Relation between the transport coefficients and the internal entropy of simple systems

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The transport coefficients of hard-sphere, soft-sphere, Lennard-Jones, and one-component-plasma systems are expressed in terms of the corresponding internal entropies, to reveal some universal characteristics. The transport of all the inverse nth-power repulsive potentials appears to be related, and can be numerically estimated by the hard-sphere model, although the hard-sphere transport is different. The entropy dependence of the coefficients of self-diffusion and (to a lesser extent) shear viscosity, for systems with purely repulsive potentials, is only slightly affected by the addition of an attractive potential.

I. INTRODUCTION

The purpose of the present work is to relate the equation of state and transport data of simple systems. We find it helpful to relate the transport coefficients to the internal entropy. This relation enables direct comparison with the hard-sphere model and has a special merit by itself since it features universal properties.

The hard-sphere model, for interpreting both static and dynamic thermodynamic properties of simple systems, is briefly discussed in Sec. II. In Sec. III this model is applied to calculate the transport coefficients of the one-component plasma (OCP). In Sec. IV we relate the transport coefficients to the internal entropy, following an indication by the variational hard-sphere model. The effect of adding attractive forces on the transport coefficients of a purely repulsive potential is discussed in Sec. V in terms of the corresponding effect on the entropy. The major findings are summarized in Sec. VI.

II. THE HARD-SPHERE MODEL

The hard-sphere approach to understanding liquids has been most successful. This model explains the observed structure factor of many liquid metals near their freezing points[1] and the experimental viscosity data of monatomic liquids.[2] The model is fruitfully applied in connection with the Lindemann law for hard spheres to yield simple melting equations[3] and additivity of melting curves.[4] In turn, systematic methods were developed for calculating fluid[5] and solid[6,7] equilibrium thermodynamic properties from interparticle potentials. Of these, the Mansoori-Canfield variational method[8] proved successful in interpreting both static[9] and dynamic[10] properties of the inverse 12th power potential and the Lennard-Jones (LJ) system. This method has also

been applied, with considerable success, to other inverse power potentials,[9] to liquid metals,[11] liquid metal alloys,[12] to the screened Coulomb potential,[13] and has been recently extended to treat also the OCP.[14]

In the variational method, one minimizes the free-energy functional with respect to ξ:

$$F(\rho, T, \xi) = F^I(\rho, T) - T S_{HS}^E(\xi)$$
$$+ 12\xi \int_1^\infty \phi(xd) g_{HS}(x; \xi) x^2 \, dx, \quad (1)$$

to get an upper bound of the free energy per particle of the system. F^I is the ideal-gas contribution, $S_{HS}^E(\xi)$ is the excess entropy per particle of the hard-sphere system, $\phi(x)$ is the pair potential of the given system, $g_{HS}(x)$ is the hard-sphere radial distribution function, and $\xi = \frac{1}{6}\pi\rho d^3$ is the hard-sphere packing fraction where d is the hard-sphere diameter and ρ is the number density. The correspondence with the hard-sphere system is obtained through a density- and temperature-dependent packing fraction $\xi(\rho, T)$ from the solution of

$$\left. \frac{\partial F(\rho, T, \xi)}{\partial \xi} \right|_{\rho, T} = 0. \quad (2)$$

The approximate excess free energy per particle is given by

$$F^E(\rho, T) \leqslant F(\rho, T, \xi(\rho, T)) - F^I(\rho, T).$$

Other thermodynamic properties are obtained by the usual thermodynamic relations. In particular, the excess entropy per particle is given by

$$S^E(\rho, T) = - \left. \frac{\partial F^E(\rho, T)}{\partial T} \right|_\rho$$

$$\geqslant - \left. \frac{\partial F^E}{\partial T} \right|_{\rho, \xi} - \left. \frac{\partial F^E}{\partial \xi} \right|_{\rho, T} \left. \frac{\partial \xi}{\partial T} \right|_\rho. \quad (3)$$

The last term in Eq. (3) vanishes because of Eq. (2), and the entropy of the system is approximated by the entropy of the hard spheres, i.e.,

$$S^E(\rho, T) \geqslant S^E_{HS}(\xi(\rho, T)).$$ (4)

It will prove useful in what follows to define the reduced coefficients of self-diffusion, D, and shear viscosity, η, which are scaled by the thermal velocity $(k_B T)^{1/2}$ and powers of the number density ρ:

$$D^*(\xi) = D\rho^{1/3}(m/k_B T)^{1/2},$$ (5)

$$\eta^*(\xi) = \eta\rho^{-2/3}(mk_B T)^{-1/2},$$ (6)

where m is the particle mass.

For hard spheres, Dymond[15] presents transport coefficients from the molecular-dynamics results of Alder et al.[17] in terms of the Enskog expressions and density-dependent correction factors. Here we do not treat other transport coefficients for lack of computer data.

III. RESULTS FOR THE OCP

The calculations by the variational HS model have the physically appealing characteristic that both transport and static properties, of the inverse 12th power potential and the LJ system, may be computed together by minimizing the free energy.[10] The situation is, however, much less favorable in the case of the OCP. In this case the packing fraction ξ, which minimizes the free energy, is related to the conventional scaled parameter for the plasma,

$$\Gamma = \frac{(Ze)^2}{kT}\left(\frac{4\pi}{3}\rho\right)^{1/3},$$

in closed form to yield[14]

$$\Gamma = 2\xi^{1/3}\frac{2-\xi}{2+\xi}\frac{(1+2\xi)^2}{(1-\xi)^5}.$$ (7)

For the dense OCP, $\Gamma > 100$, Eqs. (5), (6), and (7) predict much too high values of D and η (factor $\simeq 4$), that is, Eq. (7) gives values of ξ which are too large.

Levesque and Verlet[18] chose the hard-sphere packing fraction ξ for which the structure factor for a hard-sphere and LJ liquids had the same height in the first peak. They found that in order to reproduce the LJ molecular-dynamics data, they had to multiply the approximate expression for the self-diffusion [Eq. (5)] by a factor of 1.28. We performed similar calculations (without the 1.28 factor) for the OCP (using the Percus-Yevick[19] hard-sphere structure factors and the OCP structure factors published by Hansen[20]) to find reasonable agreement with Hansen and collaborators[21,22] (see Table I).

TABLE I. The reduced coefficients of self-diffusion, D^*, and shear viscosity, η^*, of the OCP.

Γ	D^{*a}	D^{*b}	η^{*a}	η^{*c}
10	0.4	0.43	0.5	0.3
100	0.08	0.06	2	1.7
140	0.04	0.05	4	2.7

[a] Calculated by the hard-sphere model with the "structure-factor" packing fractions.
[b] Reference 21.
[c] Reference 22.

From these results we find that the structure-factor criterion for choosing ξ has a more stable predictive character than the variational criterion. Moreover, the structure factor of real systems can be measured and can predict transport coefficients by means of the hard-sphere model. This is a crucial advantage over the variational method in cases when the effective potential is unknown.

IV. RELATION BETWEEN THE TRANSPORT COEFFICIENTS AND THE INTERNAL ENTROPY

Since we want to relate the transport coefficients to the equation of state, for which there are more readily available data for real materials, we pursue the possibility indicated by Eq. (4) and determine ξ from the excess entropy data of the system by solving Eq. (4). Beside other consequences which will be discussed later, this choice of ξ can be cast into a simple closed form upon using the Carnahan-Starling hard-sphere equation of state.[16]　Denote

$$s = -\frac{S^E(\rho, T)}{k_B} = \frac{4\xi - 3\xi^2}{(1-\xi)^2}.$$

Then Eq. (4) yields

$$\xi = \frac{s+2}{s+3}\left[1 - \left(1 - \frac{s(s+3)}{(s+2)^2}\right)^{1/2}\right].$$ (8)

We call this the "entropy" packing fraction.

Equations (5), (6), and (8) define the HS approximation for the transport coefficients with the "entropy" packing fraction. To the extent that this model can predict equally accurately the transport coefficients of different systems, we expect $D^*(s)$ and $\eta^*(s)$ to be nearly universal functions. Moreover, the accuracy of the hard-sphere model in determining D and η of various systems can be inferred directly upon plotting $D^*(s)$ and $\eta^*(s)$ together with $\eta^*_{HS}(s)$ and $D^*_{HS}(s)$.

Computer transport-coefficient data are available for the LJ system,[18,23] the inverse 12th power potential,[10,23,24] and for the OCP.[21] This data, although limited, enables one to judge the capa-
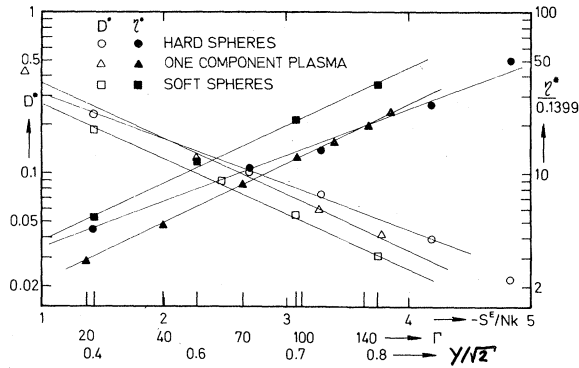
FIG. 1. Reduced coefficients of self-diffusion, D^*, and shear viscosity, η^*, as functions of the excess entropy (S^E/k_B), for hard spheres (Ref. 17), soft spheres (Ref. 23), and the OCP (Refs. 21,22). The straight lines are given as visual aids. Note the OCP point beyond the left margin.

bility of the present method for a large class of systems. The inverse 12th power potential and the OCP serve as two rather extreme test cases. The LJ data allows investigation of the effect of attractive forces added to a purely repulsive potential.

The inverse 12th power potential, $\phi(r) = \epsilon(\sigma/r)^{12}$, and the OCP, $\phi(r) = (Ze)^2/r$, have the scaling property, i.e., the excess entropy depends on only one reduced-density temperature variable, $y = \rho\sigma^3(\epsilon/kT)^{1/4}$ and Γ, respectively. For the inverse 12th power potential we use Hansen's[25] fit to the Monte Carlo data, to obtain

$$s = 1.9171y + 0.9080y^2 + 0.3091y^3 - 0.0102y^{10}. \quad (9)$$

For the OCP we can use Hansen's[20] fit to his Monte Carlo data, or preferably an excellent and simple fit by DeWitt,[26] to get

$$s = 2.4494\Gamma^{1/4} - 0.50123\ln\Gamma - 2.3148. \quad (10)$$

In Fig. 1 we plot D^* and η^* (on a logarithmic scale) versus s for the purely repulsive potentials: the hard spheres (HS), the inverse 12th power potential [i.e., soft spheres (SS)], and the OCP. For the shear viscosity η^* of the OCP we took the "H_3 super-0.02" results of Table III in Ref. 22, since they agree better with the molecular-dynamics results of Ref. 21 near the fluid-solid transition. To a good accuracy, $\log D^*$ and $\log\eta^*$ are nearly linear in s for the three systems considered. The hard-sphere model with the "entropy" packing fraction [Eqs. (5), (6), and (8)] reproduces the OCP transport coefficients to a reasonable accuracy at large s, and resembles more the soft-sphere results at small values of s. Interestingly enough, the lines representing the data of the OCP and the SS are nearly parallel,

i.e.,

$$D^*_{OCP}(s) \lesssim 1.4 D^*_{SS}(s), \quad \eta^*_{SS}(s) \approx 1.7\eta^*_{OCP}(s), \quad (11)$$

which suggests that these numbers could be related to the repulsive power index n if other nth-power transport data are available.

Figure 1 shows that the HS model with the "entropy" packing fraction can be used for quantitative estimation of the transport of dense simple systems. However it does show that for $n = \infty$ (hard spheres) the transport is distinctly different from the $n = 1$ (OCP) and $n = 12$ (SS) cases.

V. EFFECT OF ATTRACTIVE FORCES

To see the effect of adding an attractive term to a purely repulsive potential, we plot, in Fig. 2, the transport coefficients of the inverse 12th power potential and the LJ system. The self-diffusion data of the soft-sphere and the LJ systems lie on nearly the same line in the $\log D^*$-vs-s plot, i.e.,

$$D^*_{SS}(s) \cong D^*_{LJ}(s) = 0.585\exp(-0.788s). \quad (12)$$

The same trend, but to a lesser extent, is observed also for the shear viscosities, $\eta^*_{SS}(s) \approx \eta^*_{LJ}(s)$. In Ref. 23 η_{LJ} is given in terms of the transport scaling variables of the SS system.

At given ρ^*, T^* the effect of adding an attractive force to the inverse 12th power potential is to increase the diffusion coefficient. For example, at $T^* = 1$ and $\rho^* \gtrsim 0.8$ we find $D^*_{LJ} \sim 2D^*_{SS}$. Physically the reason for this is that the attractive term reduces the repulsion and decreases the size of the
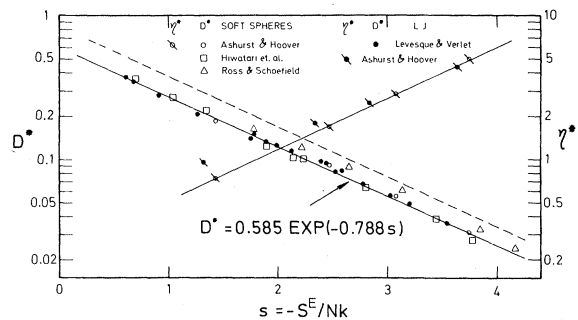

FIG. 2. Reduced coefficients of self-diffusion, D^*, and shear viscosity, η^*, as functions of the excess entropy (S^E/k_B) for the soft-sphere and LJ systems. The LJ shear-viscosity data along the saturated-vapor-pressure line is taken from Ashurst and Hoover (Ref. 23). The LJ self-diffusion data is taken from Levesque and Verlet (Ref. 18). For the soft spheres we plot the data of Ashurst and Hoover (Ref. 23), Hiwatari et al. (Ref. 24) (results for 108 particles), and Ross and Schofield (Ref. 10) (results for 500 particles). The broken line represents the results for the OCP and is given for comparison.

TABLE II. The excess entropy $[s = -S^E(\rho, T/k_B)]$ of the LJ system.

T^*	ρ^*	s Monte Carlo (Ref. 27)	Eq. (14)
2.74	0.70	1.79	1.79
	0.80	2.21	2.17
	0.90	2.65	2.60
	1.00	3.11	3.14
	1.08	3.55	3.76
1.35	0.70	2.18	2.15
	0.80	2.70	2.63
	0.90	3.28	3.27
	0.95	3.56	3.75
1.15	0.75	2.57	2.46
	0.85	3.15	3.05
	0.92	3.62	3.67
0.75	0.70	2.59	2.40
	0.80	3.24	3.01
	0.84	3.52	3.36

effective hard spheres, thereby increasing their diffusivity. We find that a completely quantitative account of this effect is taken care of by the entropy analysis: At given ρ^*, T^* the effect of adding the attractive term is to increase the entropy and thus to increase the diffusivity. A similar analysis holds also for the shear viscosity, except that there is also a long-range contribution to momentum transport from the potential in addition to the kinetic part.

To calculate the entropy of the LJ system,

$$\phi(r) = 4\epsilon \left[(\sigma/r)^{12} - (\sigma/r)^6 \right] ,$$

(reduced units $\rho^* = \rho\sigma^3$, $T^* = kT/\epsilon$), we make use of the tables of Monte Carlo data given by Verlet and Weis[27] and by Hansen,[25] and interpolate graphically when needed.

A consistency check of our calculations can be made in the following manner. Levesque and Verlet[18] fit their molecular-dynamics results of the self-diffusion of the LJ system in the region $T^* \lesssim 5$, $\rho^* > 0.65$, by a simple expression:

$$D_{LJ}^*(\rho^*, T^*) = \rho^{*1/3}(48/T^*)^{1/2}(0.006\,423T^*/\rho^{*2}$$

$$+ 0.0222 - 0.0280\rho^*) .$$

$$(13)$$

Equating the expressions (12) and (13), we obtain the following approximation for the entropy of the LJ system:

$$\frac{S_{LJ}^E(\rho^*, T^*)}{k_B} = \frac{1}{0.788} \ln \left(\frac{D_{LJ}^*(\rho^*, T^*)}{0.585} \right). \qquad (14)$$

In Table II we compare the prediction of Eq. (14) with the values obtained directly from the tables given in Ref. 27, and find good agreement.

VI. CONCLUSIONS

We find that expressing the transport coefficients of dense simple systems in terms of the internal entropy is very useful. Figure 1 shows that there is a simple relation between repulsive power transport for $n = 1$ (OCP) and $n = 12$ (SS) and suggests that other values of n will also be simply related. With transport data for some other n values, the proper interpolation could be determined and Fig. 1 would provide nearly all the nth-power transport.

Figure 2 shows that the addition of an attractive potential to the repulsive power system, does not change the functional dependence of self-diffusion upon entropy, while it does have a small effect on the shear-viscosity dependence. Thus in analyzing transport data of real materials, it is enough to have an idea of the repulsive forces.

DeWitt[26] has shown that dense repulsive-power-potential systems obey a universal equation of state in the form

$$\frac{\Delta U}{Nk_BT} \equiv \frac{U - U_s}{Nk_BT} = a\delta_E^{-1/2} + b , \qquad (15)$$

where U is the internal energy, U_s is the static fcc lattice contribution, and δ_E is the Einstein approximation for the Lindemann ratio. The constants a (≈ 0.85) and b (≈ 0.5) are nearly independent of n for $1 \leqslant n \leqslant 12$. This universality of the equation of state of the repulsive power potentials is exhibited also by the corresponding variational upper bounds.

The "universal" plot of the transport coefficients vs the internal entropy together with the "universal" equation of state [like Eq. (15)] yield a relatively simple description of transport behavior throughout the dense fluid region, and should also be useful for empirical correlations of experimental data.

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