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Relations Between Transport Coefficients in Lennard–Jones Fluids and in Liquid Metals[1]

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Several simple approximate hard-sphere relations for transport coefficients are compared with the results of molecular dynamics (MD) simulations performed on Lennard–Jones (LJ) fluids. Typically the individual transport coefficients: self-diffusion coefficients, D, shear viscosity, η_s, bulk viscosity, η_B, and thermal conductivity, λ, agree within a factor of two of the exact results over the fluid and liquid parts of the phase diagram, which seems reasonable in view of the approximations involved in the models. We have also considered the ratio, λ/η_s, and the product, $D\eta_s$, for which simple analytic expressions exist in the hard-sphere models. These two quantities also agree within a factor of two of the simulation values and hard sphere analytic expressions. Using time correlation functions, Tankeshwar has recently related the ratio λ/D to thermodynamic quantities, in particular, to the differences in specific heats, $C_p - C_V$, and to the isothermal compressibility, κ_T. Using D and thermodynamic values taken solely from LJ MD simulations, his relation was tested and found to give typically better than $\sim 20\%$ agreement at liquid densities, deteriorating somewhat as density decreases into the gas phase. Finally liquid metals are considered. In this case, λ is dominated by its electronic contribution, which is related approximately to the electrical conductivity by the Wiedemann–Franz Law. Some theoretical results for the electrical conductivity of *Na* are referenced, which allow a semiquantitative understanding of the measured thermal conductivity of the liquid metal. Shear viscosity is also discussed and, following the work of Tosi, is found to be dominated by ionic contributions; Nevertheless, at the melting temperature of *Na*, a relation emerges between thermal conductivity, electrical resistivity and shear viscosity.

KEY WORDS: diffusion; liquid metals; shear viscosity; simple liquids; thermal conductivity.

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1. INTRODUCTION

Static atomic structure in liquids is accessible through neutron experiments which allow, among other things, the stucture factor, $S(k)$ and essentially its Fourier transform, the pair correlation function or radial distribution function $g(r)$, to be extracted. Examples are given in the book by Egelstaff [1]. However, theoretical calculations of the analytic nature of $S(k)$ and $g(r)$ remain somewhat hampered by a lack of knowledge of the three-atom correlation function $g^{(3)}$ even when a pair potential, $\phi(r)$, is assumed to exist. Therefore, it is usually necessary to resort to computer simulation [Molecular Dynamics (MD), or Metropolis Monte Carlo (MC)] to obtain $g(r)$ for a particular pair potential. Early attempts to express transport coefficients in terms of essentially only $g(r)$ and $\phi(r)$ met with only partial success, and emphasis has moved into the area of the dynamical structure factor, $S(k, \omega)$ which was introduced into the theory of liquids by van Hove [2]. Its physical interpretation is outlined below. We note here first that it is accessible again by (inelastic) neutron scattering [1] or, in a more limited region of the (k, ω) plane, by light scattering. Some recent applications to metallic lithium have been reported.

The link between these scattering functions and transport coefficients is through the so-called Green–Kubo formulas [3]. These exploit the fact that $S(k, \omega)$, for example, can be related to hydrodynamic equations containing the transport coefficients in the long-wavelength (i.e., $k \to 0$) and low-frequency (i.e., $\omega \to 0$) limits. This approach is applied to metallic liquids below.

Again, as in the static structure problem, computer simulation has been applied many times to the dynamics of molecules in liquids. A considerable body of data exists on computed transport coefficients, $S(k, \omega)$, and related time correlation functions. The focus of the present work is to review the extent to which simple models can be used to account for "experimental" data obtained from "real" experiments (e.g., neutron scattering) or MD "computer" experiments.

2. SIMPLE LIQUIDS MODELED USING THE LENNARD–JONES POTENTIAL

After the above rather general considerations, we consider a specific and popular model fluid, the so-called Lennard–Jones (LJ) fluid in which the model molecules interact through the Lennard–Jones potential,

$$\phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{1}$$

where σ and ε are the length and energy scaling parameters, respectively.

In this section we consider the predictions for the transport coefficients from MD simulations and compare them with hard-sphere models for specific transport coefficients. The LJ fluid is the ideal model fluid as its transport coefficients [4, 6] and equation of state [7] are reasonably well known over the whole phase diagram.

Semiempirical expressions can,be derived for the transport coefficients in terms of thermodynamic quantities, which can be obtained independently. For example, Longuet-Higgins and Pople (LHP), have derived simple expressions for the transport coefficients based on the approximate kinetics of an equivalent hard-sphere fluid, with hard-sphere diameter, σ_{HS} [8, 9],

$$D=\frac{\sigma_{\mathrm{HS}}}{4}\left(\frac{\pi k_{\mathrm{B}}T}{m}\right)^{1/2}\left(\frac{PV}{Nk_{\mathrm{B}}T}-1\right)^{-1} \tag{2}$$

$$\eta_{\mathrm{s}}=\frac{2\sigma_{\mathrm{HS}}\rho_{\mathrm{HS}}}{5}\left(\frac{mk_{\mathrm{B}}T}{\pi}\right)^{1/2}\left(\frac{PV}{Nk_{\mathrm{B}}T}-1\right) \tag{3}$$

and for the bulk viscosity, η_{B},

$$\eta_{\mathrm{B}}=\frac{2\sigma_{\mathrm{HS}}\rho_{\mathrm{HS}}}{3}\left(\frac{mk_{\mathrm{B}}T}{\pi}\right)^{1/2}\left(\frac{PV}{Nk_{\mathrm{B}}T}-1\right) \tag{4}$$

$$\lambda=\sigma_{\mathrm{HS}}k_{\mathrm{B}}\rho_{\mathrm{HS}}\left(\frac{k_{\mathrm{B}}T}{\pi m}\right)^{1/2}\left(\frac{PV}{Nk_{\mathrm{B}}T}-1\right) \tag{5}$$

where $\rho_{\mathrm{HS}}=N\sigma_{\mathrm{HS}}^{3}/V$ and the compressibility factor is that of the equivalent hard-sphere system at the same temperature. We call Eqs. (2)–(5) the LHP transport coefficient formulas.

The problem with these expressions in Eqs. (2)–(5) is that they do not reduce to the known kinetic theory expressions in the dilute gas limit. An alternate proposal that does not have this deficiency is to use the following new expressions:

$$D=\frac{3}{8\rho\sigma_{\mathrm{HS}}^{2}}\left(\frac{k_{\mathrm{B}}T}{\pi m}\right)^{1/2}\left(\frac{PV}{Nk_{\mathrm{B}}T}\right)^{-1} \tag{6}$$

$$\eta_{\mathrm{s}}=\frac{5}{16\sigma^{2}}\left(\frac{mk_{\mathrm{B}}T}{\pi}\right)^{1/2}\left(\frac{PV}{Nk_{\mathrm{B}}T}\right) \tag{7}$$

$$\eta_B = \frac{5}{16\sigma^2}\left(\frac{mk_B T}{\pi}\right)^{1/2}\left(\frac{PV}{Nk_B T}\right) \tag{8}$$

$$\lambda = \frac{75k_B}{64\sigma^2}\left(\frac{k_B T}{\pi m}\right)^{1/2}\left(\frac{PV}{Nk_B T}\right) \tag{9}$$

We call Eqs. (6)–(9) the H transport coefficient formulas.

In Table I we compare the self-diffusion coefficients and thermal conductivities from the different approaches and in Table II the viscosities are similarly compared. The four highest density states in these tables are close to the fluid-solid coexistence line [10]. Best agreement with simulation data is found with the self-diffusion coefficients from the Longuet–Higgins and Pople (LHP) expressions. The LHP thermal conductivity is uniformly about a factor of 2 too small. The LHP and H shear viscosities are about 50% of the simulation values. Agreement, in general, between the simulation and approximate formulas is therefore reasonable considering the approximations employed in the derivations of these formulas. The use of Eqs. (6)–(9) provides the advantage of reducing to the ideal gas limits in the limit of zero density.

Table I. Comparison Between the Self-Diffusion Coefficients, D, and Thermal Conductivities, λ, of Lennard–Jones (LJ) Fluids Computed by Molecular Dynamics [4, 6] with Various Semi-empirical Predictions[a]

T	ρ	D_{MD}	D_{LHP}	D_{H}	$\lambda_{\mathrm{s,MD}}$	$\lambda_{\mathrm{s,LHP}}$	$\lambda_{\mathrm{s,H}}$	$\lambda_{\mathrm{s,T}}$
0.73	0.844	0.029	0.040	0.018	6.9	4.29	5.80	8.71
1.06	0.910	0.035	0.045	0.022	9.2	5.34	7.56	11.12
1.46	0.993	0.031	0.048	0.024	11.2	6.85	10.0	10.96
2.50	0.600	0.32	0.29	0.23	4.17	0.95	3.85	11.32
2.50	0.803	0.18	0.16	0.11	7.2	2.37	6.16	18.66
2.51	1.040	0.059	0.077	0.046	13.8	6.26	11.35	17.32
1.21	0.966	0.040	0.042	0.020	8.9	6.6	9.2	14.7
1.83	0.50	0.37	0.31	0.24	2.6	0.61	2.7	8.0
1.81	0.60	0.26	0.22	0.16	3.4	1.03	3.5	10.7
1.90	0.801	0.13	0.12	0.076	7.4	2.60	5.8	16.1
1.84	1.049	0.033	0.05	0.027	13.5	7.74	11.8	12.6

[a] Quantities here and in the next two tables are in LJ reduced units of ε, σ, and m, the mass of the LJ molecule. The LHP subscripts refer to the Longuet–Higgins and Pople expressions [8, 9]. The H subscripts refer to predictions from empirical formulas, Eqs. (6) and (7). $\lambda_{\mathrm{s,T}}$ refers to predictions of Eq. (12). The equivalent hard-sphere diameter is given by $\sigma_{\mathrm{HS}} = 1.0217(1.0 - 0.0178/T^{1.256})/T^{1.0/12.0}$ taken from Ref. 21. The hard-sphere compressibility factor was taken from the hard-sphere equation of state of Carnahan and Starling [22].

Table II. Comparison Between the LJ Shear and the Bulk Viscosities Computed by Molecular Dynamics [4, 6][a]

T	ρ	$\eta_{s,\mathrm{MD}}$	$\eta_{s,\mathrm{H}}$	$\eta_{s,\mathrm{LHP}}$	$\eta_{\mathrm{B},\mathrm{MD}}$	$\eta_{\mathrm{B},\mathrm{LHP}}$	$\eta_{\mathrm{B},\mathrm{H}}$
0.73	0.844	3.4	1.72	1.55	1.47	2.86	1.55
1.06	0.910	4.1	2.14	2.02	1.70	3.56	2.02
1.46	0.993	6.3	2.74	2.67	1.85	4.57	2.67
2.50	0.600	0.95	0.38	1.03	0.77	0.63	1.03
2.50	0.803	2.0	0.95	1.64	1.40	1.58	1.64
2.51	1.040	5.3	2.50	3.03	2.30	4.17	3.03
1.21	0.966	4.4	2.64	2.45	1.82	4.40	2.45
1.83	0.50	0.61	0.24	0.73	0.52	0.40	0.73
1.81	0.60	0.88	0.41	0.92	0.78	0.69	0.92
1.90	0.801	2.0	1.04	1.55	1.38	1.73	1.55
1.84	1.049	8.0	3.09	3.15	2.19	5.16	3.15

[a] The LHP subscripts refer to the predictions for the Longuet–Higgins and Pople expressions [8, 9]. The H subscripts are the predictions from empirical formulas, Eqs. (8) and (9).

3. LENNARD–JONES FLUIDS: TRANSPORT COEFFICIENT RATIOS

Now we focus on relations between transport coefficients which emerge from the hard-sphere theories (see Collins and Raffel [11] and Longuet–Higgins and Pople [8]) and the "exact" MD results. The first of these relationships concerns the ratio of the thermal conductivity, λ to the shear viscosity, η_s. Using the Longuet–Higgins and Pople formulas, one obtains the following relationship between the thermal conductivity and the shear viscosity,

$$\frac{\lambda}{\eta_s}=\frac{5k_B}{2m} \tag{10}$$

The ratios, λ/η_s, obtained from simulation are given in Table III, and (apart from the low-density state of $\rho=0.6$) are quite close to the value of 2.5 in reduced units predicted by Eq. (10).

The second relationship we consider is the product of the self-diffusion coefficient and the shear viscosity. Using the Longuet–Higgins and Pople formulas, we obtain

$$D\eta_s=\frac{\sigma_{\mathrm{HS}}^2}{10}\rho_{\mathrm{HS}}k_B T \tag{11}$$

Results for this product are compared with the MD LJ values in Table III. Again, the ratio given by Eq. (11) is seen to be semi-quantitative apart

Table III. Test of Eqs. (10) and (11) for the LJ Fluids Using the Thermal Conductivities and Shear and Bulk Viscosities Computed by Molecular Dynamics [4, 6]

T	ρ	$\lambda_{\mathrm{MD}}/\eta_{\mathrm{s,MD}}$	$D_{\mathrm{MD}}\eta_{\mathrm{s,MD}}$	$\sigma_{\mathrm{HS}}^2\rho_{\mathrm{HS}}k_{\mathrm{B}}T/10$
0.73	0.844	2.03	0.099	0.068
1.06	0.910	2.24	0.14	0.096
1.46	0.993	1.78	0.195	0.13
2.50	0.600	4.39	0.30	0.11
2.50	0.803	3.60	0.36	0.15
2.51	1.040	2.60	0.31	0.19
1.21	0.966	2.02	0.18	0.11
1.83	0.50	4.26	0.23	0.076
1.81	0.60	3.86	0.23	0.091
1.90	0.801	3.70	0.26	0.12
1.84	1.049	1.69	0.26	0.16

from the low density states where the right-hand side of this equation is a factor of between 2 and 3 lower than the left-hand side. Otherwise, a factor of two usually covers the deviations between the two sides of Eq. (11).

For the ratio of the thermal conductivity to the self-diffusion coefficient, Tankeshwar [12] has used time-dependent correlation functions to derive the approximate relation,

$$\lambda = \frac{2\pi\rho(C_p - C_v)\,D}{S(0)} \tag{12}$$

where we can use for the structure factor in the limit of zero k-vector, $S(0) = \rho k_{\mathrm{B}}T\kappa_T$, in terms of the isothermal compressibility, κ_T. An assessment of the accuracy of these expressions can be made for the LJ fluid using its equation of state and transport coefficients in Table I. The formula for λ in Eq. (12) gives values that are about a factor of 2 too large (see Table I) when compared with the simulation values. This relation is again of some practical use at liquid-like densities but is a factor of 2 to 3 too large at lower reduced densities ~ 0.5.

4. LIQUID METALS

The self part S_{s} of the van Hove dynamical structure factor referred to above can be written explicitly in the long-time and long-wavelength limits as Ref. 3,

$$S_{\mathrm{s}}(k, \omega) = \frac{Dk^2}{\pi(\omega^2 + (Dk^2)^2)} \tag{13}$$

which, because of the range of validity (large r and t) of the diffusion equation, applies for small k and ω. It follows from Eq. (13) that one can write for the transport coefficient D:

$$\frac{D}{\pi} = \lim_{\omega \to 0} \omega^2 \lim_{k \to 0} \frac{S_s(k, \omega)}{k^2} \tag{14}$$

which is the first of the so-called Green–Kubo formulas.

4.1. van Hove Dynamical Structure Factor $S(k, \omega)$

Having introduced a formula for diffusion, let us turn to the dynamic generalization [i.e., $S(k, \omega)$] of the static liquid structure factor $S(k)$ which has already been discussed. The first point is that $S(k, \omega)$ has the physical interpretation that it is the probability that a neutron incident on the liquid transfers momentum $\hbar k$ and energy $\hbar\omega$ to the liquid. The second point is that the integral of the dynamical structure factor $S(k, \omega)$ over all energy transfers $\hbar\omega$ leads back to $S(k)$, i.e.,

$$\int_{-\infty}^{\infty} S(k, \omega)\, d\omega = S(k) \tag{15}$$

In addition to this so-called zero-moment theorem, it can also be shown for a classical liquid consisting of ions of mass m that

$$\int_{-\infty}^{\infty} \omega^2 S(k, \omega)\, d\omega = \frac{k^2 k_B T}{m} \tag{16}$$

which is the second-moment theorem. There is a corresponding Green–Kubo formula for $S(k, \omega)$ to that of Eq. (14), namely,

$$\lim_{\omega \to 0} \omega^4 \lim_{k \to 0} \frac{S_s(k, \omega)}{k^4} = \frac{k_B T}{\pi} \frac{(\frac{4}{3}\eta_s + \zeta)}{\rho m^2} \tag{17}$$

where ρ is the ionic number density of the liquid and ζ is the bulk or compressional viscosity.

4.2. Relationships Between D and η_s for Liquid Metals Above the Freezing Point

The above Green–Kubo formulas were applied by Brown and March [13] to liquid metals as follows. For liquid metals just above the melting temperature, T_m, they exploited the fact that the self-correlation function $S_s(k, \omega)$ and the dynamical structure factor $S(k, \omega)$ entering the Green–Kubo formulas have a rather well-defined frequency range $0 < \omega < \omega_D$, the Debye frequency ω_D being analogous to that in a crystalline solid. Relating ω_D to the melting temperature T_m using Lindemann's law of melting, Brown and March obtained the approximate relations for the ionic transport coefficients at T_m:

$$\frac{Dm^{1/2}\rho^{1/3}}{T_m^{1/2}} = \text{constant} \tag{18}$$

and

$$\frac{\eta_s}{m^{1/2}\rho^{2/3}T_m^{1/2}} = \text{constant} \tag{19}$$

The formula in Eq. (19) was obtained earlier from kinetic theory by Andrade [14, 15] and which leads to reasonably quantitative results if the constant is chosen empirically as illustrated in Table IV below. However, the result from Eq. (18) is less impressive. One reason for this is that whereas Eqs. (18) and (19) yield a relation between D and η_s at melting of the form,

$$\frac{D\eta_s}{k_B T}\rho^{-1/3} = \text{constant} \tag{20}$$

Table IV. Shear Viscosities (in mPa.s) of Liquid Metals at Freezing: Theoretical Values Are Derived from Eq. (19)

Metal	Experiment	Theory
Li	0.60	0.56
Na	0.69	0.62
K	0.54	0.50
Rb	0.67	0.62
Cs	0.69	0.66
Cu	4.1	4.2
Ag	3.9	4.1
Au	5.4	5.8
In	1.9	2.0
Sn	2.1	2.1

subsequent work of Zwanzig [16, 17] discussed in March [18] yields more generally

$$\frac{D\eta_{\mathrm{s}}}{k_{\mathrm{B}}T}\,\Omega^{1/3}=0.0658\left(2+\frac{\eta_{\mathrm{s}}}{\eta_{l}}\right) \tag{21}$$

where Ω is the ionic volume and η_l is the longitudinal viscosity. When results for η_{s}/η_l eventually become available, it will be interesting to test Eq. (21) for liquid metals at T_{m} in more detail than is currently possible.

5. WIEDEMANN–FRANZ LAW RELATING THERMAL AND ELECTRICAL CONDUCTIVITY IN LIQUID METALS

The dominant contribution to the thermal conductivity, λ, of metals arises from the electrons, i.e., λ_e. The Wiedeman–Franz law relates this contribution from the electrons to the electical conductivity, σ, through

$$\frac{\lambda_e}{\sigma T}=\frac{\pi^2 k_{\mathrm{B}}^2}{3e^2}=L \tag{22}$$

where L is the so-called Lorenz number. Therefore, below we outline the weak scattering theory of electical resistivity, $R=\sigma^{-1}$.

5.1. Weak Scattering Theory of Electrical Resistivity

The idea behind weak scattering theory is to represent the total potential energy, $V(r)$, scattering the conduction electrons by a sum of screened potentials $v(r)$ at the ionic sites, $\underline{R}_i$, where one has taken a "snapshot" of the ions at a particular time:

$$V(\underline{r})=\sum_i v(|\underline{r}-\underline{R}_i|) \tag{23}$$

The resistivity R is then found by using this result and working to second order in v. As only pairs of sites $\underline{R}_i$ are then correlated, taking the liquid average, one, obtains a result in terms of the structure factor $S(k)$ and the Fourier transform of the localized potential $\tilde{v}(k)$ say in Eq. (23). The result, when one puts back all of the numerical factors, is for weak scattering with a sharp Fermi surface of diameter $2k_f$ [15] with v_f the corresponding Fermi velocity,

$$R=\frac{3\pi}{\hbar e^2 v_f^2 \rho_i}\frac{1}{(2k_f)^4}\int_0^{2k_f} S(k)\,|\tilde{v}(k)|^2\,4k^3\,dk \tag{24}$$

This is the basic formula for the electrical resistivity, R, of simple $(s-p)$ nearly free electron metals such as Na and K. In Eq. (24), ρ_i is the ionic number density and, since $S(k)$ is measurable by diffraction experiments, the only quantity needed to determine R is the Fourier transform of the localized atomic-like screened potential energy $\tilde{v}(k)$. Some discussion of the way approximations may be set up for this quantity is given in Ref. 15. It is also relevant to note that real liquid metals have blurred Fermi surfaces in accord with the Heisenberg uncertainty principle,

$$l \Delta k_f \sim 1 \tag{25}$$

where Δk_f is the blurring of k_f and l is the electronic mean free path.

Tosi et al. [19] have applied Eq. (24) to the liquid alkali metals and find excellent agreement. March and Tosi [20] have recently shown that use of the Wiedemann–Franz Law of Eq. (22) then allows the temperature dependence of the measured thermal conductivity of liquid Na to be obtained theoretically in, better than a semi-quantitative manner. These workers have also related D, λ, and η_s at the melting temperature of liquid metals.

6. SUMMARY AND FUTURE DIRECTIONS

Emphasis has been placed here on relations between transport coefficients of (a) Lennard–Jones fluids and (b) liquid metals near freezing. For case (a) the ratio of the thermal conductivity to shear viscosity is usefully given by Eq. (10) when simulation results are employed for all but the lowest density states revealed in Table III. The factor 5/2 following from the hard sphere model applies quite well to the LJ simulation derived transport coefficients (which we assume to be essentially exact). Similarly, Eq. (11) relating diffusion and shear viscosity has been found to represent the results of the LJ simulations quite well, again apart from the low-density states.

We have also tested the formula given in Eq. (12) of Tankeshwar [12], in which using time correlation functions he has related the ratio λ/D to the thermodynamic quantities including the long wavelength limit of the structure factor, $S(k)$. His relation agrees satisfactorily with the transport coefficients obtained by simulation of Lennard–Jones fluids.

Liquid metals have also been discussed, but in a much more limited way in that most of the considerations on transport currently apply at the freezing point only. However, the Wiedemann–Franz law given in Eq. (22) and the electrical resistivity (Ziman–Krishnan–Bhatia) formula of Eq. (23) are notable exceptions to this rule. The formula of Eq. (19) which was first given by Andrade [14] and derived subsequently from Green–Kubo theory by Brown and March [13] works extremely well as shown in Table IV. Equation (21) relating the product of $D\eta_s$ to the ratio η_s/η_l has not yet been subjected to careful tesing either from experiment (because of lack of data on the longitudinal viscosity) or because of the absence of systematic computer simulation results. It would clearly be of interest in the future to have data which will allow Eq. (21) due to Zwanzig to be tested.

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