Relation between transport and thermodynamic properties in liquid *sp*-electron metals near freezing

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(Received 18 February 1999)

Classical statistical mechanics based on assumed pair potentials leads, for liquid metals, to an approximate relation between shear viscosity η, surface tension σ, and thermal velocity v_T defined as $(k_BT/M)^{1/2}$, with M the ionic mass. Theory predicts for the dimensionless grouping $\sigma/\eta v_T$ evaluated at the melting temperature T_m a single value $\frac{15}{16}$; liquid *sp*-electron metals exhibit, however, a scatter from around 0.7 to 2.3. Therefore, an alternative grouping $\sigma/\eta v_s$, with v_s the velocity of sound, is considered here in detail, first using experimental data and second using both theoretical and semiempirical arguments. The scatter of $\sigma/\eta v_s$ at T_m is less than for the earlier grouping, and also insight can be gained as to various physical factors determining $\sigma/\eta v_s$. In essence, this quantity is proportional to the product of two factors, both dimensionless, namely, the surface thickness L measured in units of the mean interionic separation, and the square root of the energy Mv_s^2, measured in units of the thermal energy k_BT_m. Theoretical estimates are made of both of these factors, in fair accord with the experimental data. [S1063-651X(99)07610-2]

PACS number(s): 66.20.+d, 61.25.Mv, 68.35.Md

I. INTRODUCTION

Interest in the transport properties of liquid metals continues, as evidenced by the recent discussion of self-diffusion and the velocity autocorrelation function by Wallace [1]. While this study gives an explicit account of liquid dynamics, there has been movement recently in relating atomic transport to thermodynamic properties. Here we press further this later approach, which we shall introduce by referring first to the recent investigations by Egry [2,3] and ourselves [4].

It has been known for some time, and emphasized especially in the work of Egry [2,3], that a transport property in a dense liquid, the shear viscosity η, can be approximately related to a thermodynamic quantity, the surface tension σ, by formulas from classical statistical mechanics. For σ, the formula goes back to Fowler [5] who gave the result

$$\sigma = \frac{\pi}{8} n^2 \int_0^\infty \frac{d\phi}{dr} r^4 g(r) dr, \tag{1}$$

where n is the particle number density, $\phi(r)$ is an assumed pair potential, and $g(r)$ is the atomic pair correlation function of the bulk liquid. Turning to η, the Born-Green [6] (highly approximate) formula involves precisely the same structural integral, and using the notation of Egry the dimensionless quantity Q defined precisely at the melting temperature T_m as

$$Q = \frac{16}{15} \frac{\sigma}{\eta} \left(\frac{M}{k_BT_m} \right)^{1/2}, \tag{2}$$

where M is the atomic mass and k_B the Boltzmann constant, is predicted by the above formula to be precisely unity. In fact, we have shown [4] for about a dozen *sp*-electron metals that there is a spread of Q values at the melting point from 0.8 to 2.5. If we define the quantity $(k_BT_m/M)^{1/2}$ appearing in Eq. (2) as the thermal velocity v_T, then the above arguments indicate that at T_m the dimensionless grouping $\sigma/\eta v_T$ is very near to unity from theory but in practice has a spread of values of a factor of ~ 3 from smallest to largest.

This has led one of us [7] to propose that a study of a different dimensionless grouping, involving the velocity of sound v_s rather than v_T, defined as

$$R = \frac{\sigma}{\eta v_s}, \tag{3}$$

might be fruitful in reducing the above scatter and also in gaining further insight into the basic origin for the relation between the transport property η and the thermodynamic property σ at the melting point of *sp*-electron metals. Such a study is the focus of the present paper.

II. RELATION BETWEEN THE TWO DIMENSIONLESS GROUPINGS $\sigma/\eta v_T$ AND $\sigma/\eta v_s$ AT THE MELTING TEMPERATURE

To see a connection between the quantities Q and R defined in Eq. (2) and (3), respectively, we appeal first to the fluctuation theory result that relates the liquid structure factor $S(k)$ (essentially the Fourier transform of $[g(r)-1]$) in the long-wavelength limit $k \to 0$ to the isothermal compressibility K_T through [8]

TABLE I. Experimental values of the structure factor $S(k=0)$ at the melting temperature and the ratio of specific heats $\gamma = C_p/C_v$ for liquid *sp*-electron metals [8,9].

Metal	$S_{T_m}(0)$	γ	$\left(\frac{S_{T_m}(0)}{\gamma}\right)^{1/2}$
Li	0.031	1.20	0.16
Na	0.023	1.13	0.14
K	0.023	1.11	0.14
Rb	0.022	1.15	0.14
Cs	0.024	1.18	0.14
Cu	0.021	1.45	0.12
Ag	0.019	1.45	0.11
Be	0.047		
Mg	0.025	1.38	0.13
Ca	0.035		
Sr	0.031		
Ba	0.036		
Zn	0.015	1.25	0.11
Cd	0.011	1.23	0.09
Hg	0.005		
Al	0.017	1.25	0.12
In	0.007	1.12	0.08
Tl	0.010	1.21	0.09
Pb	0.009	1.20	0.09
Ga	0.005	1.08	0.07
Sn	0.007		
Sb	0.019		
Bi	0.009	1.15	0.09

$$S_{T_m}(0) = n k_B T_m K_T . \tag{4}$$

This formula is readily rewritten in terms of the velocity of sound, by means of the ratio $(C_p/C_v)=\gamma$ of specific heats, as

$$S_{T_m}(0) = \frac{\gamma k_B T_m}{M v_s^2}. \tag{5}$$

Thus the thermal velocity v_T defined above is related to the velocity of sound v_s by

$$v_s = v_T \left[\frac{S_{T_m}(0)}{\gamma}\right]^{-1/2} . \tag{6}$$

Because of the form of this equation we have collected in Table I experimental data for $S_{T_m}(0)$, γ and $[S_{T_m}(0)/\gamma]^{1/2}$ for *sp*-electron metals. $S_{T_m}(0)$, calculated from Eq. (4) was taken from Ref. [9]. As seen from the final column of this table, $[S_{T_m}(0)/\gamma]^{1/2}$ varies from 0.07 to 0.16, the dominant variable being the structural one, since γ only varies from 1.08 to 1.45.

Table II records the values of Q defined in Eq. (2) and $\frac{16}{15}R$ defined through Eq. (3). σ was taken from Alonso and March [10], and the shear viscosity η was collected from several sources [2,4,11,12]. Values of v_s have been directly used when available, for instance, for the alkali metals [13]. In most other cases the following formula was used [14]:

TABLE II. Values of dimensionless groupings $Q = \frac{16}{15}(\sigma/\eta v_T)$, mostly from Ref. [4], and $\frac{16}{15}R = \frac{16}{15}(\sigma/\eta v_s)$.

Metal	Q	$10(\frac{16}{15}R)$
Li	1.01	1.6
Na	0.83	1.2
K	0.83	1.2
Rb	0.78	1.2
Cs	0.78	1.0
Cu	0.85	1.0
Ag	0.82	0.9
Au	0.98	
Mg	1.01	1.3
Ca	0.73	
Zn	0.83	0.9
Cd	1.31	1.2
Hg	2.50	0.9
Al	1.60	1.9
In	1.78	1.4
Pb	1.26	1.1
Ga	2.36	1.6
Sn	1.62	1.3
Sb	1.29	
Bi	1.74	1.6

$$v_s = (\rho K_s)^{-1/2}, \tag{7}$$

where ρ is the mass density of the liquid and K_s its measured adiabatic compressibility. Data for K_s was taken from Wilson [12]. Alternatively, v_s can be obtained from Eq. (6) using data for $[S_{T_m}(0)/\gamma]^{1/2}$ from Table I. The spread of Q in Table II is a factor of 3.4, whereas the spread of R is a lower factor of 2.1. The values of $\frac{16}{15}R$ have been multiplied by 10 in the table to make the two columns easily comparable.

The data collected to calculate Q and R has been taken at the melting temperature T_m. But Wallace [15] has discovered that some of the elements in Tables I and II show anomalous melting: Ga, Sn, Sb, and Bi. This is characterized by anomalously large values of the entropy of fusion ΔS, arising from a change in electronic ground state between solid and liquid phases [15]. This change is known in Sb and Bi, that melt from a solid semimetal to a liquid metal [16]. The actual melting temperatures of these two elements are above what their T_m would be if they had melted normally from a solid metal to a liquid metal. The anomalous ΔS behavior of Ga and Sn suggest that these also have a change in electronic ground state upon melting. In the classification introduced by Wallace Ga and Sn are weakly anomalous while Sb and Bi are moderately anomalous. Consequently, it might be advisable to restrict our study to metals showing normal melting. We have left the four anomalous melting elements at the bottom of Tables I and II because the scatter in Q or R does not decrease by restricting to normal melting, but the reader should keep in mind our reservation.

III. PHYSICAL FACTORS AFFECTING THE QUANTITY $\sigma/\eta v_s$

Having shown in Table II that there is some merit in considering the dimensionless grouping $\sigma/\eta v_s$ at T_m, let us

TABLE III. Experimental values of shear viscosity η at melting temperature in cp, compared with semiempirical Eq. (10). Constant A is fitted to liquid metal Sn.

Metal	Experiment	Formula (10)
Li	0.60	0.56
Na	0.69	0.62
K	0.55	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
Mg	1.1	1.4
Ca	1.1	1.3
Zn	3.3	2.6
Cd	3.3	2.5
Hg	2.1	2.0
Al	1.1	1.9
In	1.9	2.0
Pb	2.5	2.8
Ga	1.7	3.1
Sn	2.1	2.1
Sb	1.3	2.6
Bi	1.6	2.5

next examine the physical factors that enter this particular combination of transport and thermodynamic properties. This leads us first to introduce the surface thickness L, which we take to be defined by the equation

$$\sigma K_T = L. \tag{8}$$

Egelstaff and Widom [17] studied such a relation for a variety of dense liquids in earlier work, and we have previously examined it in the context of liquid metal surfaces [9,18,19]. The main findings for liquid metals may be summarized as follows. Average values of surface thickness L go from 0.43 Å in the alkalis to 0.35 Å in the alkaline earths, the value being lower at 0.19 Å in polyvalent nontransition metals. It is worth adding that if the range of liquid metals is extended to embrace transition metals and rare earths, then the values are 0.21 and 0.23 Å, respectively [18,19]. It can thus be concluded that a universal property of liquid metals is that the liquid-vapor interface is rather sharp, with a thickness that varies relatively little between different metal groups or between the different metals within a group.

Introducing, therefore, into the definition of R in Eq. (3) the relation $\sigma = L/K_T$ and then removing K_T by means of Eq. (4) and subsequently $S_{T_m}(0)$ via Eq. (5) one is led to the form

$$R = \frac{L}{K_T \eta v_s} = \frac{L n k_B T_m}{S_{T_m}(0)\, \eta v_s} = \frac{L n (M v_s^2)}{\gamma \eta v_s}. \tag{9}$$

To progress further, we next invoke a semiempirical formula for the shear viscosity η at T_m which goes back to Da Andrade [20] and has subsequently been obtained using Green-Kubo arguments by Brown and March [21]. This formula reads

$$\eta = A T_m^{1/2} n^{2/3} M^{1/2} \tag{10}$$

and Table III shows the results obtained when the constant A is fitted to Sn, following previous work for a smaller data set [21]. An interesting observation is that the largest deviations between Eq. (10) and experiment occur precisely for the anomalous-melting elements Ga, Sb, Bi: Eq. (10) leads to large shear viscosities that can be traced back to their anomalously large T_m. In other words, the empirical equation (10) is not adequate for the anomalous-melting elements. For the normal-melting elements all the trends of η at T_m are correctly given by Eq. (10) although the formula is not fully quantitative. Hence, introducing Eq. (10) into Eq. (9) we find, at T_m

$$\frac{\sigma}{\eta v_s} \simeq \text{const} \times \left(\frac{L n^{1/3}}{\gamma} \right) \left(\frac{M v_s^2}{k_B T_m} \right)^{1/2}, \tag{11}$$

where the constant is equal to $k_B^{1/2}/A$. This equation shows that the grouping $\sigma/\eta v_s$ is itself approximately proportional to the product of two dimensionless factors: (i) $L n^{1/3}/\gamma$, which evidently involves the surface thickness L in units of the mean interatomic separation divided by the specific heat ratio γ, and (ii) the square root of a characteristic energy $M v_s^2$, measured now in units of the thermal energy $k_B T_m$ at the melting point. Equation (11) therefore exhibits the essential physical factors that determine the variation of $\sigma/\eta v_s$ shown in Table II, although we stress that the equation is approximate.

IV. USE OF SIMPLE ELECTRON THEORY PLUS KNOWN EMPIRICAL RULES

To examine the first factor on the right-hand side of Eq. (11), which is $(L n^{1/3}/\gamma)$, the simple density functional theory of a liquid ''alkali'' metal surface given by Brown and March [22] is now helpful. This theory, for these monovalent metals, first of all relates L to the Fermi energy E_F by a formula that has an elementary interpretation: the length L is in order of magnitude the length of a box giving an electron a kinetic energy of localization equal to the Fermi energy, i.e.,

$$E_F \simeq \frac{h^2}{8 m L^2} \tag{12}$$

or $L \simeq (h/2) p_F^{-1}$ where p_F is the Fermi momentum and h is Planck's constant. But the particle density n, equal to the mean electron density for the alkalis, is related to the Fermi momentum by

$$n = \frac{8\pi}{3h^3} p_F^3 \tag{13}$$

and hence the product $L n^{1/3}$ should not be far from a constant, not dependent on the material. Data for $L n^{1/3}$ given in Table IV support this assertion. Lithium, having no p elec-

TABLE IV. Values of the product $Ln^{1/3}$ for different groups. Surface thickness L is taken from Ref. [9] and particle density n from Miedema and Boom [23].

Metal	$Ln^{1/3}$	Metal	$Ln^{1/3}$
Li	0.16	Al	0.08
Na	0.11	In	0.06
K	0.10	Tl	0.06
Rb	0.09	Cu	0.08
Cs	0.10	Ag	0.06
Be	0.13	Zn	0.08
Mg	0.10	Cd	0.07
Ca	0.10	Hg	0.06
Sr	0.10		
Ba	0.11		

trons in its core, is less well described. The alkaline earths have values of $Ln^{1/3} \simeq 0.10$, similar to the alkalis (with Be deviating for the same reason as Li). Finally the trivalent group and the Cu and Zn groups have smaller values of $Ln^{1/3}$, close to 0.07. For the reasons given above, the anomalous melting elements have been excluded from this table.

The other factor $(Mv_s^2/k_BT_m)^{1/2}$ appearing in Eq. (11) is also amenable to discussion, using some empirical rules plus simple electron theory. Thus for Mv_s^2 we have in a simple metal like Na the Bohm-Staver formula [24]

$$Mv_s^2 \simeq \tfrac{2}{3} ZE_F , \tag{14}$$

where Z is the valence. One of us has shown [25] that the vacancy formation energy E_v, known for close-packed metals like Mg and Al to be such that it correlates empirically [26] with the thermal energy k_BT_m through

$$\frac{E_v}{k_BT_m} \simeq 8, \tag{15}$$

is given in terms also of ZE_F, for small Z, by

$$E_v \simeq \tfrac{4}{15} ZE_F . \tag{16}$$

Hence eliminating ZE_F between the electron theory results in Eqs. (14) and (16),

$$\frac{E_v}{Mv_s^2} \simeq \frac{2}{5}, \tag{17}$$

and finally, using Eq. (15),

$$\frac{Mv_s^2}{k_BT_m} \simeq 20. \tag{18}$$

Hence in Eq. (11),

$$\left(\frac{Mv_s^2}{k_BT_m}\right)^{1/2} \simeq 4.5. \tag{19}$$

This estimate is evidently a rough one when comparing to experiment due to the assumptions made (close packing; low Z). In fact, from Eq. (6) we can write

$$\left(\frac{Mv_s^2}{k_BT_m}\right)^{1/2} = \left(\frac{\gamma}{S_{T_m}(0)}\right)^{1/2}. \tag{20}$$

The inverse of this latter quantity is already recorded in Table I and hence $(Mv_s^2/k_BT_m)^{1/2}$ has values ranging between 6 for Li and 12 for ln (excluding again anomalous-melting elements). The Li value, or the values of 7 for other alkali metals, are in fair agreement with the estimate of Eq. (19). The gist of the variation of $\sigma/\eta v_s$ at T_m can hence be understood in terms of the two dimensionless factors entering Eq. (11).

V. SUMMARY AND FUTURE DIRECTIONS

We have considered in some detail the properties of the dimensionless grouping $\sigma/\eta v_s$ defined in Eq. (3) and evaluated at T_m, which relates a transport property, namely, shear viscosity, to thermodynamically derivable quantities. The final column of Table II records this grouping for a number of liquid *sp*-electron metals and shows it has a spread from 0.09 to 0.19, that is, a factor of 2. Attention has then been focussed on the factors that lead to this ''approximate constancy.'' Equation (11) is then the most important result, showing that $\sigma/\eta v_s$ can be viewed as approximately proportional to the product of two other dimensionless quantities, namely, $(Ln^{1/3}/\gamma)$ and $(Mv_s^2/k_BT_m)^{1/2}$. Both these quantities change themselves rather weakly as one spans the liquid *sp*-electron metals for which suitable experimental data are available. Electron theory plus semiempirical rules give a basis for the relative constancy of these two factors separately.

It will be of obvious interest for the future to gather suitable experimental data on outstanding liquid *sp*-electron metals and thereby to complete the as yet missing entries in Tables I and II. It would seem worth investigating whether Eq. (11) had wider utility than just for *sp*-electron metals, even though electron theory formulas such as Eqs. (14) and (17) are not useful for, say, liquid transition or rare-earth metals.

ACKNOWLEDGMENTS

This work was supported by DGES (Grant No. PB95-0720-C02-01) and Junta de Castilla y León (Grant No. VA 72/96). N.H.M. wishes to acknowledge extended visits to the University of Valladolid and also thanks Professor G. R. Freeman (University of Alberta) and Dr. D. M. Heyes (University of Surrey) for discussions.

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