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Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

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Online publication date: 27 October 2010

To cite this Article Zhang, Ming-Liang, March, N. H. and Van Doren, V. E. (2002) 'Transport Properties of Monatomic Insulating Liquids and Liquid Alkali Metals from a Cage Model', *Physics and Chemistry of Liquids*, 40: 3, 295 – 316

To link to this Article: DOI: 10.1080/0031910021000004874

URL: <http://dx.doi.org/10.1080/0031910021000004874>

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TRANSPORT PROPERTIES OF MONATOMIC INSULATING LIQUIDS AND LIQUID ALKALI METALS FROM A CAGE MODEL

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(Received 1 May 2001)

A cage model is used to calculate the shear viscosity η_s and the thermal conductivity κ for insulating monatomic liquids and for liquid alkali metals. Three empirical laws: (i) $\eta_s \propto (1/\sqrt{T})$ for liquid alkalis; (ii) $\kappa/\eta_s \sim \text{constant}$ for Rb and Cs respectively; (iii) $(\gamma/\eta_s) \sim \sqrt{k_B T_m/M}$ for liquid alkalis at the melting temperature T_m , where γ is the surface tension and M the ionic mass, are naturally explained.

Keywords: Viscosity; Thermal and electrical conductivity; Surface tension

I. INTRODUCTION

The investigation of the transport properties of dense fluids such as viscosity and thermal conductivity and their mutual relationship has a long history. The Chapman–Enskog method solved similar problems for gases with satisfactory accuracy [1]. But for liquids, some important problems remain unsolved. From the Liouville equation of non-equilibrium statistical mechanics, Kirkwood, Born, Green and others obtained an explicit formulation of the fluxes of conservative quantities

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in terms of the intermolecular forces and the non-equilibrium pair distribution function [2]. However, the method remains difficult to apply and only very few calculations have been carried out to date.

Various models have been suggested to obtain useful results in concrete situations. More than sixty years ago, Eyring *et al.*, applied the theory of absolute reaction rates to various transport coefficients [3]. The central idea of the Eyring model is most obviously reflected in their derivation [3] of the shear viscosity. The work done by the external force on the liquid decreases (increases) the activation energy of atomic jump along (reverse) the external force direction. These changes in activation energy influence the jump rates in the two inverse directions. The momentum transferred to the second layer of the liquid from the first layer is implicitly represented in the expression of the molecular velocity through the atomic jump rate. However, they did not use this idea thoroughly. For instance to derive thermal conductivity, they used the sound velocity and the mean free path in the liquid in the corresponding places in the expression for the thermal conductivity of a gas. In this way the energy transferred by the molecular force field is only partly taken into account. Nevertheless, the Eyring model has been widely applied to organic liquids, liquids of inert elements and to liquid metals.

More recently, Zwanzig and others thought of (i) the configuration space of a many-body system as being divided into “cells”, each one associated with a local minimum on the system’s potential energy surface, the configuration of liquid remaining in one of these cells for a time, performing approximate harmonic oscillations about the local minimum, until it suddenly finds a saddle-point or bottleneck on the potential surface and jumps to another cell; (ii) the volume of the entire system consists of a number of equivalent sub-volumes. One effect of a cell jump is to rearrange the equilibrium positions of the particles in a particular sub-volume while the equilibrium positions of the remaining particles are unchanged (We will refer to these two assumptions as a cage model) [4,5]. Zwanzig used this model and another two assumptions to estimate the self-diffusion coefficient D_{self} through considering the auto-correlation of the molecular velocity [4]. The cage model can be regarded as a generalization of the early cell model relating to equilibrium phenomena (for a brief review see pp. 271–293 of [2]) to transport properties.

By introducing a transit parameter to characterize the ionic transition probability and the correlation of two successive jumps, Wallace suggested a two-parameter formula for D_{self} in the cage model, which works well for the simple *sp* metals (Hg and In are two exceptions) [5]. With the help of Wallace's formula, March and Tosi related $D_{\text{self}}\eta_s/k_B T \rho_n^{1/3}$ to this transit parameter at the melting point T_m , where η_s is the shear viscosity and ρ_n is the number density [6].

From an experimental viewpoint, three puzzles that remain are (i) the shear viscosities of liquid Na, K, Rb, Cs universally collapse on to a common curve and are proportional to the inverse square root of temperature over a wide temperature range (Fig. 2 of [7]); (ii) the ratio of thermal conductivity to the shear viscosity for both Rb and Cs is nearly constant over a wide temperature range (Table 11.2 of [8]); (iii) $\gamma/\eta_s \sim \sqrt{k_B T_m/M}$ [9] or $\gamma/\eta_s \sim v_{\text{sound}}^{\text{liquid}}$ [7,10] for simple metals, where T_m is the melting temperature, γ is the surface tension and M is the ionic mass.

Stimulated by these experimental findings (i) to (iii) above, in this article we further explore the consequences of the cage model. Making use of energy barrier height E_b as the single parameter, the waiting time t_w which determines all transport coefficients, is given in Section II for insulating liquids. E_b can easily be extracted from available experimental data for one thermodynamic state (T, p) (Section II.C). With the help of the cage model, the molecular force field contribution to the transport coefficients [2] is formulated by means of a work-energy principle. Results for these transport coefficients are explicitly expressed in terms of t_w . We compare our results with Eyring's; the difference between the two physical pictures is specifically discussed in Section II.C and Section II.D. Liquid alkali metals are composed of ions and electrons. Therefore the long-range Coulomb force between charges and screening effects introduce essential corrections into the waiting time t_w and the sound velocity v_{sound} . Section III discusses the transport coefficients of liquid metals. Besides the force field contribution to the shear viscosity, the electronic contribution to thermal and electrical conductivity must be treated. The mean free path of an electron is derived in an Appendix. The three empirical laws for liquid alkalis mentioned in the previous paragraph are naturally derived from the cage model. Our aim throughout is to expose the key characteristic physical parameters needed to estimate

the order of magnitude of the transport coefficients. It is a task for the future to make the resulting formulae fully quantitative.

II. MONATOMIC INSULATING LIQUIDS

In this paper we restrict ourselves throughout to monatomic liquids such as Ar or Na. The generalization to diatomic molecules, polyatomic molecules or long chain organic liquids seems to pose no major difficulties. Let us consider first a monatomic insulating liquid such as Ar. We denote its atomic mass by M . Let $d/2$ be the atomic scattering length in the liquid or the radius of hard sphere in a rigid sphere model, and then the scattering cross section between two atoms will be of order πd^2 .

We denote the number density of atoms at temperature T and pressure p as $\rho_n(T, p)$. In the following it is convenient to take (T, ρ_n) as independent variables rather than (T, p) . However, since most experimental data are measured at specific values of (T, p) , we need the corresponding density $\rho_n(p, T)$ to compare theoretical results with such experiments. The mass density $\rho_m = M \rho_n$ is also a quantity frequently used. When the number density is ρ_n , the average distance r between two nearest-neighbor atoms is about $d + [1/\rho_n - (4/3)\pi(d/2)^3]^{1/3}$.

A. Energy Barrier Height E_b

According to the cage model of a liquid [4,5], a cage is to be visualized as an environment around the considered atom with approximately spherical symmetry, each atom in a liquid being surrounded by a cage of nearby atoms for a waiting time t_w . To leave such a cage, the considered atom must overcome an energy barrier of height E_b . The most difficult point in the transitional process is the moment that the escaping atom passes between two adjacent atoms in the wall of the cage and inserts itself into the space between these two 'wall' atoms. Therefore, the barrier height E_b is mainly determined by two factors: (i) the excluded-volume effect of the atom itself and (ii) the attraction produced by the surrounding atoms when the considered atom wants to move. The excluded volume effect of atom

depends on the ratio Ω_a/Ω_f of the atomic volume $\Omega_a = (4/3)\pi(d/2)^3$ to the free volume $\Omega_f = 1/\rho_n - (4/3)\pi(d/2)^3$ and the polarizability α which describes how difficult it is to deform the atomic outer shell electron cloud, roughly speaking $E_b^{(i)} \propto (\Omega_a/\Omega_f)/\alpha$. $E_b^{(i)}$ is a function of $\rho_n(T, p)$ and the atomic polarizability α . The factor (ii) for monatomic insulating liquid is the van der Waals force and is usually proportional to the instantaneous coordination number. However, for some liquids, hydrogen bonds between molecules and/or dipole-dipole forces are also involved. The contribution (ii) to the barrier height E_b is also a function of the number density $\rho_n(T, p)$ through the distance between atoms. $E_b^{(ii)}$ is proportional to the heat of vaporization [3] or the thermal energy at melting $k_B T_m$. $E_b = E_b^{(i)} + E_b^{(ii)}$ will determine the correlation time of a two-particle positional correlation function.

B. Characteristic Times t_w and t'_w

For the situation $E_b(\rho_n)/k_B T \gg 1$, the picture of an atom confined in a cage is a good description. At the thermodynamic state (T, ρ_n) , an atom has a probability $e^{-E_b(\rho_n)/k_B T}$ to escape its cage, the probability of staying in the cage being evidently $(1 - e^{-E_b(\rho_n)/k_B T})$. The escaping atom will move freely until it collides with another atom, just like the molecules in a gas. The atom in its cage will jump to another cage after waiting a time t_w with a thermal velocity of order $\sqrt{k_B T/M}$. Before its jump motion, the atom in its cage executes a certain number of vibrations. The time t_{jump} needed for an atom to jump from one cage to a neighbouring cage by a jump motion is $\sim r/\sqrt{k_B T/M}$. The long-range jump motions in which the jump distances are longer than the average atomic distance r are neglected for obvious reasons in a dense liquid. The amplitude of the instantaneous vibration A_{iv} is about r . If we assume the activation energy $E_b(\rho_n)$ as the elastic energy of the cage, then the period of an instantaneous vibration may be estimated as $t_{\text{vib}} \sim r\sqrt{M/E_b}$. From the Maxwellian velocity distribution, the waiting time t_w is

$$t_w \sim \frac{r\sqrt{k_B T M}}{E_b(\rho_n)} \exp\left(\frac{E_b(\rho_n)}{k_B T}\right). \quad (1)$$

For the alternative situation $E_b(\rho_n)/k_B T < 1$, it is better to describe the motion of a considered atom as being delayed rather than as confined by a cage of surrounding atoms. The effect of such a shallow atomic potential well of surrounding atoms is that the potential delays the free motion of an atom from one potential well to another by producing a negative acceleration. If t_1 is the time needed from one atomic potential well to another with a negative acceleration due to the shallow well, and t_2 is the time needed to move the same distance in absence of the well, then $t'_w = t_1 - t_2$ will describe the effect of the cage of the surrounding atoms. This characteristic time t'_w is then in order of magnitude

$$t'_w \sim \frac{rM}{E_b} \left[\sqrt{\frac{k_B T}{M}} - \sqrt{\frac{k_B T}{M} - \frac{2E_b}{M}} \right] - \frac{r}{\sqrt{k_B T/M}}. \quad (2)$$

If $E_b(\rho_n)/k_B T \ll 1$, t'_w can be simplified to read $t'_w \sim r\sqrt{(M/k_B T)} \times (E_b/2k_B T)$ by expanding the second square root in the bracket to order $[E_b(\rho_n)/k_B T]^2$. The transition from a jump-like transport to transport by free motion occurs when t'_w is close to the interaction time $d/\sqrt{k_B T/M}$ i.e., $r(E_b/2k_B T) \leq d$.

The correlation time of the two-particle positional correlation function or the stress correlation function in order of magnitude is t_w for $E_b(\rho_n)/k_B T \gtrsim 1$, and is t'_w for $E_b(\rho_n)/k_B T < 1$. t_w and t'_w are crucial in determining self-diffusion coefficient, viscosity and thermal conductivity of the monatomic liquids considered.

C. Shear Viscosity

In a liquid, there are three ways to transfer momentum (i.e. there are three contributions to the viscosity): (i) the momentum transferred by the internal force field of atoms in the liquid: in this type of momentum transfer there is no accompanying mass transfer and we shall denote the corresponding contribution to the shear viscosity as η_s^{field} ; (ii) the momentum transferred by the free jump motion of the atoms: we denote the corresponding contribution to the shear viscosity by η_s^{jump} ; (iii) the momentum transferred by the free motion of the atoms: the corresponding contribution to the shear viscosity being η_s^{free} .

For the last two types of momentum transfer there is accompanying mass transfer. The corresponding contributions to the kinematic viscosity from the last two modes of momentum transfer are proportional to self-diffusion coefficient D_{self} . The force field part of the viscosity relates to the two-particle positional correlation function. It is different from the random walk contributions which are determined by the single-particle positional correlation.

The correlation length ξ of the two-particle positional correlation function, in order of magnitude, is just the distance in which a disturbance is propagated in a waiting time t_w for $E_b/k_B T \gtrsim 1$ (for $E_b/k_B T < 1$, t_w must be replaced by t'_w). Since the propagation velocity of such a disturbance is the sound velocity v_{sound} , the correlation length ξ relates to t_w through $\xi \sim v_{\text{sound}} t_w$ for $E_b/k_B T \gtrsim 1$ (or $\xi \sim v_{\text{sound}} t'_w$ for $E_b/k_B T < 1$).

The atomic force field part of the shear viscosity η_s can be found from a work-energy principle. For convenience of presentation, we restrict ourselves to the case $E_b/k_B T \gtrsim 1$: to obtain the corresponding results for $E_b/k_B T < 1$, we need only replace t_w by t'_w . Let us consider a small volume element of fluid with area S_y and edge length ξ , with another identical volume element close below. The mass m of such a block of fluid is $\rho_m S_y \xi$. The total force acting on the second block due to the first block is equal to the number of atoms in the interface multiplied by the force acting on one atom, namely $(S_y/\pi r^2) \times (E_b/r^2) t_w \xi (\partial v_x / \partial y)$. In a time interval t_w , the work done by the first block on the second block is a product of the driving force and the displacement induced by that driving force, namely $((S_y/\pi r^2) \times (E_b/r^2) t_w \xi (\partial v_x / \partial y)) ((F_x/m) t_w - \xi (\partial v_x / \partial y)) t_w$. This work partly gives the second block kinetic energy while a part is dissipated as thermal energy used to break some cages, with corresponding increase of entropy. This is expressed by the following energy conservation equation:

$$\begin{aligned} & \left(\frac{S_y}{\pi r^2} \frac{E_b}{r^2} t_w \xi \frac{\partial v_x}{\partial y} \right) \left(\frac{F_x}{m} t_w - \xi \frac{\partial v_x}{\partial y} \right) t_w \\ &= \frac{1}{2} \rho_m S_y \xi \left(\frac{F_x}{m} t_w - \xi \frac{\partial v_x}{\partial y} \right)^2 + \eta \left(\frac{\partial v_x}{\partial y} \right)^2 (\xi S_y) t_w. \end{aligned} \quad (3)$$

This determines the shear viscosity η_s and can be used for arbitrary ratio $E_b/k_B T$. An analysis shows that $E_b t_w^2 / \rho_m \pi r^4 \gtrsim (1 + \sqrt{2}) \xi$ is the

condition to ensure that η_s is both real and positive. In this derivation, the energy output from the second block to the block below it and higher order effects are neglected.

If $E_b t_w^2 / \rho_m \pi r^4 \gg (1 + \sqrt{2})\xi$, the second term on the RHS of Eq. (3) will be much bigger than the first term, i.e., the dissipation is very strong, the input energy being mainly used to break the molecular cages. Under this strong dissipation condition, the contribution to shear viscosity from momentum transfer by the force field is

$$\eta_s \sim \rho_m \frac{\xi^2}{t_w} \left[1 + \left(\frac{E_b t_w^2}{\xi \rho_m \pi r^4} \right)^{-1} \right].$$

For a liquid with large E_b near to its melting point, the confinement by the cage is much stronger than the influence of the external force in any realistic accessible velocity gradient. On a length scale r , the single atomic jump is a rare case when the external force is much smaller than the binding force of the atomic cage. Then the motion of atomic groups (several atoms) will be the dominant process. In contrast, according to Eyring's considerations, the work done by an external force changes the activation energy of the atomic jump rate [3] in the nearest neighbor atomic layer, the distance between two atomic layers being taken as r . Maybe the best applicable range of the "two atomic layers" picture of Eyring is to those liquids where E_b is not too large but yet is still larger than the atomic thermal energy $k_B T$. The increase of entropy (i.e. dissipation) in the Eyring model is realized in the relaxing of the jump equilibrium along and opposite the external force direction [3]. Whereas in the present approach, the energy barrier height E_b is an intrinsic quantity of the liquid, the effect of the external force is to break the cage (i.e. to induce changes in microscopic states and to increase entropy) in an accumulative way for a thickness ξ and an action time t_w . The variation of E_b is reflected in the variation of ξ : the correlation length ξ is just a measure of how many atomic layers below a specific atom are involved in dynamic motions. Similarly, the correlation time t_w which is also determined by E_b , is a measure of the sustaining time of the effect of the change in state of an atom affecting other atoms.

If $E_b t_w^2 / \rho_m \pi r^4$ is not much larger than $(1 + \sqrt{2})\xi$, the first term on the RHS of Eq. (3) is the dominant contribution and this is

the case of weak dissipation. The shear viscosity in this situation is given by

$$\eta_s \sim \frac{\rho_m \xi^2}{t_w} + \frac{\rho_m \xi^2}{t_w} \frac{2E_b t_w^2}{\rho_m \pi r^4 \xi},$$

the second term on the RHS being of the same order of magnitude as the first term, the sum of the two terms in consequence being several times bigger than $\rho_m \xi^2/t_w$.

Thus in order of magnitude, the shear viscosity is

$$\eta_s \sim \frac{\rho_m \xi^2}{t_w} \sim \rho_m v_{\text{sound}} t_w, \tag{4}$$

in both strong and weak dissipation cases. Because η_s , ρ_m and v_{sound} are all accessible quantities for experiments, t_w is easily determined by Eq. (4). Then from Eq. (1) one can find the parameter E_b of the cage model.

We can also characterize t_w through the adiabatic bulk modulus B_{ad} and η_s . B_{ad} is an accessible quantity, according to thermodynamics: $B_{ad}^{-1} = B_T^{-1} - (T\alpha_d^2/C_p)$, where α_d is thermal expansion coefficient, C_p is heat capacity per unit volume constant pressure, B_T is the isothermal bulk modulus. In fact $B_{ad} \sim \rho_m v_{\text{sound}}^2 \sim \rho_m (\xi^2/t_w^2)$. Combining this expression with Eq. (4), we have $t_w \sim \eta_s/B_{ad}$.

For $E_b/k_B T \gtrsim 1$, we may easily check $\eta_s^{\text{jump}} \ll \eta_s^{\text{field}}$ and $\eta_s^{\text{free}} \ll \eta_s^{\text{field}}$. η_s^{jump} and η_s^{free} are not important for dense fluids. The viscosity produced by the atomic force field η_s^{field} is dominant in the liquid.

To leading order in $E_b/k_B T$, $\eta_s^{\text{field}} \sim \rho_n^{2/3} \sqrt{M k_B T} \exp(E_b/k_B T) [1 - (\rho_n(4\pi/3))(d/2)^3]^{-2/3}$ which is not very different from Eyring's classical result $\eta_s \propto \rho_n \exp(E_b/k_B T)$ [3].

It is interesting to note that in the situation where $E_b/k_B T \ll 1$, by calculating t'_w to order of $(E_b/k_B T)^2$ (to the first order of $E_b/k_B T$, t'_w is zero), the force field contribution to the shear viscosity is given by

$$\eta_s^{\text{field}} \sim E_b \rho_n^{2/3} \sqrt{\frac{M}{k_B T}} \left[1 - \rho_n \frac{4\pi}{3} \left(\frac{d}{2}\right)^3 \right]^{-2/3}. \tag{5}$$

The jump contribution to the shear viscosity is $\eta_s^{\text{jump}} \sim E_b \rho_n^{2/3} \sqrt{M/k_B T} (1 - E_b/2k_B T)$ to first order in $E_b/k_B T$, and hence

$\eta_s^{\text{jump}} \ll \eta_s^{\text{field}}$. The free motion contribution to the shear viscosity is $\eta_s^{\text{free}} \sim (\sqrt{k_B T M} / \pi d^2) \exp(-E_b/k_B T)$, and therefore $(\eta_s^{\text{free}} / \eta_s^{\text{field}}) \sim \exp((-E_b/k_B T)(k_B T/E_b)([1/\rho_n - (4/3)\pi(d/2)^3]^{2/3} / \pi d^2))$. η_s^{free} becomes comparable with or surpasses η_s^{field} in some situations. $\eta_s^{\text{free}} > \eta_s^{\text{field}}$ means in fact a gas-like viscosity.

D. Thermal Conductivity

Just as for shear viscosity, according to the cage model there are also three contributions to the thermal conductivity: (i) energy transferred by the free motion of particles; (ii) energy transferred by jump motion; (iii) energy transferred by the atomic force field. The free motion contribution to the thermal conductivity is $\kappa^{\text{free}} \sim k_B \sqrt{((k_B T)/M)} / \pi d^2 \exp(-E_b/k_B T)$, which satisfies $\kappa^{\text{free}} \propto \eta^{\text{free}} C_m$, where C_m is the heat capacity per unit mass for constant pressure. For $E_b/k_B T \gtrsim 1$, the jump contribution to thermal conductivity is $\kappa^{\text{jump}} \sim k_B ((\rho_n^{1/3}) / (t_w + t_{\text{jump}}))(1 - \exp(-E_b/k_B T))$; for $E_b/k_B T < 1$, the corresponding result can be obtained just by substituting t_w by t'_w in the above expression. The jump part of the thermal conductivity also satisfies $\kappa^{\text{jump}} \propto \eta^{\text{jump}} C_m$.

The force field contribution to the thermal conductivity can be estimated from an energy balance argument: the energy transferred by the molecular force field to a place distant from the interface equals the difference between the input internal energy and the energy used to raise the temperature locally.

Let us consider a block of fluid with cross section S_x (perpendicular to x axis) and length ξ , in its right hand side, and a close neighbor as another identical fluid block. To set up a temperature gradient $\partial T/\partial x$ along the negative x axis, the required input energy in a time interval t_w is $t_w S_x q_x = t_w S_x \kappa (\partial T/\partial x)$, where q_x is the heat flux along the positive x direction and κ is the thermal conductivity. A part of the input energy is transferred to a distant place and the remainder is used to raise the temperature locally, the energy balance condition being

$$t_w S_x \kappa \frac{\partial T}{\partial x} = (\rho_m S_x \xi) C_m \xi \frac{\partial T}{\partial x} + \frac{S_x k_B \xi (\partial T/\partial x)}{\pi r^3} t_w \sqrt{\frac{E_b}{M}}. \quad (6)$$

The first term on the RHS of Eq. (6) is the energy used in raising the temperature in the second block, the second term on the RHS of Eq. (6)

being the thermal energy transferred by the force field to a place far from the interface between two blocks. After some simplifications we obtain the thermal conductivity κ as

$$\kappa = \rho_m C_m \frac{\xi^2}{l_w} + k_B \frac{\xi}{\pi r^3} \sqrt{\frac{E_b}{M}}. \quad (7)$$

It is easily verified that for both $E_b/k_B T \gtrsim 1$ and $E_b/k_B T < 1$, the second term on the RHS of Eq. (7) is much smaller than the first term. The empirical relation $\kappa^{\text{field}} \propto \eta^{\text{field}} C_m$ is recovered. All the comments concerning the relative order of magnitude of η_s^{free} , η_s^{jump} and η_s^{field} are applicable to κ^{free} , κ^{jump} and κ^{field} in corresponding situations $E_b/k_B T \gtrsim 1$ and $E_b/k_B T < 1$.

To obtain the thermal conductivity in the liquid state, Eyring *et al.* made the following substitution ($l_{\text{gas}} \rightarrow r$; $v_{\text{sound}}^{\text{gas}} \rightarrow v_{\text{sound}}^{\text{liquid}}$) in the thermal conductivity expression for a gas, where l_{gas} is the mean free path of gas. Their result is $\kappa_{\text{Eyring}} = \rho_m C_m r v_{\text{sound}}^{\text{liquid}}$, where $v_{\text{sound}}^{\text{liquid}} \sim [1 - \rho_n (4\pi/3)(d/2)^3]^{-1/3} \sqrt{k_B T/M}$ [3]. The present result is $\kappa = \rho_m C_m \xi v_{\text{sound}}^{\text{liquid}}$. Since instead of the correlation length ξ , the distance r between atoms enters into κ_{Eyring} , the force field effect is only partly taken into account in their expression for the thermal conductivity.

III. ALKALI METALS

Due to the long-range character of the Coulomb interaction and the screening effects, two characteristics of liquid metals such as Na are different from insulating liquids (e.g. Ar): (i) the size of an ionic cage is about a_{TF} (the Thomas-Fermi screening length), rather than the cage size in an insulating liquid where it is about the average distance r between atoms; (ii) in the same reduced temperature T/T_m , the ratio $E_b/k_B T$ of the energy barrier height E_b to thermal energy $k_B T$ for liquid alkalis is smaller than $E_b/k_B T$ for most monatomic insulating liquids. (i) and (ii) will produce some special behavior of the transport coefficients of liquid metals compared with the insulating liquids discussed above.

Since we expect the excluded volume effect of an ion in a liquid alkali metal to be small, the correlation time of the two-particle correlation function will be largely determined by the screened Coulomb inter-

action alone. The single-ion waiting time (t_w , say) within a cage is just the correlation time of the positional correlation function between two different particles. Since the interaction range in liquid metals is the order of the Thomas–Fermi screening length a_{TF} and the characteristic velocity of an ion is $v_{\text{thermal}}^i \sim \sqrt{k_B T/M}$ with M the ionic mass, two ions will lose their correlation in a time $t_w \sim a_{TF}/v_{\text{thermal}}^i$.

A. Shear Viscosity

Local electrical neutrality allows us still to regard a liquid alkali as a relatively hard sphere liquid in a time scale larger than ω_p^{-1} where ω_p is the electronic plasma frequency and a length scale larger than atomic radius. Some empirical evidence exists which supports such a viewpoint: the ratio of the Ornstein–Zernike direct correlation function at zero range to the value at zero wave number is near to the corresponding ratio for a hard sphere liquid [7] (Table I). The empirical law of ‘reduced fluidity’ in alkalis Na, K, Rb, Cs (Fig. 1) is qualitatively explained by Eq. (5), the corresponding hard sphere result for $E_B/k_B T \ll 1$.

Evidently, a liquid alkali metal is a two-component system: ions and electrons. The momentum transfer comes from the motion of individual electrons, the motion of individual ions and the force field of their mixture. The first two contributions are accompanied by the corresponding mass transfers and are much smaller than the last contribution. We first estimate the momentum transfer by individual motion of the particles. The local electrical neutrality condition ensures that the average velocity of electrons is related to the average velocity of ions*. If a block of liquid metal has a velocity \bar{v} , the

TABLE I Values of Ornstein–Zernike direct correlation function c at $r=0$ and $k=0$ for liquid alkalis near freezing points (after [7])

<i>Liquid metals</i>	$-c(r=0)$	$-c(k=0)$
Na	43	41
K	42	40
Rb	45	42
Cs	50	38

*Note added on proof. See also the Bohm-Staver formula given later.

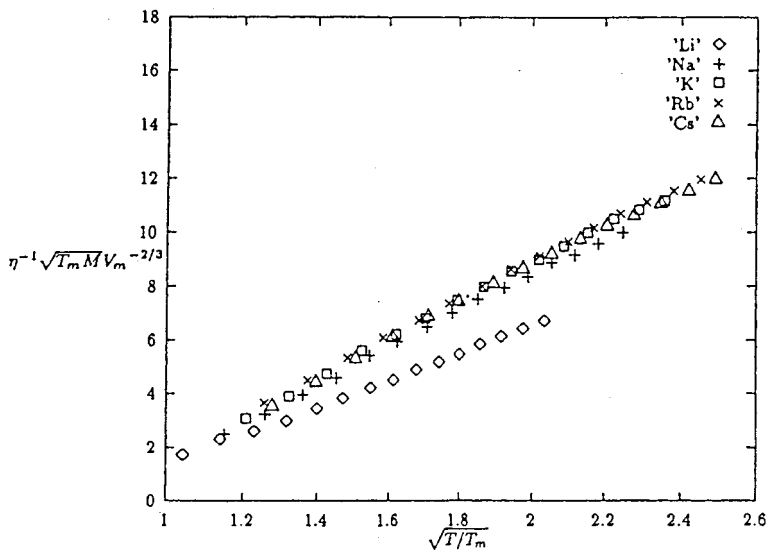


FIGURE 1 Reduced fluidity $\sqrt{T_m} M V_m^{-2/3} / \eta$ versus $\sqrt{T/T_m}$ for liquid alkalis, where $V_m = \rho_n^{-1}(T_m)$. (after [7])

momentum current transferred by the electronic individual motions is $n_e(k_B T/E_F)(m_e \bar{v})v_F$, the momentum current transferred by the ionic individual motions is $n_i(M \bar{v})v_i$, the ratio of the former to the latter is $Zv_i/v_F \ll 1$, where for v_i we take the thermal velocity of the ions.

The momentum transfer by the force field in a liquid metal has some new characteristics which are different from those of a monatomic insulating liquid. However, these corrections are small compared with $\sim \rho_m v_{\text{sound}} t_w$. The long-range effective attraction between ions has been subsumed into E_b . Here we consider another attraction due to the instantaneous dipoles produced by the deviation from local electrical neutrality. The relative displacement of two blocks is $\xi(\partial v_x/\partial y)t_w$, in the interface of two blocks each atom has a induced instantaneous dipole $(v_i/v_F)\xi(\partial v_x/\partial y)t_w Ze$, where the factor v_i/v_F gives the deviation from local electrical neutrality. The electric field by this dipole at a distance a_{TF} is about $(1/4\pi\epsilon_0)(1/a_{TF}^3)[(v_i/v_F)\xi(\partial v_x/\partial y)t_w Ze]$, so that the force acting on the electron cloud in the second block by one interfacial atom is in order of magnitude $(1/4\pi\epsilon_0)(1/a_{TF}^3)(v_i/v_F)\xi(\partial v_x/\partial y)t_w Ze(en_e a_{TF}^3)$, where the screened

Coulomb force acting on a range $\sim a_{TF}$ is not like the short-range force which evidently only acts on the nearest neighbors. Here we have neglected the force acting on the ions, since if we apply a similar force in an equal time interval to two different masses, the kinetic energy obtained by the body with the larger mass is smaller than the body with smaller mass: $E_1/E_2 = m_2/m_1$. The ion in the second block is drawn through its surrounding electron cloud in the above instantaneous dipole mechanism.

The number of atoms on S_y is $\sim S_y/\pi r^2$, and the total force by the atoms on S_y acting on the second block is $S_y/\pi r^2[(1/4\pi\epsilon_0)(1/a_{TF}^3) \times ((v_i/v_F)\xi(\partial v_x/\partial y)t_w Z e)(en_e a_{TF}^3)]$. The displacement of the second block is $((F_x/m)t_w - \xi(\partial v_x/\partial y))t_w$, where $m = \rho_m S \xi$ is the mass of block and F_x is the force acting on the first block to keep a velocity gradient $(\partial v_x/\partial y)$, $(F_x/S_y) = \eta(\partial v_x/\partial y)$. The work done by the first block on the second block due to the electrostatic force by the interfacial induced dipole when the second block moves relative to the first block is given by $(S/\pi r^2)(Ze^2 n_e/4\pi\epsilon_0)(v_i/v_F)((\partial v_x/\partial y)t_w)^2 \xi((\eta t_w/\rho_m \xi) - \xi)$. The total work done by the first block on the second block is a sum of this work of interfacial instantaneous induced dipoles plus the work done by the binding force of the ionic cage (coming from E_b). To obtain the corresponding formula for a liquid metal, we need only make the following substitution in the expression of insulating liquid:

$$\frac{E_b t_w^2}{\xi \rho_m \pi r^4} \rightarrow \frac{E_b t_w^2}{\xi \rho_m \pi r^4} + \frac{1}{\pi r^2} \frac{Ze^2 n_e}{4\pi\epsilon_0} \left(\frac{v_i}{v_F}\right) \frac{t_w^2}{\xi \rho_m}.$$

We have estimated various contributions to the momentum transfer: the force field part, the electronic part and the ionic part. The force field part of the shear viscosity is dominant. The shear viscosity can be written as $\eta_s \sim M n_i v_{\text{sound}}^2 t_w$, where n_i is the number density of ions, v_{sound} is the sound velocity. v_{sound} in the liquid metal is determined by the Bohm–Staver formula: $v_F \sqrt{Z m_e/M}$, where v_F is the Fermi velocity of the electrons, m_e is the mass of an electron and Z is the number of valence electrons in an atom. Substituting t_w and v_{sound} into the expression of η_s , we have

$$\eta_s(T, n_i) \sim (Z n_i)^{2/3} \sqrt{M k_B T_m} \left(\frac{T}{T_m}\right)^{-1/2} \left[\frac{(\hbar^2/m_e)(Z n_i)^{2/3}}{k_B T_m}\right]^{-1/2} \sqrt{a_0 (Z n_i)^{1/3}}, \quad (8)$$

where a_0 is Bohr radius of hydrogen atom and T_m is melting temperature. Eq. (8) gives a natural explanation for the empirical law $\eta_s \propto \sqrt{1/T}$ presented in Fig. 1 for the shear viscosity of Na, K, Rb, Cs in a rather wide temperature range from T_m to $2.6 T_m$.

The thermal conductivity from the molecular force field also needs a similar correction:

$$\kappa = \rho_m C_m \frac{\xi^2}{t_w} + k_B \frac{\xi}{\pi r^3} \sqrt{\frac{E_b}{M}} + k_B \frac{\xi}{\pi r^3} \sqrt{\frac{k_B T}{M}} \frac{1}{4\pi} \frac{v_{\text{thermal}}^j}{v_F}.$$

B. Scattering of Electron-Ionic Density Fluctuation, Electrical Conductivity and Thermal Conductivity

The electrical conductivity from ions is much smaller than that from electrons. In various contributions to the mean free path of electrons, the electron-ionic positional fluctuation scattering plays the most important role in reducing the mean free path and is the main reason for the observed resistivity. The electrical conductivity σ of a liquid metal is

$$\sigma \sim n_i^{5/3} (k_B T)^{-3/2} M^{-1/2} Z^{-1/3} \langle \phi(q) \rangle e^2, \quad (9)$$

$\phi(q)$ being the Fourier transformation of the free energy of the ionic density fluctuation. $\langle \phi(q) \rangle$ is an average over wave-vector q . The electronic part of the thermal conductivity in a liquid alkali metal is also dominant (see the Appendix):

$$\kappa \sim n_i^{5/3} (k_B T)^{-1/2} Z^{-1/3} M^{-1/2} \langle \phi(q) \rangle k_B, \quad (10)$$

Experiment shows that there is an intimate relation between thermal conductivity κ and the shear viscosity η_s in liquid metals: in a wide temperature range 400–1500 K and fixed pressure ~ 10 MPa, $\kappa/\eta_s \sim 1.10$ – 1.27 for liquid Rb and $\kappa/\eta_s \sim 5.38$ – 8.49 for Cs (Table II).

Comparing Eq. (10) with Eq. (8), we have

$$\frac{\kappa}{\eta_s} \sim n_i^{1/6} M^{-1} Z^{-11/6} \langle \phi(q) \rangle \left(\frac{e^2}{\epsilon_0} \right)^{1/2} \frac{m_e^{3/2}}{\hbar^3} k_B. \quad (11)$$

TABLE II The ratio of thermal conductivity to shear viscosity for Rb and Cs (after [8])

T (K)	<i>Rb</i>	<i>Rb</i>	<i>Cs</i>	<i>Cs</i>
	ρ_m (Kg m ⁻³)	$(\kappa/\eta_s)10^4$ Kg JK ⁻¹	ρ_m (Kg m ⁻³)	$(\kappa/\eta_s)10^4$ Kg JK ⁻¹
400	1452	1.10	1791	5.38
500	1411	1.13	1738	5.93
600	1370	1.15	1685	6.54
700	1328	1.19	1630	7.16
800	1286	1.23	1575	7.76
900	1242	1.25	1518	8.14
1000	1198	1.27	1461	8.49
1100	1152	1.27	1401	8.39
1200	1105	1.25	1346	8.18
1300	1056	1.21	1277	7.86
1400	1005	1.17	1211	7.19
1500	752	1.12	1140	6.52

Equation (11) indicates that for a specific element, κ/η_s is a temperature-independent constant and is weakly density dependent ($\sim n_i^{1/6}$). This is consistent with observations. On the other hand, Eq. (11) suggests that κ/η_s strongly depends on ionic mass $\sim M^{-1}$. The mass ratio of the Cs to the Rb atom is $(M_{Cs}/M_{Rb}) \sim 1.55$, therefore Eq. (11) gives $((\kappa/\eta_s)_{Rb})/((\kappa/\eta_s)_{Cs}) \sim 1.55$ if we neglect the weak dependence on the number density n_i . This is close to the observed κ/η_s ratio Rb and Cs: $((\kappa/\eta_s)_{Rb})/((\kappa/\eta_s)_{Cs}) \sim 1.50$ – 2.04 .

We may obtain a relation between electrical conductivity σ and viscosity η by comparing Eqs. (8) and (9):

$$\frac{\eta_s}{k_B T \sigma} \sim n_i^{-1/6} M Z^{11/6} \frac{1}{\langle \phi(q) \rangle} \left(\frac{\epsilon_0}{e^2} \right)^{1/2} \frac{\hbar^3}{m_e^{3/2} e^2}, \quad (12)$$

where ϵ_0 is permittivity of free space. For a specific liquid alkali, the RHS of Eq. (12) has no dependence on temperature and is weakly density dependent. For different elements, both mass M and valence Z dependences are strong.

In fact Eq. (12) is a direct consequence of two experimental laws: Eq. (11) and the Wiedemann–Franz law $\kappa/\sigma \sim (k_B T/e^2) k_B$. It is common knowledge that the Wiedemann–Franz law does not depend on the concrete scattering mechanisms of the electrons provided that in both thermal conductivity and electrical conductivity the electronic part is dominant: $\kappa/\sigma \sim [(n_e (k_B T/E_F) k_B t v_F^2)/(n_e e^2/m_e) t] \sim [k_B^2 T/e^2]$,

where t is the collision interval of electrons whatever the type and number of the scattering mechanisms. For liquid simple metals, $\kappa/\sigma \sim (k_B T/e^2)k_B$ is well satisfied (Table 7.1 of [11]). However Eqs. (9) and (10), and therefore Eqs. (11) and (12), rely on (i) the electronic contribution dominating both the electrical conductivity and thermal conductivity; (ii) the main scattering mechanism being the electron-ionic positional fluctuation collisions.

C. Surface Tension and its Relation with the Shear Viscosity at the Melting Point

The repulsion force suffered by an ion from other ions in a range a_{TF} is $\sim ((Ze)^2/(4\pi\epsilon_0 a_{TF}^2))(n_i a_{TF}^3)$ when the system is compressed near to the equilibrium configuration. An equal and inverse attraction force exists when the system is expanded. Let us pull a line on a surface of liquid alkali with length L perpendicular to the direction of line; the total force needed on this line is just $(L/r)(1 - \exp(-E_b/k_B T)) \cdot ((Ze)^2/(4\pi\epsilon_0 a_{TF}^2))(n_i a_{TF}^3)$, where r is the distance between the atoms and L/r is the number of ions on this line. At temperature T , the occupation probability of an ionic position is $1 - \exp(-E_b/k_B T)$, only the occupied positions contributing to the attraction. From its definition, the surface tension γ is $\sim (1 - \exp(-E_b/k_B T))((Ze)^2/(4\pi\epsilon_0))n_i^{4/3} a_{TF}$. For a liquid alkali metal whose $E_b/k_B T \ll 1$, $\gamma \sim ((-E_b/k_B T)(Ze)^2/4\pi\epsilon_0)n_i^{4/3} a_{TF}$. The shear viscosity can be written as $\eta_s \sim \rho_m(\xi^2/t_w) \sim n_i M v_{\text{sound}}^2 (a_{TF}/\sqrt{(k_B T/M)} \sim n_i Z E_F (a_{TF}/\sqrt{(k_B T/M)})$. Therefore, the ratio between surface tension γ and shear viscosity η_s is

$$\frac{\gamma}{\eta_s} \sim \frac{E_b}{k_B T} \frac{(Ze)^2 n_i^{1/3} / 4\pi\epsilon_0 M}{v_{\text{sound}}^2} \sqrt{\frac{k_B T}{M}}. \quad (13)$$

For an insulating liquid whose $E_b/k_B T \ll 1$, the shear viscosity is $\eta_s \sim (E_b/k_B T)\rho_n^{2/3} \sqrt{k_B T_m M} (T/T_m)^{-1/2} [1 - (\rho_n(4\pi/3)(d/2)^3)]^{-2/3}$. If we combine this η_s at melting point T_m with the Andrade [12] relation $\eta_s(T_m) \sim \text{constant} \times \rho_n^{2/3} \sqrt{k_B T_m M}$ (p. 152 of [8]), then $E_b/k_B T_m$ is universal at melting point for simple metals. The second factor on RHS of Eq. (13) (the ratio of Coulomb energy to Fermi energy) is

TABLE III (16/15) $(\gamma/\eta_s v_T)$ and (16/15) $(\gamma/\eta_s v_{\text{sound}})$
(after [9,10])

<i>Metal</i>	(16/15) $(\gamma/\eta_s v_T)$	(16/15) $(\gamma/\eta_s v_{\text{sound}})$
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

weakly density dependent ($\sim n_i^{-1/3}$); we may expect the product of these two factors of Eq. (13) to be nearly constant. Both the Eyring relation $\gamma/\eta_s \sim \sqrt{k_B T/M}$ [9] and the Alonso–March relation $\gamma/\eta_s \sim v_{\text{sound}}$ [7,10] are in quite reasonable agreement with experimental observations at the melting point T_m . Eq. (13) is in some sense intermediate between them (Table III).

IV. SUMMARY

We have here used a cage model to estimate transport coefficients for both monatomic insulating liquids and the liquid alkali metals. A work-energy principle is adopted to make the transported part and the dissipated part the input energy more clear for both η_s and κ . The force field contribution is explicitly characterized by the correlation time of the two-particle positional correlation function (waiting time t_w for $E_b/k_B T \gtrsim 1$ or characteristic time t'_w for $E_b/k_B T < 1$) and the correlation length ξ (through t_w and sound velocity v_{sound}). For $E_b/k_B T \gtrsim 1$, we have obtained similar results to the classical Eyring method. This is consistent with the fact that the Eyring model is the strong dissipation limit of the present treatment. The minor differences concerning the temperature dependence of η_s , and the difference in κ between the two models remains to be clarified by more experimental data, when this becomes available.

The liquid alkali metals belong to the regime in which $E_b/k_B T < 1$. Three empirical laws: (i) $\eta_s \propto 1/\sqrt{T}$ for alkali metals; (ii) $\kappa/\eta_s \sim \text{constant}$ for Rb and Cs respectively and (iii) $\gamma/\eta_s \sim \sqrt{k_B T_m/M}$ for simple metals at melting point, are naturally explained.

Making use of partial structure factors in the liquid metal (Chapter 14 of [11]) affords a more rigorous approach by means of which to

formulate the transport problems in the two-component systems like the liquid alkali metals. The results of the cage model presented here may supply some useful information for the dynamical generalization of such partial structure factors and aid in making suitable approximations in wave vector space. Such work is currently in progress.

Acknowledgements

One of us (NHM) wishes to acknowledge numerous valuable discussions on the area embraced by this article with Professors J.A. Alonso and M.P. Tosi and with Dr. K. Tankeshwar. MLZ was supported by STWW-project Computerontwerp van moleculen en materialen (EV 48.88).

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APPENDIX

Electron-Ionic Density Fluctuation Scattering

Mean Free Path of Electron under Born Approximation

In a dense liquid metal, the electron-ionic density fluctuation scattering is the main scattering mechanism to determine the mean free path of electrons. A two-component treatment in term of partial structure factors was suggested by March and Tosi [11]. To directly relate the mean free path l_e with intrinsic material parameters (Z, M) and external conditions (n_i, T), we mimic the famous critical opalescence consideration modeling the collisions between the electronic de Broglie wave with the ionic density fluctuations. Since the typical interaction range in liquid metal is the Thomas–Fermi screening radius a_{TF} , we divide the whole liquid metal into many small parts, each cell having volume a_{TF}^3 .

In the critical opalescence case, the light wavelength is much bigger than the distance between molecules, the effect of the motion of the individual molecules is not obvious, only a spatial average about the corresponding spatial density fluctuation in cell being necessary. However, for the electron-ionic density fluctuation scattering in liquid metal, the wavelength of electronic de Broglie wave is of the same order of magnitude as the average distance between ions, is smaller than a_{TF} . The ionic motion therefore strongly influences the scattering potential of the cell: some kind of time average must be included to take care of the ionic motion. We include a factor t_w/t_e in the scattering cross section, where $t_e \sim a_{TF}/v_F$ is the time needed for an electron to cross the scattering cell. In fact $1/t_e \sim \omega_p$ and $1/t_w \sim \sqrt{(k_B T/Z E_F)} \omega_{IP} \sim v_{\text{thermal}}/v_{\text{sound}} \omega_{IP}$, where

$$\omega_{IP} = \sqrt{(Ze)^2 n_i / \epsilon_0 M}$$

is the ionic plasma frequency. The scattering cross section A between electron and a cell evaluated in the Born approximation is $A(q) \sim (m_e^2/h^4) |V(q)|^2 (v_F/v_{\text{thermal}}^i) a_{TF}^3 (k_B T/\phi(q))$, where $V_\alpha(q)$ is the Fourier transform of the scattering potential from the α th ion. Since all the ions are equivalent in a pure liquid metal, we neglect the index α on $V_\alpha(q)$. $a_{TF}^3 (k_B T/\phi(q))$ is the correlation of the static

number density fluctuation in each cell with wave number q [13], while $\phi(q)$ is the Fourier transformation of the free energy change due to the density fluctuation.

The mean free path of electron is given by

$$l_e \sim \frac{E_F}{k_B T} \frac{1}{n_{\text{cell}} A} \sim \frac{E_F}{k_B T} \frac{\hbar^4 \langle \phi(q) \rangle v_{\text{thermal}}}{m_e^2 \langle |V(q)|^2 \rangle k_B T v_F} \quad (\text{A1})$$

$$\sim (k_B T)^{-3/2} M^{-1/2} Z^{-1} n_i \langle \phi(q) \rangle \hbar,$$

where $n_{\text{cell}} = a_{TF}^{-3}$ is the number of cells in per unit volume. We have taken an average for both $\phi(q)$ and $V(q)$. The Heine formula for the effective electron-ion interaction is $z/v(0)$, where $v(0)$ is the density of states per unit energy per unit volume at the Fermi surface [13]. We have used this result in the last step of Eq. (A1).

Electrical Conductivity

The electrical conductivity σ_e due to electrons is

$$\sigma_e \sim \frac{n_e e^2 l_e}{m_e v_F} \sim \frac{Z n_i (k_B T)^{-3/2} \langle \phi(k) \rangle \hbar^4 e^2}{\sqrt{M} \langle |V(q)|^2 \rangle m_e^2} \quad (\text{A2})$$

$$\sim n_i^{5/3} (k_B T)^{-3/2} M^{-1/2} Z^{-1/3} \langle \phi(q) \rangle e^2.$$

To give an upper limit for the ionic electrical conductivity, we imagine that the increase of the electron density ahead of the ion is made up from the decreasing density behind it. Then the upper limit of the total force on an ion is $Z e \vec{E}$, where \vec{E} is the strength of electric field [14,15]. The upper limit of the ionic electrical conduction σ_i is $(n_i (Z e)^2 / M) \tau_i$, where τ_i is the collision interval (or mean free time) of ion, about $r / \sqrt{k_B T / M}$. It follows that $\sigma_i \sim (n_i^{2/3} (Z e)^2 / \sqrt{k_B T M})$. Comparing with Eq. (A2), we find that, even in the minimum conductivity limit $l_e \sim r$, $(\sigma_i / \sigma_e) \sim Z (P F / \sqrt{M k_B T}) \ll 1$. Therefore, the electrical conductivity mainly comes from the electronic part.

Thermal Conductivity

In a non-degenerate plasma, the density of ions and electrons is very dilute; hence the collision probability is very small. The mean free path of electrons and ions is much longer than the range of the

interaction, so that an ion meeting an electron is a rare event. In a liquid metal, the concentration of electrons and ions is so large that local neutrality is satisfied very well in a length scale of the order of the ionic radius. Then the separation between the electron cloud and ions is very small. We assume that the local energy exchange between electrons and ions in a distance of a Bohr radius is very fast, since in this range, an electron is easily captured into and released from an individual ionic well. This is in marked contrast to the dilute plasma, where the energy exchange is very slow due to the huge difference electron and ionic mass.

For liquid metals, the dominant contribution to thermal conductivity comes from the free motion of electrons. By means of Eq. (A1), the thermal conductivity due to the free motion of electrons is given by

$$\begin{aligned} \kappa_e &\sim n_e \frac{K_B T}{\varepsilon_F} k_B l_e v_F \sim \frac{Z n_i k_B}{\sqrt{M k_B T}} \frac{\phi(k)}{|V(q)|^2} \frac{h^4}{m_e^2} \\ &\sim n_i^{5/3} (k_B T)^{-1/2} Z^{-1/3} M^{-1/2} \langle \phi(k) \rangle k_B. \end{aligned} \quad (\text{A3})$$

The thermal conductivity due to the ions' free motion is of order $n_i(3k_B)l_i v_i \exp(-E_b/k_B T)$, where the mean free path of ion $l_i \sim r$ (the average distance between ions). Since all the degrees of freedom of ions are excited in a liquid, the heat capacity per ion is $3k_B$. The thermal conductivity contributed by the ions' random walk (jump from one cage to another) is $n_i(3k_B)(r^2/(t_w + l_{\text{jump}})[1 - \exp(-E_b/k_B T)])$. The ratio of the ionic thermal conductivity to the electronic part is $(\kappa_i/\kappa_e) \lesssim Z^{-1}(E_F/k_B T)(v_i/v_F)$. Even in the worst case $l_e \sim r \sim l_i$, for all the liquid metals $(E_F/k_B T) < 30$ and $(v_i/v_F) \sim 10^{-3}$, the electronic part of thermal conductivity is always dominant. The force field part of the thermal conductivity $\kappa_f^i = \kappa_f^e \sim \rho_m C_m (\xi^2/t_w) \sim n_i(3k_B)v_{\text{sound}}^2 (a_{TF}/\sqrt{k_B T/M})$ in order of magnitude. The force field part of thermal conductivity is smaller than the contribution of the free motion of the electrons: $(\kappa_f^i/\kappa_e) \sim (E_F/k_B T)(\rho_F/\sqrt{k_B T M}) < 1$.

To conclude this Appendix, we draw attention to the interest in developing the present approach to throw further light of the processes of electro- and thermo-mixation (14)–[16].