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# On the Calculation of Atomic Transport Coefficients in Liquid Metals

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The paper treats two topics: namely (a) the relation between shear viscosity  $\eta$  and bulk viscosity  $\zeta$  implied by the simplest, one-component plasma, model with some of the essential features to describe the liquid alkalis and (b) the incorporation of electron-ion interaction by means of another simple model, leading to linear dissipative ionic motion. The results of (a) should have potential relevance to experiments especially on Na and K, while (b) should be of interest for the lightest liquid alkali metal, Li.

## 1 INTRODUCTION

March and Suhl<sup>1</sup> have recently argued that the measurements of shear viscosity  $\eta$  in pure isotopes Li<sup>6</sup> and Li<sup>7</sup> by Ban *et al.*,<sup>2</sup> some twenty years ago, demonstrate that dynamical interactions between screened ions must play a role in determining transport coefficients in light liquid metals. They proposed that sound wave attenuation and neutron scattering experiments should also reveal departures from the scaling with isotopic mass that one would expect from a conventional theory.

In this paper, we pursue further (a) the consequences of a simple model, the so-called one-component plasma (OCP), for sound wave attenuation and (b) the influence of electron-ion interaction on atomic dynamics.

Ideally, one would like to start from the OCP model which, as we discuss below, has well studied transport properties, and, after investigating this fully from the standpoint of sound wave attenuation say, switch on the electron-ion interaction. Though statically this procedure leads to good results, dynamically there appear to be problems with current approaches to atomic transport in liquid metals by this route. Therefore, while not directly utilizing the OCP Hamiltonian as starting point, we shall consider the role of electron-ion interaction on atomic dynamics, with the objective of demonstrating for an explicit, though admittedly oversimplified, Hamiltonian, that single ion motion, in the presence of electron-ion interaction such as exists in a liquid metal like Li, can be represented by a conventional Newtonian equation of motion, but with a linear dissipative term proportional to the ionic velocity. The inclusion of such a term in molecular dynamical simulation of the atomic transport coefficients in light liquid metals such as Li is therefore proposed, the motivation for doing this being the viscosity measurements of Ban *et al.*<sup>2</sup> already referred to.

The outline of the paper is as follows. Immediately below, in Section 2, we use the thoroughgoing study of the OCP model by Vieillefosse and Hansen<sup>3</sup> to derive a relation between the longitudinal and shear viscosities. This may have relevance at least to the heavier liquid alkali metals and, we hope, might stimulate further efforts to measure precisely the bulk viscosity in these liquids. In this model however, with its unresponsive background of uniform neutralizing electronic charge, the atomic transport coefficients scale in the appropriate classical manner with atomic mass and therefore one cannot explain the results of Ban *et al.*<sup>2</sup> on the isotopes of Li. This makes it imperative for this lightest alkali metal to introduce electron-ion interaction, which is indeed known from a variety of evidence to be strong in Li metal.

Therefore, in Section 3, a suitable model Hamiltonian is introduced, into which electron-ion interaction is incorporated from the outset. With this, admittedly oversimplified, model Hamiltonian, the formalism of Lindenberg and Seshadri<sup>4</sup> can be used to derive an explicit equation of motion for an ion. Then, in Section 4, by plausible additional assumptions, this equation is recast into a form with a linear dissipative term. Section 5 constitutes a brief summary, plus proposals for incorporation of a linear dissipative term in molecular dynamical calculations of atomic transport in light liquid metals. The interest in neutron inelastic scattering from suitable light isotopes of liquid metals is finally re-emphasized. Though, for self-motion, the two lowest order sum rules are not expected to be affected by linear dissipation, it would be interesting to plot the deviations of the self-function  $S_s(k, \omega)$  from the

simple mass scaling result (cf. Eq. (5.1) below) valid in the absence of velocity dependent forces.

## 2 RELATION BETWEEN SHEAR AND BULK VISCOSITY IN ONE-COMPONENT PLASMA

By way of motivation, we merely note that for a one-component system the dynamical structure factor  $S(k, \omega)$ , accessible via neutron scattering, the Kubo-Green formula<sup>5</sup>

$$\frac{4}{3}\eta + \zeta \propto \lim_{\omega \rightarrow 0} \omega^4 \lim_{k \rightarrow 0} k^{-4} S(k, \omega) \quad (2.1)$$

leads to the combination of bulk viscosity  $\eta$ , and shear viscosity  $\zeta$ , which enters the interpretation of sound wave attenuation data. There is another, closely related Kubo formula for the shear viscosity, but we shall not need it directly in the present paper.

While the experimental situation with respect to the shear viscosity of liquid metals as a function of temperature is quite satisfactory, very little definitive information is available on the bulk viscosity.

Therefore, the work of Vieillefosse and Hansen<sup>3</sup> on the OCP model has considerable potential interest for the alkali metals. In particular, these workers give explicit expressions for reduced shear viscosity  $\eta^*$  and longitudinal viscosity  $b^*$ , related directly to  $(\frac{4}{3}\eta + \zeta)$  in Eq. (2.1). These quantities  $\eta^*$  and  $b^*$  are given explicitly in their Eqs (50) and (63) respectively. All the quantities entering these formulae can be attributed direct physical significance within the OCP model, except for the parameter they denote by  $H_3$ . This latter quantity, therefore, Vieillefosse and Hansen<sup>3</sup> estimate using the superposition approximation for the triplet correlation function  $g_3$ , which enters the expression for  $H_3$ .

As these workers demonstrate, at high values of the usual dimensional coupling constant  $\Gamma$  for this OCP model, the individual values of  $\eta^*$  and  $b^*$  are very sensitive to small variations in  $H_3$ . Thus, their Table III shows that, around the critical coupling  $\Gamma \sim 160$  for transition from liquid to crystal,  $\eta^* = 0.14$ , estimated from use of superposition, could vary with estimated uncertainties from 0.25 to 0.11. Similar large variations of  $b^*$  between 0.31 and 0.15, around their estimate  $b^* = 0.19$  are possible.

Therefore, the procedure we prefer to adopt below is to forego the possibility of obtaining fully quantitative estimates of  $\eta^*$  and  $b^*$  individually, which will clearly necessitate solving the still somewhat complicated problem of transcending the superposition approximation for  $g_3$ , and to content ourselves with relating  $b^*$  and  $\eta^*$  by eliminating  $H_3$  between their Eqs (50) and (63).

After some algebra, and use of definitions in the pioneering work,<sup>3</sup> we find the explicit relation

$$\frac{5}{\Gamma} = \frac{3\pi}{450} \left[ \frac{3}{b^{*2}} \left\{ \frac{15}{\Gamma} + 2I_1 - 15\gamma d \right\}^3 - \frac{4}{\eta^{*2}} \left\{ \frac{5}{\Gamma} - I_1 \right\}^3 \right]. \quad (2.2)$$

We note that, in terms of  $\Gamma$  and the excess of internal energy per particle  $U/N$ , the quantity  $I_1$  is given by

$$I_1 = \frac{2}{3\Gamma} \frac{U}{Nk_B T}. \quad (2.3)$$

The quantity  $\gamma$  as usual denotes the ratio of specific heats  $c_p/c_v$ , while  $d$  is given by

$$d = \frac{1}{3\Gamma} \frac{\beta}{\rho K_T} \equiv \frac{1}{3\Gamma} \beta \left( \frac{\partial p}{\partial \rho} \right)_T. \quad (2.4)$$

Motivated by the statement of Vieillefosse and Hansen<sup>3</sup> that they find  $b^*/\eta^* \simeq \frac{4}{3}$  over the entire range of  $\Gamma$  by numerical use of their Eqs (50) and (63) directly, we have investigated Eq. (2.2) above and have found that in the limit  $\Gamma$  tends to infinity, Eq. (2.2) does indeed lead back to  $b^*/\eta^* = \frac{4}{3}$ . Of course, near the freezing point of liquid alkali metals,  $\Gamma$  is  $\sim 160$  to  $200$  and is therefore indeed large.

Though, as already referred to above, we have now restricted ourselves to relating  $b^*$  and  $\eta^*$ , we have next used the numerical studies in Ref. 3 to evaluate explicitly this relation. Thus, Figure 1 shows a plot of  $b^*$  versus  $\eta^*$ , curves of constant  $\Gamma$  having been drawn in. Using a value of  $\eta^*$  quoted above, around 0.2, the spread due to the variation of  $b^*$  with coupling strength  $\Gamma$  is seen to be relatively small, confirming the main findings of Ref. 3, while avoiding the use of superposition. The fact that in Figure 1 the curve labelled  $\Gamma = 1$  is out of sequence with the others seems to be connected with the remark of the authors of Ref. 3 that the isothermal compressibility changes sign here.

It would, of course, be interesting if a satisfactory method could be found for handling the dynamics when electron-ion interaction is switched on to the above OCP model. However we have not, so far, seen how to proceed satisfactorily with that. Below therefore we shall explore another, not unrelated, route to the treatment of electron-ion interaction, essential for understanding transport in Li, if probably unimportant for Na and K, the most ideally free-electron metals for which the OCP model is very appropriate.

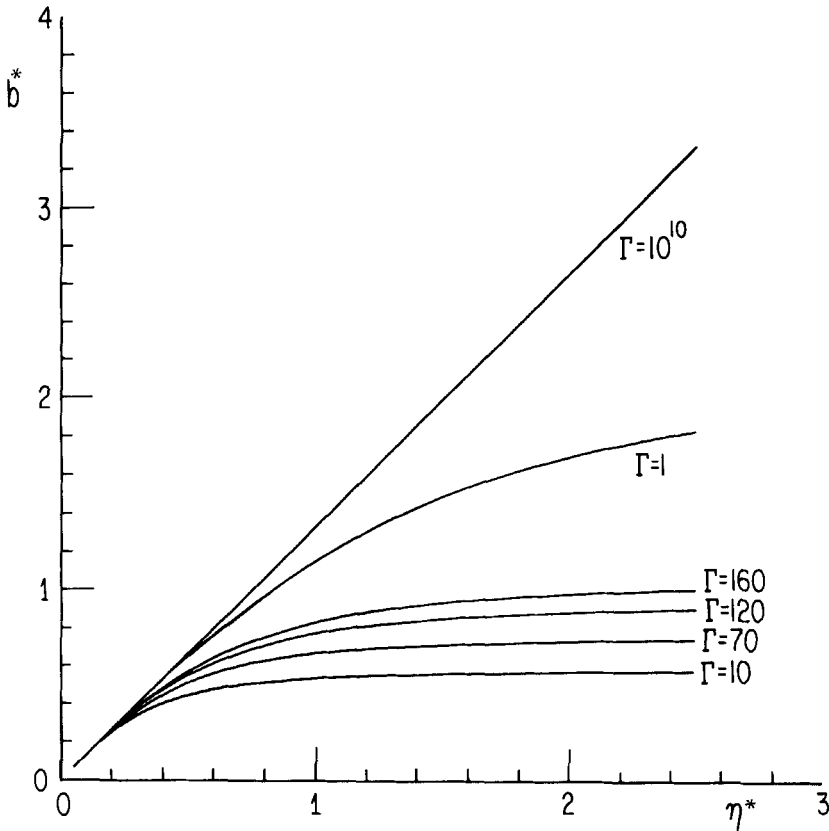


FIGURE 1 Reduced longitudinal viscosity  $b^*$  versus reduced shear viscosity  $\eta^*$  for different values of the OCP coupling strength  $\Gamma$ .

### 3 HAMILTONIAN OF COUPLED ION-ELECTRON ASSEMBLY

We consider the motion of an ion of mass  $M$  coupled to other ions of the same species, and also coupled to the conduction electrons of the metal, to be described by the Hamiltonian:

$$H = H_I(x) + H_e(y) + H_{Ie}(x, y). \quad (3.1)$$

The Hamiltonian for the ions will be of the general form

$$H_I = \sum_{i=1}^N \left[ \frac{M_i \dot{x}_i^2}{2} + V(x_i) \right] \quad (3.2)$$

while for the electrons it is convenient to follow a somewhat special approach. Normally, the conduction electrons will have a mean square displacement  $D_e t$ , where  $D_e$  is the diffusion coefficient. It is not our intention here to evaluate  $D_e$ , but rather to demonstrate that it separates into an electron-ion part and a contribution due to self-diffusion (and similarly for ionic diffusion). Therefore, we adopt the following simplification of treating the electrons as harmonic oscillators:

$$H_e = \frac{1}{2} m \sum_{i=1}^N (\dot{y}_i^2 + \omega_i^2 y_i^2). \quad (3.3)$$

In the limit  $\omega_i$  tends to zero, our results should yield the free-electron limit. In conjunction with this approximation, it will turn out to be useful to approximate the ion-electron interaction by the expression

$$H_{Ie} = \sum_{ij} (mM)^{1/2} \gamma_{ij} y_i x_j \quad (3.4)$$

The usefulness of this form is that in the limit  $\omega_i \rightarrow 0$ ,  $\gamma_{ij} \rightarrow 0$ , subject to the restriction that  $\gamma_{ij}/\omega_i$  is finite, we can obtain the desired separation of the diffusion coefficient into its two contributions.

Given the above choice of Hamiltonian, consider the equation of motion of a single ion, denoted  $x(t)$ , and the oscillators to which it is coupled:

$$M\ddot{x} + \frac{\partial V(x)}{\partial x} + \sum_{n=1}^N (Mm_n)^{1/2} \gamma_n y_n = 0 \quad (3.5)$$

$$\ddot{y}_n + \omega_n^2 y_n + \gamma_n x (M/m_n)^{1/2} = 0. \quad (3.6)$$

The  $y_n$  coordinates refer to all the degrees of freedom to which the "tagged" ion is coupled according to the bilinear form given in Eq. (3.4). In principle, this may be used to represent not only the electronic background, but also that of the other ions in the system.

Following Lindenberg and Seshadri,<sup>4</sup> these equations can be combined to yield the equation of motion for the ion in the presence of the background oscillators:

$$M\ddot{x} + \frac{\partial V}{\partial x} + \sum_{n=1}^N (Mm_n)^{1/2} \gamma_n y_n^{(0)}(t) + \sum_{n=1}^N M\gamma_n^2 \int_0^t ds G_n(t-s)x(s) = 0. \quad (3.7)$$

In Eq. (3.7),  $y_n^{(0)}(t)$  is the homogeneous solution to the equation of motion for the  $n$ th background oscillator, while  $G_n$  is the appropriate Green function. Explicitly, these are:

$$y_n^{(0)}(t) = q_n^{(0)} \cos \omega_n t + \frac{\dot{q}_n^{(0)}}{\omega_n} \sin \omega_n t \quad (3.8)$$

$$G_n(\tau) = \frac{1}{2i\omega_n} \exp(i\omega_n \tau) - \exp(-i\omega_n \tau) \quad (3.9)$$

With the aim of expressing the ionic motion in a manner that displays the dissipative contribution, it is convenient to define the kernel

$$G_n(t - s) = \frac{d}{ds} F_n(t - s). \tag{3.10}$$

Then, if we integrate by parts, the new form for the equation of motion for the tagged ion may be expressed as:

$$\begin{aligned} M\ddot{x} + \frac{\partial V}{\partial x} + \left[ \sum_{n=1}^N M\gamma_n^2 f_n(0) \right] x(t) - \sum_{n=1}^N \gamma_n^2 M \int_0^t ds F_n(t - s) \dot{x}(s) \\ = f(t) + \left[ \sum_{n=1}^N M\gamma_n^2 F_n(t) \right] x(0). \end{aligned} \tag{3.11}$$

In Eq. (3.11),  $f(t)$  and  $F_n(t)$  are given by:

$$f(t) = \sum_{n=1}^N y_n^{(0)}(t) (Mm)^{1/2} \gamma_n \tag{3.12}$$

$$F_n(t) = -\frac{1}{2\omega_n^2} [\exp(i\omega_n t) + \exp(-i\omega_n t)]. \tag{3.13}$$

All this follows without approximation, from the choice of model Hamiltonian in Eqs (3.1) and (3.4). Before proceeding further, two comments should be made. First, had the equation of motion for  $y_n$  contained non-linear terms, we would have had to construct a perturbative solution for  $y_n(t)$  involving convolutions over powers of  $G_n(\tau)$ . Rewriting  $G_n$  in terms of  $F_n$  would add non-linear dissipation terms to the equation for  $x(t)$ . In principle such contributions will be present, but will not alter our conclusions concerning the coefficient of the linear dissipation term.

Secondly, we see that there is a “renormalization” of the oscillator frequency for  $x$ , and from this we conclude that the harmonic oscillator model which we have chosen is likely to be less restrictive than might appear at first sight. This contribution is in the form of a sum over terms like  $F_n(0)$ .

#### 4 MARKOVIAN ASSUMPTION AND LINEAR DISSIPATION

To move from the above formalism to some specific results which can be interpreted directly, it is necessary to invoke some plausible approximations. Central to the treatment below is the Markov assumption. This will motivate then a number of approximations which are made in order to allow an explicit determination of the resulting correlation functions.



The Markov approximation appears directly through the requirement that the effective “external” source be delta correlated:

$$\langle f(t)f(t') \rangle = C_0 \delta(t - t'). \quad (4.1)$$

A reasonable starting point in achieving this form is to take the initial phase coordinates of the set  $\{q_n^{(0)}, \dot{q}_n^{(0)}\}$  to be determined by the canonical distribution:

$$P = Z^{-1} \exp\left(-\frac{\beta}{2} \sum_{n=1}^N m_n (\dot{q}_n^{(0)})^2 + \omega_n^2 q_n^{(0)2}\right) \quad (4.2)$$

From this, we have:

$$\langle f(t)f(t') \rangle = \sum_{n=1}^N M \gamma_n^2 \frac{k_B T}{\omega_n^2} \cos[\omega_n(t - t')]. \quad (4.3)$$

Therefore, if we take  $\gamma_n^2$  proportional to  $\omega_n^2$ , say  $\gamma_n^2 = D_0 \omega_n^2$ , then

$$\langle f(t)f(t') \rangle = D_0 k_B T \sum_{n=1}^N \cos[\omega_n(t - t')]. \quad (4.4)$$

In the limit of large  $N$  and assuming that the  $\omega_n$  are uniformly spaced, we have the desired result

$$\langle f(t)f(t') \rangle = D_0 k_B T M \delta(t - t').$$

The sum over  $n$  is a sum over all background oscillators, so if this set is divided into ions and electrons, it is clear that there are two components to the correlation function for  $f(t)$ :

$$\langle f(t)f(t') \rangle = (D_s + D_{Ie}) M k_B T \delta(t - t'). \quad (4.5)$$

The first contribution is the self-part, or ion–ion interaction; the second contribution is due to the ion–electron interaction.

#### 4.1 Consequence of fluctuation–dissipation theorem

We next note that the nature of the fluctuation–dissipation theorem is that any assumption about the additive noise necessarily determines the multiplicative noise also. Inspection of Eq. (3.11) indicates that, having determined the statistical properties of  $f(t)$ , we are also in a position to simplify the coefficients of  $x(t)$  and  $\dot{x}(s)$  as well. The new equation of motion is:

$$M \ddot{x} + \frac{\partial V}{\partial x} + \Omega^2 x(t) + b \dot{x}(t) = f(t) \quad (4.6)$$

which has been arrived at by putting

$$\Omega^2 = \sum_{n=1}^N M \frac{\gamma_n^2}{\omega_n^2} = N D_0 M \quad (4.7)$$

and by making the assumption

$$M \sum_{n=1}^N \frac{\gamma_n^2}{\omega_n^2} \cos[\omega_n(t - t')] = b\delta(t - t') \tag{4.8}$$

The term proportional to  $x(0)$  in Eq. (3.11) can be omitted since the initial position of the ion can be taken to be zero when averaged. By the fluctuation-dissipation theorem, it follows that:

$$b = D_0 M. \tag{4.9}$$

If we therefore simply consider the equation of motion

$$M\ddot{x} + b\dot{x} + \Omega^2 x = f(t) \tag{4.10}$$

then the solution is readily expressed in terms of the Green function and the external source as:

$$x(t) = \int_0^t ds G_0(t - s)f(s) \tag{4.11}$$

where

$$G_0(\tau) = \frac{1}{a_1 - a_2} [\exp(a_1\tau) - \exp(a_2\tau)] \tag{4.12}$$

and  $a_1$  and  $a_2$  are given by:

$$a_1 = -\frac{b}{2} + \frac{1}{2}(b^2 - 4\Omega^2)^{1/2} \equiv B + (B^2 - \Omega^2)^{1/2} \tag{4.13}$$

$$a_2 = -\frac{b}{2} - \frac{1}{2}(b^2 - 4\Omega^2)^{1/2} \equiv B - (B^2 - \Omega^2)^{1/2}$$

with  $B = -b/2$ . From Eq. (4.11) we can calculate the correlation function for  $x(t)$  in the long time limit:

$$\langle x(t)x(t) \rangle = \frac{k_B T}{2ND_0 M} \equiv \frac{k_B T}{2N} \frac{\tau^2}{M} \tag{4.14}$$

In this expression, we have redefined the proportionality constant given earlier:

$$\frac{\gamma_n^2}{\omega_n^2} \equiv \frac{1}{\tau^2} \tag{4.15}$$

The nature of this definition should be clear if it is interpreted as an effective mean free lifetime  $\tau$ . Of course, it would be more appropriate to have  $\tau$  depend on  $n$ , for example:

$$\frac{\gamma_n^2}{\omega_n^2} = \frac{\Gamma_0^4}{\omega_0^2 + \omega_n^2}$$

which would lead to exponentially correlated additive noise. Further elaboration is possible, the main observation being that the manipulations given above can be used as a reasonable starting point for investigating the dissipative effect of coupling the electron system to the ions.

The separation of  $D_0$  into an ion-ion and an ion-electron part:

$$D = D_{II} + D_{Ie} = \frac{1}{\tau_I^2} + \frac{1}{\tau_E^2} \quad (4.16)$$

is an important refinement on which computer simulation may yield useful information, since our model does not give a basis for determining the ratio  $\gamma_n/\omega_n$ . At low temperatures, quantum effects, absent in this calculation, will be significant and the mean free lifetime of the particles will diverge. At high temperatures, the mean lifetime has a different dependence on  $T$ ; therefore a purely mechanical choice for  $\gamma_n/\omega_n$  is not sufficient, but can act only as a guide for a given temperature regime.

## 5 SUMMARY AND PROPOSALS FOR FURTHER WORK

The main achievements of the present work can be summarized as follows. First, for Na and K, the predictions of Figure 1 for  $\Gamma \sim 160$  are relevant.  $b^*/\eta^*$  can be marginally less than  $4/3$  in the relevant range of  $\eta^*$ . As stressed in Ref. 3,† however, the conclusion from the study is that  $\zeta$  makes only a small contribution to sound wave attenuation for these simple, free-electron, metals. Mass scaling in this treatment is as in conventional classical theory, and therefore this model cannot suffice for the correct treatment of atomic transport in liquid  $\text{Li}^6$  and  $\text{Li}^7$ .

The further achievement of the paper is then to demonstrate that, for the admittedly simple model Hamiltonian summarized by Eqs (3.1)–(3.4), electron-ion interaction can be, essentially, subsumed into a rather simple equation of motion for the tagged ion with (a) a modified conventional force field, which we might liken to “static electron screening” of bare ions, and (b) a linear dissipative term proportional to the ionic velocity.

Of course, it is true that the electrons in a liquid metal just above its melting point form a completely degenerate electron gas. However, because of the close similarities between assemblies of harmonic oscillators treated classically or quantum mechanically, we do not expect our main conclusions to be altered by quantum mechanics, within our Drude-like modelling of the electrons. Furthermore, of course, our work should be viewed within the

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† Presumably the Gaussian approximation made in this reference for the memory function is responsible for the non-physical  $b^*/\eta^* \lesssim 4/3$ .

context of the usual treatment, say by molecular dynamical computer simulations, of ionic dynamics based on effective ion-ion pair interactions. Naturally these “static” pair interactions are mediated by the electrons and must be calculated by treating the electrons quantum mechanically.<sup>5</sup> But over and above these effective static forces, the additional dissipative term arising from electron-ion interaction must modify the scaling property noted by Brown and March,<sup>6</sup> namely

$$S_s(k, \omega) = M^{1/2}f(k, \omega M^{1/2}) \tag{5.1}$$

It will, we believe, be interesting, with reasonable choices of the linear dissipative constant  $b$ , as motivated by the present work, to calculate the self-diffusion constant  $D$  in pure Li<sup>6</sup> and pure Li<sup>7</sup>,  $D$  being related by the Kubo-Green formula (cf. Eq. (2.1) for sound wave attenuation)

$$\frac{D}{\pi} = \lim_{\omega \rightarrow 0} \omega^2 \lim_{k \rightarrow 0} k^{-2} S_s(k, \omega) \tag{5.2}$$

to the self function  $S_s$ . Of course, the complete self-function  $S_s(k, \omega)$  for two isotopes, for varying values of  $b$ , will be of some interest too.

But returning to the starting point of the present work, experimental data on the shear viscosity  $\eta$  for pure Li<sup>6</sup> and pure Li<sup>7</sup> is already available as a function of temperature.<sup>2</sup> Molecular dynamical simulation of  $\eta$ , including linear dissipation, seems therefore the first priority. We must emphasize that while, at first, it would seem sensible to work simply with one constant  $b$ , the work of McCaskill and March<sup>7</sup> relates dynamic interactions between screened ions to the sharpness of the Fermi surface. In a liquid metal, the Heisenberg Uncertainty Principle links the degree of Fermi surface blurring to the electronic mean free path. This would mean that velocity dependent terms in the ionic equations of motion could have a magnitude dependent on the electronic mean free path and therefore temperature dependent.

In conclusion, the present work on electron-ion interaction, though based on a simple model Hamiltonian, can leave little doubt that it will not be possible to treat atomic transport in liquid metals in a fully correct manner with the customary “static” effective ion-ion interactions. We expect, however, that the effects discussed in the present paper will only be of quantitative importance for really light liquid metals. Li is already of considerable interest: Be would be potentially also a metal worthy of careful study, but its toxicity means that little experimental information is available. Mg and Al are outside candidates to study experimentally. Overall, and following the pattern already evident from experiments on Li, measurements on different isotopes of the same light liquid metal seem the most promising, experiments in the present context embracing molecular dynamical simulation.

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