS AND DISCUSSION

As an illustration of this approach to dense fluid transport, we have calculated the viscosity and thermal conductivity of argon using the Carnahan–Starling[8] hard-sphere equation of state $Z_0 = (1 + y + y^2 - y^3)/(1 - y)^3$ and the Wertheim–Thiele[9] solution for the Percus–Yevick hard sphere radial distribution function, $g_d(y, r)$. The temperature range covered was 85–375 K, with densities ranging from the dilute gas to approximately 1.25 g/cm^3 (2.5 ρ_c). The dilute gas viscosities and thermal conductivities were evaluated by using Lennard–Jones 12–6 collision integrals in Eqs. (4) and (5).

Figure 1 displays the results thus obtained for the isochoric and saturated argon viscosity. The results are extremely good for temperatures above critical (150.86 K) and densities below approximately twice critical ($\rho_c \cong 0.5235$ g/cm^3). As one would expect, the results for the saturated vapor are quite good but rather large discrepancies are seen for the saturated liquid (approximately 40% near the triple point). This latter disagreement can be explained by considering the primary physical assumption made in the statistical mechanical perturbation theory, viz., that the repulsive intermolecu-
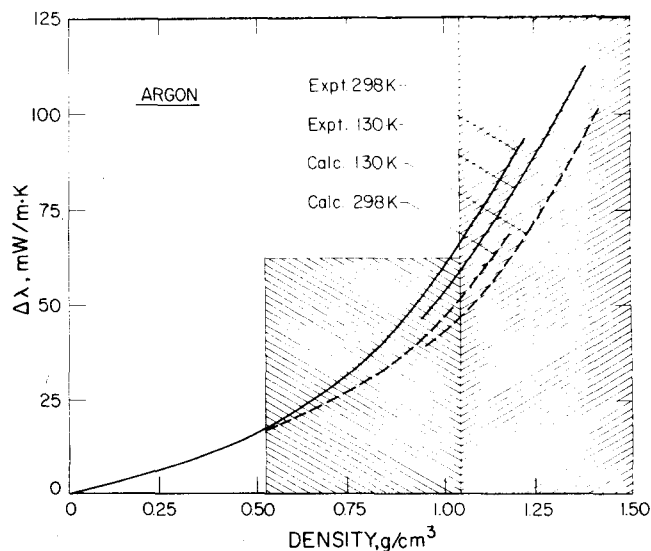

FIG. 4. Excess argon thermal conductivity, $\Delta\lambda = \lambda - \lambda_0$. The solid lines are smoothed experimental results and the dashed lines show the corresponding calculations.
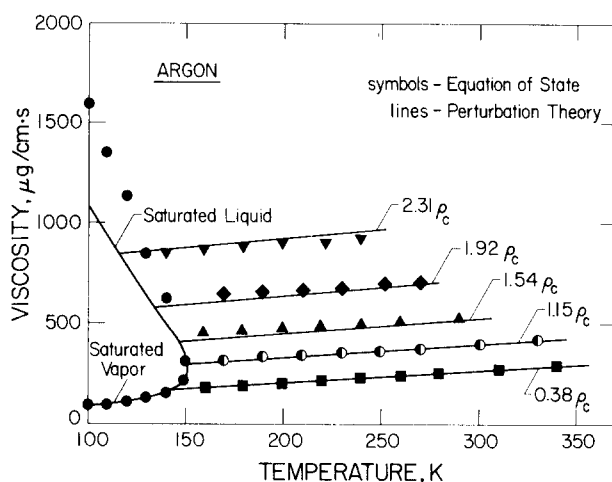
FIG. 5. Isochoric and saturated argon viscosity. The symbols were calculated using a Benedict–Webb–Rubin equation of state for argon and the modified Enskog theory and the dashed lines were calculated using the statistical mechanical perturbation theory equation of state and the modified Enskog theory.

lar forces determine the fluid structure with attractive forces providing an internal pressure which holds the fluid together at some specified density. This assumption, although generally valid, must break down along the saturated liquid boundary where there are two phases existing at virtually zero pressure.

Figure 2 shows the corresponding results for the argon thermal conductivity coefficient. In this case, the results are satisfactory for temperatures above 225 K and densities below $1.5 \rho_c$. The deviations at the highest density considered are approximately 20% at 200 K. Rather large deviations are observed below 175 K owing to the failure of the MET to predict the critical point anomaly in the thermal conductivity.[10] It is interesting to note that away from the critical point, the calculated saturated liquid thermal conductivities are in much better agreement with experiment than the corresponding viscosity calculations. This agreement, however, must be considered to be fortuitous due to the fact that the modified Enskog theory tends to predict saturation thermal conductivities which are too large.[4]

Figure 3 shows the excess viscosity, $\Delta\eta = \eta - \eta_0$, for the 139.7 and 373 K isotherms. It can be seen that the agreement with experiment is quite good over the entire density range at the higher temperature and that the agreement at 139.7 K, although not outstanding, is satisfactory even at $2\rho_c$.

Figure 4 shows the excess thermal conductivity, $\Delta\lambda = \lambda - \lambda_0$, along the 130 and 298 K isotherms. The agreement in this case is not quite as good as for the viscosity, but again should be considered satisfactory.

It has been shown[4,11] that the modified Enskog theory breaks down for densities above $2\rho_c$ and it is interesting in this regard to compare our calculations with those obtained using an equation of state based on experimen-

tal pvT data in the MET. This not only effectively removes the errors of the MET but also provides a good check on the perturbation theory equation of state. Figure 5 displays the results of this comparison with the symbols being calculated with the MET and a Benedict–Webb–Rubin equation of state for argon[12] and the solid lines being calculated with the perturbation theory. The results are seen to be extremely good over virtually the entire surface which would imply that the perturbation theory provides a very good representation of the thermal pressure.

In summary, we have presented a simple method of calculating argon viscosities and thermal conductivities and have shown that the results thus obtained compare very favorably with those obtained using experimental pvT data. As compared to experiment, the results are quite good except along the saturated liquid boundary, where the equilibrium statistical mechanical perturbation theory appears to break down. This approach provides us with a method of predicting transport properties of dense fluids using fundamental molecular theory. The results thus obtained should be sufficiently accurate for many technical applications. Work is currently in progress to extend the technique to more complex molecules (O_2, N_2, etc.) and mixtures, for which relatively little experimental data is available.

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