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Corresponding states for thermal conductivities via nonequilibrium molecular dynamics[a)]

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We follow Rosenfeld in comparing fluid-phase thermal conductivities for several simple pair potentials. Within about ten percent these (nonelectronic) conductivities satisfy a corresponding states relation involving the equilibrium entropy. This corresponding states relation, deduced directly from the results of computer simulations, is also suggested by hard-sphere perturbation theory and by the quasiharmonic cell-model approach. The conductivity-entropy relation should be useful for estimating transport coefficients from the equation of state of monatomic fluids with arbitrary pair potentials.

I. INTRODUCTION

About ten years ago several groups[1] suggested that hard-sphere perturbation theory could be used to calculate accurate thermodynamic properties for dense fluids. This approach has been refined. Now energies and pressures can be reliably estimated with uncertainties of order 0.05 in E/NKT and PV/NKT.[2]

An accurate, theoretically based, approach to dense-fluid transport coefficients is still lacking. No convergent perturbation theory of transport has been found. The alternative to analytic work, brute-force computer methods can be used to estimate transport coefficients. But the computer methods are considerably more time consuming, for the same accuracy, than are those designed to measure equilibrium properties.

Shock wave experiments have been an invaluable source of high-pressure thermodynamic information. Unfortunately equally-precise experiments measuring transport properties have not been developed.

On the theoretical side, Enskog's ideas, more than half a century old, are still as good as any for estimating the diffusion, viscosity, and thermal conductivity coefficients. As an alternative, approximate transport coefficients can be estimated from cell or "Einstein" models. Either method, Enskog's or Einstein's, can be used to suggest corresponding-states treatments of transport coefficients. Here, in considering thermal conductivity, we closely follow the approach Rosenfeld[3] used in analyzing diffusion and viscosity coefficients.

In computer simulation, molecular dynamics methods are used to get reliable estimates of transport coefficients. The molecular dynamics simulations, either "equilibrium" ones using the Green–Kubo formulas, or "nonequilibrium" ones generating steady fluxes, make it possible to estimate viscosity and heat conductivity with uncertainties on the order of a few percent.[4] The nonequilibrium methods pioneered by Ashurst[5] are more promising than is the equilibrium Green–Kubo approach.[6] *Any* computational technique is complicated by unavoidable fluctuations and number dependence. These difficulties are gradually eroding in significance with the increase in computer speeds and the gaining of experience in extrapolating small-system results with large fluxes to macroscopic zero-flux values.

The first direct use of molecular dynamics results to estimate transport coefficients for fluids was provided by the hard-sphere system for the high-temperature gas and liquid transport properties of molecular fluids. It was found, for instance by Dymond,[7] that experimental transport properties along an isotherm could be represented by molecular dynamics results with a fixed hard-sphere diameter over a wide density range. Such hard-sphere models, however, are not suited to estimating fluid properties in the "dense fluid region," where any such parameters must be both density and temperature dependent. This region can be defined as the relatively "low temperature" fluid region where the temperature is below about twenty times the melting temperature. This corresponds generally to regions of higher than normal density and pressure.

In the dense fluid region the molecular dynamic study of the inverse-power potentials has been rewarding.[8] In addition to the usual corresponding-states relations for potentials which are linear in an energy parameter and in a function of distance, the inverse powers also exhibit the simplification that a single isochor, isotherm, or isobar is sufficient to generate equation-of-state and transport properties over the whole phase diagram.

A similar simplification holds for nonequilibrium systems of inverse-power particles arbitrarily far from equilibrium. It is only necessary that all four kinds of forces entering into nonequilibrium dynamical simulations—interparticle forces, boundary forces, constraint forces, and driving forces—simultaneously satisfy the same scaling relations.

Corresponding states relationships linking dissimilar, nonscaling force laws can only be approximate, not exact. But these approximate relationships can be useful both in making estimates of unknown constitutive properties and for suggesting theoretical analyses of regularities found empirically. Rosenfeld[3] correlated shear viscosity and diffusion with the excess entropy in the dense liquid region. This approach was motivated by the success of the fluid-phase hard-

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sphere perturbation theory in which the hard-sphere diameter—or equivalently, the entropy—was used to parametrize the structure of equilibrium fluids. As a justification for expecting transport coefficients to have similar correlations away from equilibrium, one can site Maxwell's relaxation-time approach. In fact, Rosenfeld's empirical correlations suggest that diffusion and viscosity can be estimated within about 30% by using corresponding states values based on the excess entropy. This approach is as useful as Enskog's original recipe relating transport coefficients to the thermal pressure.

Here we extend Rosenfeld's ideas to heat conductivity, correlating old data and adding a few new points calculated using the new Evans–Gillan[9] nonequilibrium molecular dynamics method. We compare our entropy correlation with several alternatives based on Enskog's model. We find that the correlation of the conductivity data, over a range of force laws, is even better than that found by Rosenfeld for diffusion and viscosity. We report three additional viscosity calculations for the inverse sixth-power potential. Together with previous results these improve somewhat the applicability of the corresponding states law to real fluid viscosities.

In Sec. II we discuss the available data and display it in corresponding-states form. In Sec. III we discuss the properties of entropy correlations in terms of hard-sphere and simple cell models. Finally the applicability to real fluids of the corresponding-states relations derived from molecular dynamic calculations is discussed.

II. THERMAL CONDUCTIVITIES

Thermal conductivities have been generated using three different kinds of computer simulations. The Green–Kubo fluctuation-dissipation approach is least direct, and has been applied sparingly. There is some Green–Kubo data for the inverse first-power potential[11] (one-component plasma) and for hard spheres.[7] The direct simulation of the flow of heat between a hot reservoir and a cold one was described by Ashurst in his thesis.[5] He studied the whole range of fluid thermodynamic states, from low-density gas to the melting line, for both the Lennard-Jones 12–6 potential and for its purely repulsive 12th-power component, the "soft-sphere" potential.

These data from the Green–Kubo method and the direct-simulation method have been augmented, in the past two years, by using external driving forces.[9,10] These external forces generate a homogeneous heat flow without any accompanying temperature gradient (so that periodic boundaries can be used in all three directions, including the flow direction). To generate a heat flow consistent with the Green–Kubo formula and with irreversible thermodynamics, the driving force must have the form

$$F_d = \lambda\,(\Delta E + \Delta P^{\phi}_{xx}\,V, \Delta P^{\phi}_{xy}\,V, \Delta P^{\phi}_{xzv}) \qquad (1)$$

for a heat current flowing in the x direction. ΔE is the energy of a particle, less the instantaneous mean value of that quantity, where the pairwise interaction energy is divided equally between the two interacting particles. Similarly, ΔP^{ϕ}_{xx}, ΔP^{ϕ}_{xy}, and ΔP^{ϕ}_{xz} represent the pressure-tensor contributions of each particle's intractions, again less the instantaneous mean values of these quantities. The rate at which these external driving forces do work is exactly equal to the product of the heat flux vector, the volume V, and the driving force coefficient λ.[9] This external work would cause substantial irreversible heating in the absence of stabilizing steady-state constraints. A steady state is imposed through constraint forces. $-mv\zeta$, applied to each particle, with ζ chosen to keep either the temperature or total energy constant. The one-component plasma, hard-sphere, soft-sphere, and Lennard–Jones[5,12] conductivities mentioned above have been augmented in the present work by the inverse sixth-power calculations listed in Table I. The latter calculations were carried out in order to test the number dependence of the results and the sensitivity of inverse-power conductivities to the replusive exponent. The additional sixth-power viscosity calculations reported in Table I provide analogous data for viscosity.

All of the data are plotted in Figs. 1 and 2, corresponding-states style, as suggested by Rosenfeld's study of diffusion and viscosity. We plot the logarithm of a dimensionless heat conductivity $\kappa d^2/k\,(kT/m)^{1/2}$ and a dimensionless viscosity $\eta d^2/(mkT)^{1/2}$, where d^3 is the volume per particle and k is Boltzmann's constant, as a function of the excess entropy $S^e = S - S_{\text{ideal}}$. The excess is measured relative to that of an ideal gas at the same density and temperature. This form of

TABLE I. Transport coefficients for the inverse-sixth-power potential $\phi = \epsilon(\sigma/r)$.[6] The reduced density ρ for $n = 6$ is $(N\sigma^3/\sqrt{2}\,V)(\epsilon/kT)^{1/2}$. S^e is the excess entropy. The thermal conductivity κ and shear viscosity η are expressed in units with σ, m, ϵ, and k set equal to unity. The time t, and viscous strain rate $\omega = du_x/dy$, and conducting driving force λ are also given in these same units. Most viscosity and conductivity calculations were done on 64 and 108 particle systems, respectively.

ρ	$\frac{-s^{e\,a}}{nk}$	κ	λ	t	κ_r	η^c	t	η_r
0.5	1.32	2.2 ± 0.2	0.05	500	2.8 ± 0.3	0.37 ± 0.02	600	0.47 ± 0.03
1.0	2.60	8.5 ± 2	0.03	1600[d]	6.8 ± 1.5	1.6 ± 1	240	1.3 ± 0.1
1.4	3.47	16.7 ± 2	0.03	310	10.6 ± 1.3	...	...	...
1.5[b]	3.69	...	...	...	...	5.8 ± 0.2	300	3.6 ± 0.15

[a] See Fig. 1.

[b] Liquid phase could not be stablized at this density for conductivity calculations.

[c] $\omega = 0.2$ for all cases.

[d] This is a total time for 32, 108, and 256 particle conductivities, which were consistent with a weak number dependence.

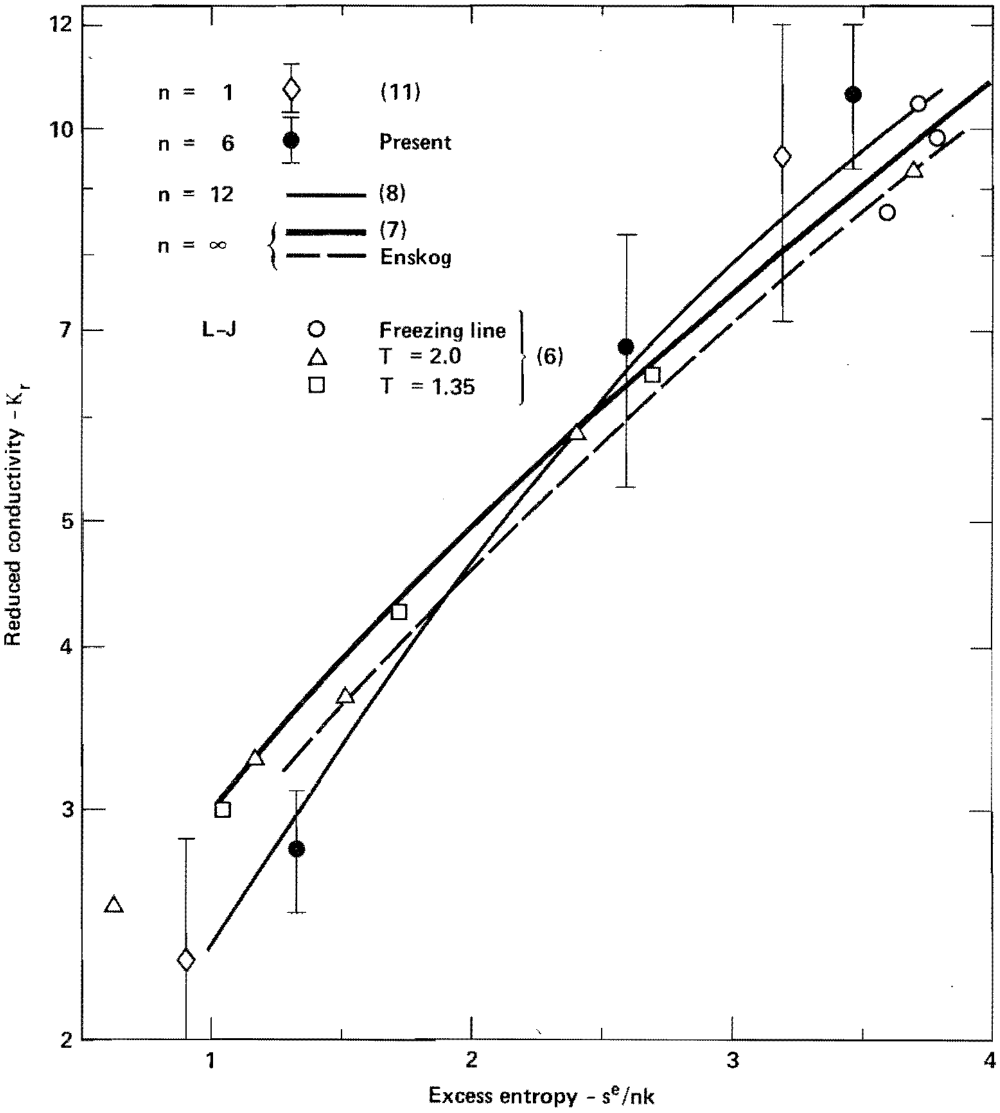

FIG. 1. Summary plot of fluid conductivities for dense fluids with various pair potentials. Lennard–Jones values have small uncertainties of about 2%.[5,12] Excess entropies are from standard sources as follows: $n = 1$: W. L. Slattery *et al.*, Phys. Rev. A **21**, 2087 (1980). $n = 6$: D. A. Young and F. J. Rogers, J. Chem. Phys. **81**, 2789 (1984). $n = 12$: W. G. Hoover *et al.*, J. Chem. Phys. **52**, 4931 (1970). $n = \infty$: Carnahan–Starling representation. Lennard–Jones: Y. Rosenfeld, Phys. Rev. A **26**, 3633 (1982).

the reduced transport coefficients is suggested by elementary kinetic theory to be appropriate to a dense medium in which the carriers are atoms, with scattering occurring after a motion of order the average interparticle distance. The residual variation of the reduced transport coefficients with the excess entropy is relatively weak.

It is apparent that a single, straight, corresponding-states line would describe all the conductivity data shown in Fig. 1 with an accuracy of order 10%. (The straight line approach is qualitatively wrong at very low density, where the excess entropy vanishes. In this limit our reduced conductivity diverges.) The slope of the approximating line would be about 0.45. This number lies relatively close to the value, 1/3, derived from the Einstein model, as discussed in the next section. In Fig. 2 similar straight line fits are seen to be consistent with viscosity data for each power law. Moreover, the slopes for all potentials except the hard-sphere system are about the same, 0.66 ± 10%. However, for the softer potentials computer viscosities are systematically lower. A single corresponding states representation of viscosities is therefore less accurate than for conductivities.

III. APPROXIMATE MODELS FOR CONDUCTIVITY AND VISCOSITY

Enskog used the "thermal pressure" $T(\partial P/\partial T)_v$ to estimate a hard-sphere diameter. He then approximated the ratio of each of the transport coefficient to its low-density limiting value through a universal function of a reduced, dimensionless density based on this hard-sphere diameter. An alternative approach to Enskog's is to use the difference between the pressure and the zero-temperature pressure as a "thermal pressure." This approach fails for densities lying outside the stabilty range of the solid phase. Variational, hard-sphere perturbation theory supplies perhaps the best definition of an effective hard-sphere diameter. In this theory the excess entropy is precisely that of the hard-sphere fluid. Because the hard-sphere entropy, relative to an ideal gas, is a function of the reduced density, entropy can replace density as a corresponding-states variable. Entropy is also experimentally accessible and is for that reason a more appealing choice than a variable depending explicitly on a hard-sphere diameter.

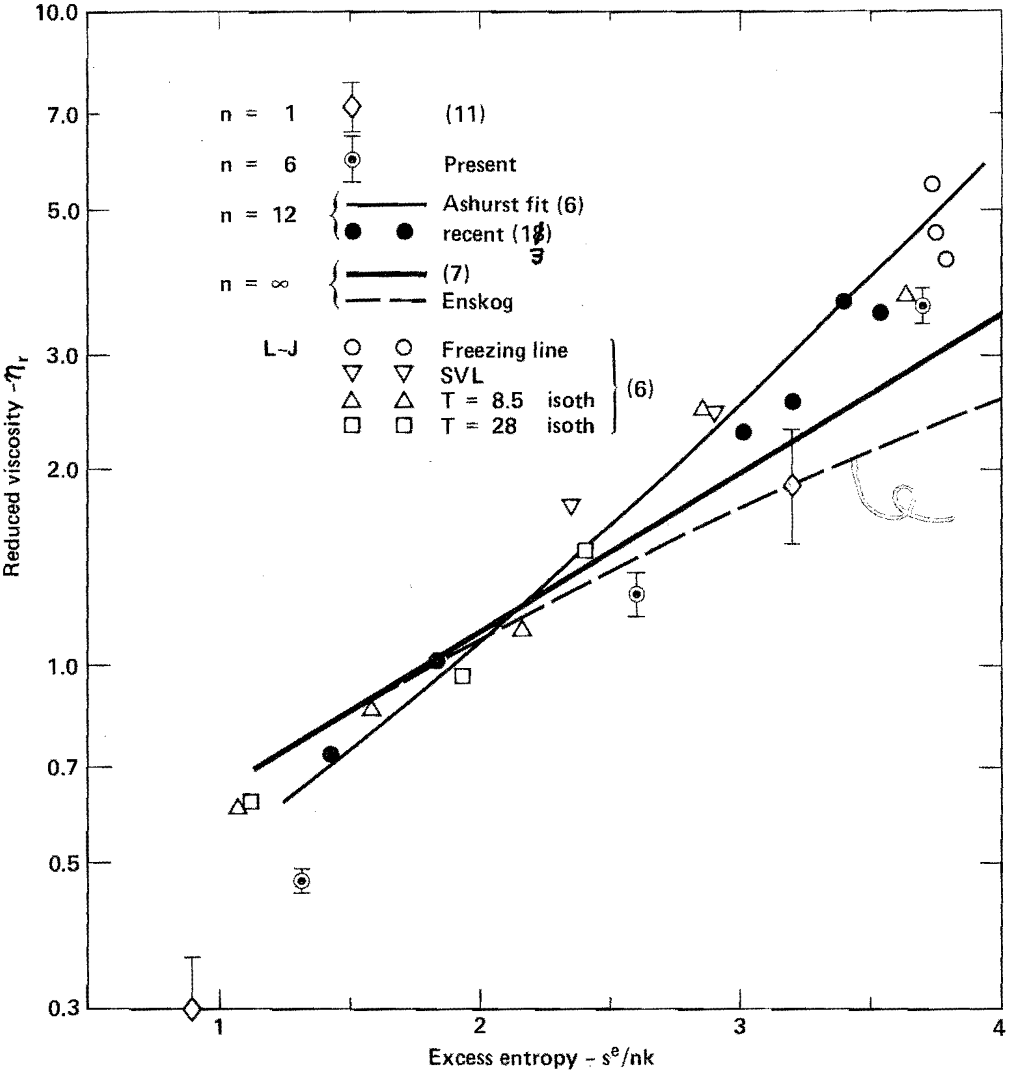

FIG. 2. Summary plot of fluid viscosities from molecular dynamics. The Lennard–Jones isotherm calculations[5] have errors of 5%–10%. The present results for the inverse-sixth power repulsive potential were calculated at a moderate strain rate (see Table I). The highest-density (right-most) point, near melting, is probably several percent lower than the zero-strain-rate limit.

Some features of the dependence of the conductivity on entropy (shown in Fig. 1) can also be understood in terms of a quasiharmonic Einstein model. Completely analogous arguments hold for viscosity. In the Einstein model the excess entropy has the form

$$-S^e/Nk = 3\ln(\nu) + 3\ln(d) - (3/2)\ln(kT) + c_s, \quad (2)$$

where the additive constant c_s is material independent and ν is the "Einstein frequency," the frequency at which a single particle vibrates in the fixed field of its neighbors. This frequency varies as the $(n+2)/6$ power of the density for inverse-power potential interactions.

The Einstein frequency can also be related to the thermal conductivity, as was suggested by Horrocks and McLaughlin.[5,14] The analog for viscosity is due to Andrade.[5] Suppose that a vibrating particle transports energy from its hotter to its cooler neighbors, through an area of order d^2. The transport occurs at the Einstein frequency. The logarithm of the resulting conductivity has the form

$$\begin{aligned}\ln(\kappa^*) &= \ln[\kappa d^2/k(kT/m)^{1/2}]\\ &= \ln(\nu) + \ln(d) - (\tfrac{1}{2})\ln(kT) + c_k, \quad (3)\end{aligned}$$

where the constant c_k too is material independent. Comparing relations (2) and (3) for S^e/nk and $\ln\kappa$ reveals the same proportionality for all materials with a slope of 1/3.

Because a more rigorous justification cannot at present be given by theory for these approximate corresponding states relationships, the evidence for their generality must depend mainly on the computer data. While the inverse powers do represent fluids with a wide variety of Grüneisen "lattice" gammas $\langle\partial\ln\nu/\partial\ln\rho\rangle$, these gammas do not vary with density. Realistic potentials (Lennard–Jones, exponential-six) lead to gammas which decrease rapidly with density. The existing Lennard–Jones conductivity calculations shown in Fig. 1 provide a thorough test of corresponding state behavior for fluids with high gammas. For viscosity, however, the high temperature isotherms for the Lennard–Jones potential in the excess entropy range of Fig. 2 lie at high densities where the potential is effectively repulsive, close to the $n = 12$ soft-sphere potential. The agreement with the 12th-power results on these isotherms is thus not surprising. Viscosity calculations at the lower reduced temperatures used in the conductivity work is desirable to see the effect of the inverse-sixth part of the potential.

The Lennard–Jones potential is in one sense, however, a relatively poor example of a typical pair potential. Its repulsions are too strong and its lattice gammas (greater than 7/3) too large at high compression. It would be desirable to test further the generality of the corresponding states relationship by carryng out calculations using a more realistic potential like the exponential-six potential with its weaker repulsions at close distances.

In spite of its large scatter, the available viscosity data also support the usefulness of a corresponding states law for monatomic fluids. This can been seen in Fig. 2 where the viscosities appear to have a maximum near $n \simeq 12$. This corresponds to the range of gammas in typical solids and liquids, $1.5 < \gamma < 2.5$. The possibility of lower, hard-sphere-like, reduced viscosities due to large gammas would occur mainly at high temperature expanded states where, however, available Lennard-Jones results show no anomalies. The main deviations from corresponding states behavior in fluid viscosity should thus occur at very high densities and pressures when pair potentials will soften and gamma is expected to decrease to its plasma value of 0.5.

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