Dense Fluid Shear Viscosity and Thermal Conductivity—The Excess

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We have developed a nonequilibrium molecular dynamic method to directly simulate dense fluid transport (Ashurst and Hoover, 1975). The trajectories of N interacting atoms in a fixed volume V are numerically computed. External forces, which are restricted to special boundary regions, do work and extract heat in order to maintain the hydrodynamic boundary conditions which produce a steady shear-momentum or heat flux. The transport coefficient is determined from the time average of the flux and corresponding gradient in the volume V.

Experimental observation of dense fluid shear viscosity and thermal conductivity data reveals that the excess coefficient, that part above the temperature-dependent dilute gas value, is almost temperature independent (Diller et al., 1970; Hanley et al., 1972). In order to calculate representative dense fluid transport coefficients, we have selected the Lennard-Jones potential (twelfth-power repulsion with sixth-power attraction) as a simple, yet realistic, atomic potential. Most atomic interactions occur with energy of order kT; thus, for high temperatures, the Lennard-Jones potential is effectively a single inverse power potential. The single inverse nth power potentials have special scaling features since the potential and its derivatives depend only upon the combination of energy and particle size $\epsilon \sigma^n$. Thus, if the density and temperature are combined into one variable x [$\equiv$ (density) (temperature)$^{-3/n}$], then all systems with identical scaled initial conditions and the same x value will have identical dynamic evolution (Hoover et al., 1971). The reduced excess transport coefficients times $(\epsilon/kT)^{1/2+2/n}$ are functions of x only, not density and temperature separately, throughout the fluid phase.

Since, at high temperature, the repulsive core potential dominates momentum transport, the high-temperature Lennard-Jones shear viscosity must approach the scaling behavior of the inverse-12th-power viscosity. Nonequilibrium molecular dynamic calculations for the Lennard-Jones shear viscosity have shown this to be true and we have found that the scaling is successful even at the triple point ($N\sigma^3/V = 0.85$, $kT/\epsilon = 0.70$). The Lennard-Jones shear viscosity has been calculated (with 108 and 216 atoms) along two isotherms corresponding to room temperature for hydrogen and helium ($kT/\epsilon = 8.5$ and 28) for densities up to freezing ($N\sigma^3/V \simeq 1.5$), see Figure 1. The calculated reduced excess shear viscosity $\Delta\eta$ for $x > \sim 0.5$ is well described by the simple expression

$$\Delta\eta\sigma^2(m\epsilon)^{-1/2}(\epsilon/kT)^{2/3} = 7.0\, x^4 \qquad (1)$$

which clearly reveals two features: (1) weak temperature dependence, and (2) a negative temperature derivative at constant density, $(d\ln\Delta\eta)/(d\ln T) = -1/3$. Notice that

the temperature derivative is negative if the power of x is greater than 8/3. While both of these features have been experimentally observed in simple-fluid-shear-viscosity data (for example, argon, helium, hydrogen, oxygen and carbon dioxide; see Diller et al., 1970 and Hanley et al., 1972) their cause has not been previously traced to the dominance of the repulsive core potential. For all x, a slightly better fit is given by the empirical relation

$$\Delta\eta\sigma^2(m\epsilon)^{-1/2}(\epsilon/kT)^{2/3} = 0.024\,[\exp(6x) - 1] \qquad (2)$$

(dashed line in Figure 1). Notice that the temperature derivative is positive for low density-high temperature combinations and only becomes negative for x greater than 0.41.

The single-inverse-12th-power (soft sphere) shear viscosity has also been calculated and a fit similar to Equation (2) produces coefficients of 0.0152 and 7.02, where the product of the coefficients was required to equal the soft-
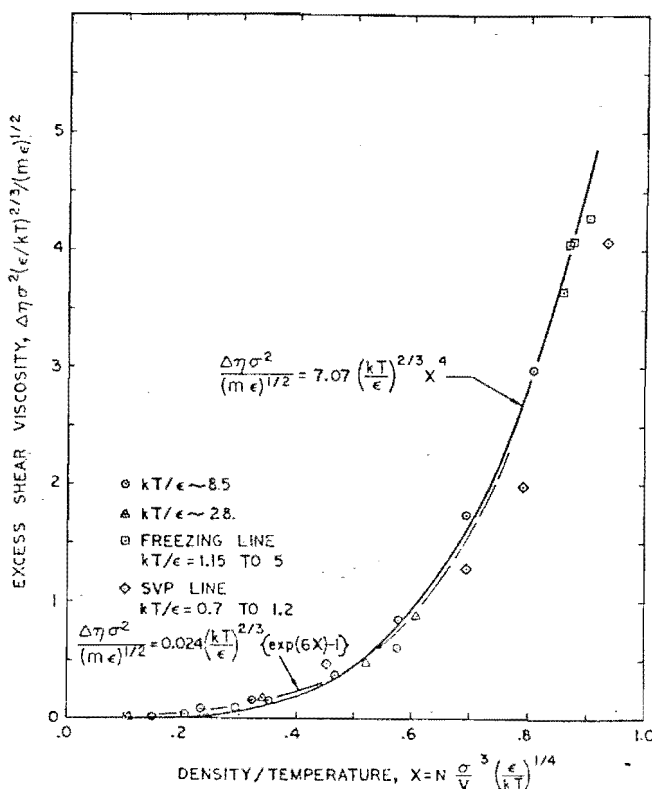

Fig. 1. Calculated Lennard-Jones excess shear viscosity along the isotherms $kT/\epsilon = 8.5$ and 28; expressed in terms of the single-repulsive-12th-power scaling variables. Also shown, but not used in determining the curve fits, are calculated Lennard-Jones shear viscosities along the (L-J) freezing line and the saturated vapor pressure line (of argon). The standard error is about 10% of the total coefficient.

sphere Enskog first density correction to the dilute-gas shear viscosity (0.1066—see Equation (26) of Hanley et al., 1972). For x less than 0.5, the Enskog theory provides a good soft-sphere shear viscosity estimate; however, for higher densities, the molecular dynamic results are 2 to 3 times the Enskog values. There is a small discrepancy in the soft-sphere coefficient values and the Lennard-Jones values [Equation (2)] since at infinite temperature they must be equivalent. Procrustean fitting (guided by the inverse-square-root temperature expansion of the second and third Lennard-Jones virial coefficients, which determine the Enskog first density correction) of all the nonequilibrium molecular dynamic results yields the empirical relation

$$\Delta\eta\sigma^2 (m\epsilon)^{-1/2}(\epsilon/kT)^{2/3} = 0.0152\,[1 - 0.5(\epsilon/kT)^{1/2}$$
$$+ 2.0(\epsilon/kT)] \times \{\exp\,[7.02\,x(1 - 0.2\,(\epsilon/kT)^{1/2})] - 1\}$$
$$(3)$$

with a fit error of 5 to 10% of the excess or dilute shear viscosity (whichever is larger). The experimental hydrogen and deuterium shear viscosity data (pressure up to 2000 atm.) of Michels et al. (1953) are reproduced within 2% by Equation (3) [classical Lennard-Jones parameters from Hirschfelder et al. (1964)]. This equation also reproduces (within 5%) the experimental argon shear viscosity data of Michels et al. (1963). Thus soft-sphere scaling of the computer results yields a relatively simple function which should be useful for describing simple-fluid shear viscosity throughout the fluid phase.

Experimental excess thermal conductivity data resemble excess shear viscosity data (strong density with weak temperature dependence) except the isochoric temperature derivative is positive, the opposite of shear viscosity [see Diller et al., 1970; Hanley et al., 1972]. The Lennard-Jones thermal conductivity coefficient has been calculated by nonequilibrium molecular dynamic simulation of heat flow (Ashurst, 1974). For reduced temperatures greater than one the results can be represented by curve A in Figure 2. Similar fitting of experimental argon thermal

conductivity data (Michels et al., 1963) yields the same second coefficient and only changes the first coefficient from 0.36 to 0.335. The second coefficient determines the x value at which the isochoric temperature derivative changes sign. Thus the calculated Lennard-Jones and the experimental argon excess thermal conductivity both have a positive isochoric temperature derivative for densities less than twice critical (for $kT \sim 2\epsilon$).

Therefore, this new way of scaling excess coefficients yields relatively simple functions for describing transport behavior throughout the fluid phase and should also be useful for empirical correlations of experimental transport data.

ACKNOWLEDGMENTS

NOTATION

k = Boltzmann constant
m = mass of atom
n = power of repulsive potential ($n = 12$ for this work)
N = number of atoms
T = temperature
V = volume
x = reduced number density/(reduced temperature)$^{3/n}$ [$\equiv (N\sigma^3/V)\,(\epsilon/kT)^{1/4}$ for this work]

Greek Letters

Δ = excess coefficient, that part above temperature-dependent dilute gas limit
ϵ = energy parameter of pair potential
η = shear viscosity
λ = thermal conductivity
σ = length parameter of pair potential

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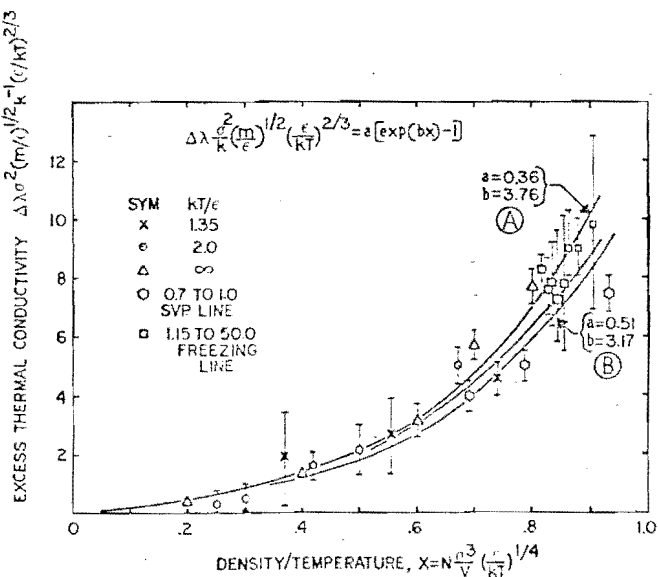
Fig. 2. Calculated Lennard-Jones excess thermal conductivity expressed in terms of the single-repulsive-12th-power scaling variables. Curve A is a nonlinear fit of all Lennard-Jones results for which $kT > \epsilon$, while curve B is for the condition $kT < 3\epsilon$ (corresponding argon fit yields 0.52 and 3.1). Also shown are the calculated infinite-temperature (that is, soft-sphere) thermal conductivities. The vertical lines denote one standard error.