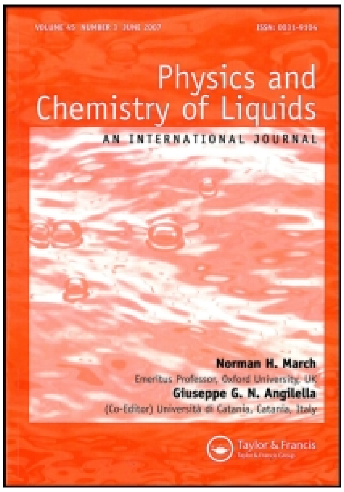

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Letter

Enskog's Modification of Hard Sphere Theory Related to Andrade's Melting Point Formula for Shear Viscosity

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It is pointed out that by using Enskog's modification of the formula given by Longuet-Higgins and Pople for the shear viscosity η of a dense fluid of hard spheres, the form of Andrade's melting point expression for η can be extracted.

Key Words: Kinetic pressure, Joule's Law, packing fraction.

Transport in dense fluids continues to present considerable problems for analytical theory, although computer experiments have certainly led to deeper insight into such non-equilibrium properties.[1]

A long time ago, using the Green–Kubo-type approach, Brown and March[2] gave arguments appropriate to those liquid metals with a rather well-defined Debye frequency which led to the approximate formula for the shear viscosity $\eta(T)$:

$$\eta(T_m) = \text{const.}\,\frac{T_m^{1/2}M^{1/2}}{\Omega^{2/3}} \tag{1}$$

at the melting temperature T_m, M being the atomic mass and Ω the atomic volume. This formula was in fact given earlier by Andrade[3] from a kinetic theory argument which no longer finds ready acceptance.[4] However, as can be seen from Table 2 of Ref. 2, the formula (1) remains useful also for liquified rare gases, for which the assumption of a well-defined Debye frequency is not appropriate.

It therefore seems of interest to attempt a more general justification of the form of Eq. (1) than was given by Brown and March.[2] This will be done in a sequence of steps as follows:

i) The starting point is the result derived for the shear viscosity η of a dense fluid of hard spheres by Longuet-Higgins and Pople,[5] namely

$$\eta = \frac{4a}{5}\left(\frac{Mk_BT}{\pi}\right)^{1/2}\left(\frac{p}{k_BT} - \frac{N}{V}\right) \tag{2}$$

with M and a the mass and radius of the spheres; a rather similar formula also emerges from free volume considerations.[6]

ii) Enskog's modification of replacing p in Eq. (2) by the so-called "kinetic pressure" $T(\partial p/\partial T)_V$ is adopted[5] as an approximate way to characterize attractive forces.

iii) Thermodynamics is used to relate the kinetic pressure to departures from Joule's Law, described by the magnitude of $(\partial U/\partial V)_T$, with U the internal energy.

iv) Departures from Joule's Law are estimated from specific heat data plus the long-wave limit $S(0)$ of the liquid structure $S(k)$.

Following the above procedure, steps (ii) and (iii) lead almost immediately to the result, with $\rho = N/V$,

$$\eta = \frac{4a}{5}\left(\frac{Mk_BT}{\pi}\right)^{1/2}\rho\left[\frac{1}{\rho k_BT}\left(\frac{\partial U}{\partial V}\right)_T + \frac{p}{\rho k_BT} - 1\right]. \tag{3}$$

Now one takes step (iv), which is facilitated by reference to recent work of the writer[7] on departures from Joule's Law in dense liquids near freezing related to vacancy properties in hot crystals. In particular, when $p/\rho k_BT \ll 1$, as it is in the dense liquids under discussion, then $1/\rho k_BT(\partial U/\partial V)_T$ can be estimated from specific heat data and $S(0)$ as

$$\frac{1}{\rho k_BT}\left(\frac{\partial U}{\partial V}\right)_T \simeq \left\{\frac{(\gamma - 1)C_v/k_B}{S(0)}\right\}^{1/2} \tag{4}$$

with $\gamma = C_p/C_v$. As noted in Ref. 7, estimates of Eq. (4) for liquid metal rubidium near freezing, or for liquid argon near the triple point, lead to a value ~ 7. Thus, the formula (1) is regained, at least qualitatively, when it is noted that the liquid packing fraction is almost constant for dense liquids near freezing.[4]

In summary, the form of Eq. (1), due originally to Andrade,[3] is shown to emerge from Enskog's modification of hard sphere theory, given (a) the approximate constancy of Eq. (4) at the melting point and (b) the similarity of the packing fractions of dense liquids near freezing.

Modifications and refinements of the present approach are currently under quantitative examination by Chapman and March[8] in relation to the thermal conductivity λ of dense insulating fluids. The hard sphere theory of Ref. 5 predicts the ratio η/λ to be $2M/5k_B$ and this relation is currently being explored as a possible route to calculating thermal conductivity in such systems.

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