PHYSICAL REVIEW B VOLUME 33, NUMBER 10 15 MAY 1986

Temperature dependence of atomic transport in less-simple liquid metals

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(Received 18 December 1985)

We report on the atomic transport properties, viz., the coefficients of shear viscosity and self-diffusion for certain less-simple liquid metals at various temperatures. The basic assumption made is that these properties of a liquid metal resemble those of an appropriate hard-sphere system. The temperature dependence of the basic ingredients, i.e., the hard-sphere diameters and packing fraction, is considered via a full thermodynamic perturbation theory. The optimal values of these basic ingredients are employed in calculating the atomic transport coefficients of Cu, Cd, In, and Pb. The calculated results are found to be in good agreement with the experimental and available theoretical results.

I. INTRODUCTION

The study of the transport coefficients of liquid metals is important for various chemical and metallurgical purposes. Over the last few decades there have been a variety of experiments[1] and theoretical developments[2] along this stream of investigations.

In the present investigation we model the liquid metal by a hard-sphere description and the relevant formalism for the transport coefficients is correlated with this model and the pair potentials derived from the pseudopotential theory. It is mentioned here that there is a variety of expressions available in the literature to consider the temperature dependence of the hard-sphere diameters and packing fractions.[3,4] Since these parameters are the basic ingredients for computing the transport coefficients, we believe that they should be determined by a full thermodynamic variational method so that they inherit self-consistency. Consequently, we use a perturbative treatment and the so-called Gibbs-Bogoliubov inequality based on a third-order theory in the pseudopotential formalism. This procedure incorporates the temperature dependence in these ingredients via the standard variational technique.[5]

It is reiterated here that to ensure the best yield of the basic ingredients one should include in the formalism all possible features inherited by the structural properties of the relevant systems. In this respect, if we look at the electronic structures of Cu, Cd, In, and Pb, we note that the occurrence of the d bands in the close vicinity of the respective Fermi levels necessitates an inclusion of the band hybridization effects in the electron-ion interactions.[6] On the other hand, in accordance with the so-called *cancellation theorem,* the nonlocal effects in these interactions are significant, and they should be included precisely in the formalism. In view of these inferences we have employed an on-Fermi-sphere model potential[7] that adequately takes care of the effects of hybridization and partial nonlocality. Furthermore, for cohesive reasons we have included a term in the free-energy expression that accounts for the exchange and overlap energy.

The optimal values of the basic ingredients obtained through the standard minimization procedure of the upper bound of the free energy are employed to calculate the coefficients of self-diffusion and shear viscosity for Cu, Cd, In, and Pb.

II. FORMULATION

A. Basic ingredients: Pseudopotential theory

We consider a metal consisting of N atoms having valency Z^* contained in a volume Ω. Using a standard third-order perturbation theory, the upper bound of the Helmholtz free energy in terms of the hypothetical hard-sphere (HS) diameter σ for a finite temperature T is given by

$$F(T,\Omega,\sigma)=F_0(\Omega,T)+\langle U_2\rangle_{\mathrm{HS}}+\langle U_M\rangle_{\mathrm{HS}}+\langle U_3\rangle_{\mathrm{HS}}+U_{\mathrm{eov}}-NTS_{\mathrm{HS}}\;, \tag{1}$$

where $\langle\,\rangle$ denotes the ensemble average. The first term in this equation consists of the structure-independent but volume-dependent contributions. The other terms are the second-order band-structure contribution

$$\langle U_2\rangle_{\mathrm{HS}}=\frac{N}{4\pi^2}\int_0^\infty[\chi_0(q)-\chi_0^2(q)U_{ee}(q)]\times[v_{\mathrm{sc}}(q,2k_F)]^2S(q)q^2\,dq\;, \tag{2}$$

where $\chi_0(q)$ is the static Lindhard function, $U_{ee}(q)$ the electron-electron interaction function, $v_{\mathrm{sc}}(q,2k_F)$ the screened quasilocal pseudopotential, and $S(q)$ is the static structure factor. The Madelung contribution[8] is

$$\langle U_M\rangle_{\mathrm{HS}}=\frac{N}{4\pi^2}\int_0^\infty\frac{4\pi e^{*2}Z^{*2}}{q^2}[S(q)-1]q^2\,dq\;. \tag{3}$$

The third-order contribution[9] is

$$\langle U_3\rangle_{\mathrm{HS}}=\frac{16N}{\pi^3}(4/q\pi)^{1/3}r_s\int\int d\omega_1\,d\omega_2\,W(-\omega_1)W(\omega_1-\omega_2)W(\omega_2)H^3(\omega_1,\omega_2)P(\omega_1,\omega_2)\;, \tag{4}$$

where

$$W(\omega) = v_{sc}(\omega)/4\pi e^{*2}\omega^2, \quad \omega = q/2k_F \ ,$$

and r_s is the electron gas density parameter given by $4\pi r_s^3/3 = \Omega/NZ$. Here H^3 and P are, respectively, the third-order response function and the three-body structure factor; the latter is calculated by using the so-called geometric approximation.[10] The exchange and overlap repulsive energy is

$$U_{ee} = \frac{4\pi N^2}{\Omega}\int_0^\infty g(r) v_{\rm eov}(r) r^2\,dr \ , \tag{5}$$

where $v_{\rm eov}$ is an exchange and overlap function derived in the analytic form.[11] The various components of the effective entropy $S_{\rm HS}$ are available in the closed forms.[12]

B. Transport coefficients: Self-diffusion and shear viscosity

We employ the standard statistical theory[13] of a fluid combined with the pair potential $\phi(r)$, the radial distribution function $g(r)$, and the static structure factor $S(q)$ in writing an expression for the self-diffusion coefficient

$$D_S = k_B T/(\zeta^H + \zeta^S + \zeta^{SH}) \ . \tag{6}$$

The various friction coefficients appearing in Eq. (6) are due to the hard-core contribution

$$\zeta_H = \tfrac{8}{3} n g(\sigma)\sigma^2(\pi m k_B T)^{1/2} \ , \tag{7}$$

the soft-core interaction between the neighboring atoms in the linear-trajectory approximation

$$\zeta^S = -n(\pi m/k_B T)^{1/2}/3(2\pi)^2\int_0^\infty q^3 \Phi^S(q)\tilde{G}(q)\,dq \ , \tag{8}$$

and the cross effect between the hard and soft forces in the pair potential

$$\zeta^{SH} = -n g(\sigma)(m/\pi k_B T)^{1/2}/3 \times\int_0^\infty [(q\sigma)\cos(q\sigma) - \sin(q\sigma)]\Phi^S(q)\,dq \ , \tag{9}$$

where n is the number density of atoms, $g(\sigma)$ is the value of $g(r)$ at $r=\sigma$ (the hard-sphere diameter), and m the ionic mass. The functions $\Phi^S(q)$ and $\tilde{G}(q)$ appearing in Eqs. (8) and (9) are, respectively, the Fourier transforms of the soft part of the pair potential and $[g(r)-1]$; the former is taken to be the Yukawa shouldered potential.[14]

The coefficient of shear viscosity μ_{ra} is given by[15]

$$\mu_{ra} = \mu_{ra}^{(1)}(\sigma) + \mu_{ra}^{(2)}(\sigma) + \mu_{ra}^{(3)}(r > a) + \mu_{ra}^{(4)}(a) \ . \tag{10}$$

In this equation the first two contributions,

$$\mu_{ra}^{(1)}(\sigma) = \frac{5k_B T}{8g(\sigma)}\left(\frac{2\pi n\sigma^3}{15}\right)\left(1 + \frac{4\pi n\sigma^3}{15}g(\sigma)\right) B_\sigma^{(1)} \tag{11}$$

and

$$\mu_{ra}^{(2)}(\sigma) = \frac{8\pi}{15} n^2\sigma^6 g(\sigma) k_B T/B_\sigma^{(2)} \ , \tag{12}$$

arise due to the hard part of the pair potential. The soft-part contribution is

$$\mu_{ra}^{(3)}(r > \sigma) = \frac{4\pi m n^2}{30\zeta^s}\int_0^\infty r^4\left(\frac{\partial^2\phi}{\partial r^2} + \frac{4}{r}\frac{\partial\phi}{\partial r}\right) g(r)\,dr \ . \tag{13}$$

Finally, the kinetic part in μ_{ra} is given by

$$\mu_{ra}^{(4)}(\sigma) = 5k_B T[1 + (4\pi\sigma^3 g(r)/15v]/8g(\sigma)\{B_\sigma^{(1)} + [5\zeta^s v/4mg(\sigma)]\} \ , \tag{14}$$

where v is the thermal velocity of an ion given by $mv^2/2 = 3k_B T/2$. The quantities $B_\sigma^{(1)}$ and $B_\sigma^{(2)}$ appearing in Eqs. (11) and (12) are

$$B_\sigma^{(1)} = [B_\sigma^{(2)} + 5\zeta^s/8nmg(\sigma)]^{-1} \times(1 + 4B_\sigma^{(2)}/\{4B_\sigma^{(2)} + [5\zeta^s/nmg(\sigma)]\}) \tag{15}$$

and

$$B_\sigma^{(2)} = (4\pi k_B T/m)^{1/2}\sigma^2 \ . \tag{16}$$

The final expressions for the self-diffusion and shear viscosity coefficients are

$$D = C_{\rm AW}^D(\eta) D_s \tag{17}$$

and

$$\mu = C_{\rm AW}^\mu(\eta)\mu_{ra} \ , \tag{18}$$

where $C_{\rm AW}^D(\eta)$ and $C_{\rm AW}^\mu(\eta)$ are the scaling corrections that take care of the relaxation process in the back scattering situation. Since there is no simple way of determining these functions theoretically for the hard-sphere fluid, we follow the Alder-Wainwright approach in extrapolating them from the tabulated values.[16]

III. RESULTS AND DISCUSSIONS

In calculating the structural free energies we employ the on-Fermi-sphere pseudopotential due to Animalu[7] and the exchange correlation function of Geldart and Vosko.[17] The optimal values of the hard-sphere diameter σ and packing fraction η are evaluated by minimizing the free energy expressed by Eq. (1). These optimal ingredients are then used in calculating the pair distribution functions, structure factors, and the relevant parts of the pair potentials. These functions are finally employed in computing the transport coefficients.

The results for the coefficients of self-diffusion and shear viscosity are presented in Figs. 1 and 2, respectively. The self-diffusion coefficients for all of the four metals are found to be in good agreement with the experimental[18-22] as well as with the previous theoretical results.[3,23-27] The present results are found to be closer to experiments than most of the previous semiempirical calculations. This may be expected, because while there remains a considerable uncertainty in the temperature dependence of the hard-sphere ingredients in the previous theories, the present calculations succeeded in removing this uncertainty through self-consistency.

The results for the shear viscosity coefficients are presented in Fig. 2 together with the experimental and the available theoretical results. After proper scaling the present results are found to be in reasonable agreement with experiments[2,28] and previous theories;[3,4,27] without scaling, however, the results are higher than the measured values for all of the metals. This is also true for the self-diffusion coefficients. Finally, it may be mentioned that the differences

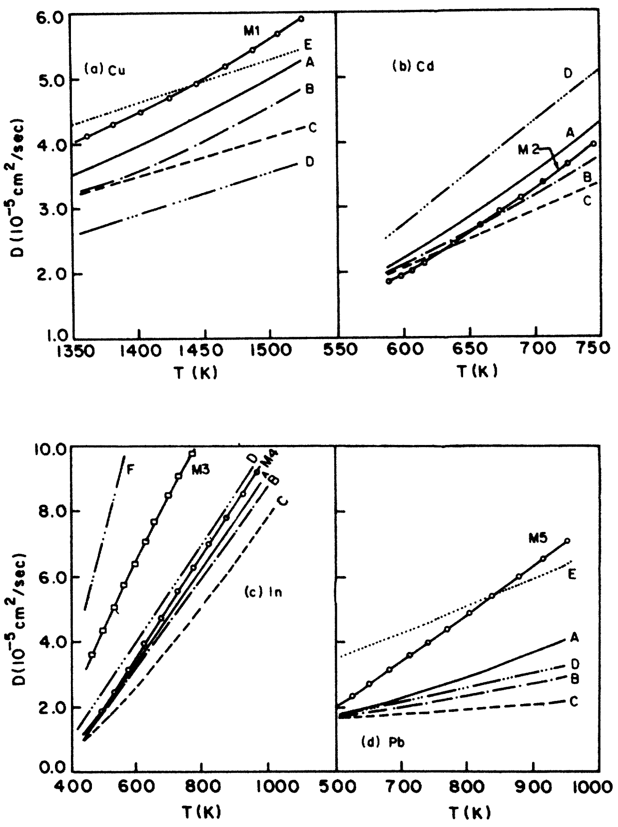

FIG. 1. Self-diffusion coefficient $D(10^{-5}\,\text{cm}^2/\text{sec})$ for (a) Cu, (b) Cd, (c) In, and (d) Pb. Here curve A denotes the present results and B, C, D, E, and F denote the calculated results due to Refs. 3, 23, 24, 25, and 26, respectively. Curves M1, M2, M3, M4, and M5 denote the measured values obtained from Refs. 18, 19, 20, 21, and 22, respectively.

noted between the present and other theoretical values, as noted earlier, are due to the scale of temperature dependence encountered by the basic hard-sphere ingredients.

IV. CONCLUSIONS

In conclusion, we may mention that the present variational calculations have generated the best possible values of the hard-sphere ingredients in a self-consistent fashion by incorporating into the formalism the essential features reflected in the electronic and atomic properties of the relevant metals. This self-consistency is also essential for thermodynamic and structural considerations. As an example it may be mentioned here that inclusion of the third-order contributions in the formalism generates the free energies more consistently; this in turn ensures more refined values of the hard-sphere ingredients. It has been noted that these ingredients obtained from the second-order theory alone reproduce results for the atomic transport which deviate by a few percent from those calculated using the ingredients obtained from the third-order theory; this deviation is also noted when a comparison is made with experiments. In addition, the structural details included in the formalism through the linear-trajectory approximation[15] via the pair distribution functions and the pair potentials, are somewhat left out by the conventional Enskog theory used by many of the previous authors.[3,4]

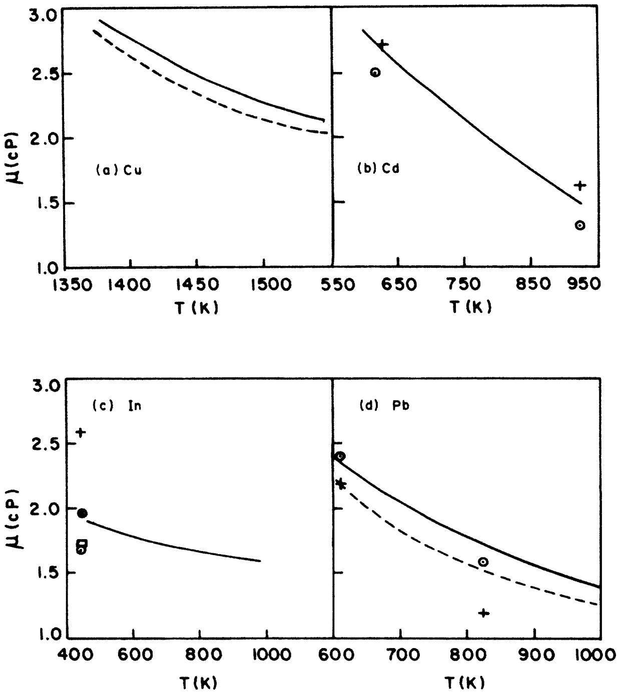

FIG. 2. Coefficient of shear viscosity $\mu(cP)$ for (a) Cu, (b) Cd, (c) In, and (d) Pb. Here — denotes the present results while ---, □, and + denote the calculated results due to Refs. 4, 2, and 27, respectively. ⊙ and ⊗ denote the experimental values.

ACKNOWLEDGMENTS

We would like to thank Professor W. H. Young and Dr. M. Silbert for many useful discussions. One of us (S.M.M.R.) is grateful to the Royal Society of England for financial support, and thankful to the British Council for making the travel arrangements.

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