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Transport coefficients of liquids from first principles

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Abstract

The use of first-principles molecular dynamics to calculate the viscosity of liquid metals using the Green–Kubo relations is described. The first-principles techniques are based on density functional theory, the pseudopotential approximation, and plane-wave basis sets. The statistical-mechanical basis of the Green–Kubo relations is summarised, and extensive first-principles molecular dynamics simulations of liquid aluminium are presented to demonstrate that the method works in practice. Calculated viscosity results are reported for two important systems: liquid iron at Earth's core conditions, and liquid selenium at states on the liquid–vapour curve. The significance of the viscosity results for an understanding of these systems is discussed. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

First-principles molecular dynamics (FPMD) has become a widely used simulation method for studying liquid metals and a variety of other condensed-matter systems. Since the pioneering work of Štich et al. on liquid Si [1], a large amount of simulation work has been published on all kinds of liquid metals, including Cu [2], Al [3], Ge [4], Hg [5] and Se [6], as well as liquid alloys such as Ag/Se [7]. Comparisons with diffraction data show that in many cases the structure of the real liquid is precisely reproduced by FPMD simulations. Atomic diffusion coefficients are generally well reproduced as well. But up to now, rather little attention has been paid to transport coefficients such as viscosity, even though these quantities are often very important for practical reasons or for understanding the dynamics of the liquid.

The aim of this paper is to show that the FPMD calculation of the viscosity of liquid metals is now becoming feasible. In Section 2, we summarise the statistical–mechanical background, emphasising the Green–Kubo relations used in this work. Section 3 reports results on three systems: liquid Al, chosen for our initial tests because of its simplicity; a liquid Fe/S alloy at Earth's core conditions, which illustrates the geological importance of viscosity calculations; and liquid Se, a case where the viscosity is intimately related to the unusual structure of the liquid. Discussion and conclusions are presented in Section 4 and Section 5, respectively.

2. Theoretical ideas

The technique of FPMD [8], based on density functional theory (DFT), the pseudopotential

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approximation and plane-wave basis sets, is now very well established, and we do not describe it in detail here. The main idea is to calculate the total energy of a system and the forces on all the atoms for each set of atomic positions by solving Schrödinger's equation to find the electronic ground state. The forces are then used to generate the time evolution of the atomic positions using Newton's equation of motion, with the ground state being recalculated at every time step. The key approximation – indeed the only significant one – is the functional used to represent the electronic exchange-correlation energy. It is important to stress that although FPMD is well established, liquid metals (and particularly transition metals) pose special problems. Our practical calculations rely heavily on the technical advances made by Kresse and Furthmüller as implemented in the VASP code [9–11]. General reviews of DFT and FPMD are given in Refs. [12,13]; a non-technical review of FPMD and its multifarious applications is given in Ref. [14]. In the rest of this section, we give a brief review of the statistical mechanics needed to calculate transport coefficients, and we then summarise the technical details that apply to all the simulations presented. Further details particular to each simulation will be given in the appropriate place in Section 3.

2.1. Statistical mechanics

The most obvious way to calculate the viscosity is to subject the simulated system to a steady shear rate, calculate the average shear stress, and divide one by the other. However, this is not necessarily easy to do in practice; we prefer a more indirect approach, which exploits the relation between transport coefficients and equilibrium correlation functions. This approach has been widely used in classical molecular dynamics simulation [15], but has so far been little discussed in the first-principles context. It will therefore be useful to give a brief summary of the basic ideas.

There is a branch of statistical mechanics known as 'linear response theory', concerned with the response of a system to a weak external perturbation. (The meaning of 'weak' will be made clear below.) The corner-stone of linear response theory is the fluctuation–dissipation theorem [16], which gives a rigorous relation between the response to a perturbation and spontaneous fluctuations in the absence of the perturbation. Many external perturbations can be described by a time-varying term added to the Hamiltonian. If H_0 is the Hamiltonian of the system without the perturbation, then an external perturbation varying at frequency ω can be described by adding a term $A\exp(\mathrm{i}\omega t)$, so that the total Hamiltonian is

$$H(t) = H_0 + \lambda A \exp(\mathrm{i}\omega t). \tag{1}$$

Here A is a dynamical variable describing the perturbation, and λ is a parameter specifying the size of the perturbation. Now we want to know how some other variable B responds to this perturbation. Denote by $\langle B(t)\rangle$ the average value of B at time t. Because of the perturbation, $\langle B(t)\rangle$ varies in time at frequency ω. If the perturbation is weak enough, this variation will be proportional to λ, so that we can write

$$\langle B(t)\rangle = \lambda \chi_{BA}(\omega) \exp(\mathrm{i}\omega t), \tag{2}$$

where $\chi_{BA}(\omega)$ is a so-called response function characterising the frequency-dependent response of B caused by A. (The requirement that the response is proportional to λ defines what is meant by a 'weak' perturbation.) We assume here that the average of B in the absence of the perturbation is zero.

The fluctuation–dissipation theorem says that the response function $\chi_{BA}(\omega)$ can be rigorously expressed in terms of a correlation function describing the fluctuations of A and B when the system is in thermal equilibrium with no perturbation applied. For systems in which the movement of the atoms can be described by classical mechanics, the theorem says

$$\chi_{BA}(\omega) = \frac{1}{k_{\mathrm{B}}T} \int_0^\infty \mathrm{d}t e^{\mathrm{i}\omega t} \frac{\mathrm{d}}{\mathrm{d}t} \langle B(t)A(0)\rangle. \tag{3}$$

Now transport coefficients are a special kind of response function concerned with a special kind of variable. In general, the dynamics of atoms happens on a time-scale of ps. But there are some degrees of freedom that vary on time-scales of seconds, minutes or even longer. The origin of this remarkable behaviour lies in the existence of conserved quantities. For example, energy is conserved, so the energy in one region of the system can only change by the flow of energy from surrounding regions. The same is true of other conserved quantities such as particle number and momentum. But the flux of such quantities is caused by gradients in the system, so that it depends on the wavevector of the disturbance. As the wavevector gets smaller, the time rate of change gets smaller. Transport coefficients specify the proportionality between the flux of a conserved quantity and the gradient of a thermodynamic variable.

Since transport coefficients describe the response to a disturbance, the fluctuation–dissipation theorem tells us that they can be expressed in terms of correlation functions. It turns out that the dynamical variables entering these correlation functions are none other than the fluxes of the conserved quantities. The resulting general formulas expressing transport coefficients in terms of equilibrium correlation functions of the fluxes of conserved quantities are called Green–Kubo relations. The huge advantage of calculating transport coefficients this way in a simulation is that we never have to apply any disturbance at all. We simply do a normal simulation and calculate the correlation functions.

Viscosity is about the transfer of momentum, and the flux of momentum is the stress tensor $P_{\alpha\beta}$, so it is not surprising to find that the Green–Kubo formula for the shear viscosity η is [15]

$$\eta = \frac{V}{k_B T} \int_0^\infty \mathrm{d}t \langle P_{xy}(t) P_{xy}(0) \rangle, \tag{4}$$

where V is the total volume of the system. Here P_{xy} is the off-diagonal component of the stress tensor, with x and y the Cartesian components. The fluctuating stress tensor P_{xy} at any instant of time can be calculated in FPMD, as it can in classical molecular dynamics, so this formula gives us a fundamentally based procedure for calculating the viscosity of a liquid from first principles. We refer to the quantity $\langle P_{xy}(t) P_{xy}(0) \rangle$ in the following as the stress autocorrelation function (SACF). In fact, there are five independent SACFs corresponding to the five components of the traceless stress tensor: P_{xy}, P_{yz}, P_{zx}, $\frac{1}{2}(P_{xx} - P_{yy})$ and $\frac{1}{2}(P_{yy} - P_{zz})$. In a large system, the five SACFs would be statistically identical by spherical symmetry, but the cubic periodic boundary conditions that we use break this symmetry slightly. In the practical calculations, each SACF like $\langle P_{xy}(t) P_{xy}(0) \rangle$ is computed as an average of the quantity $P_{xy}(t + t_0) P_{xy}(t_0)$ over time origins t_0 for given time differences t.

2.2. Practicalities of FPMD

The results we shall present all come from FPMD simulations done with the pseudopotential plane-wave code VASP [9–11]. As noted above, metallic systems pose special technical problems, which the VASP code has been specifically designed to overcome. Unlike the FPMD technique originally proposed by Car and Parrinello [8], VASP performs an iterative minimization to the electronic ground state at every molecular-dynamics step. Particularly important in VASP is a charge-mixing scheme based on ideas proposed by Pulay and others (see Ref. [10]) which plays a crucial role in accelerating the search for the ground state. Also important is an efficient iterative matrix-diagonalization scheme based on residual minimization. A smearing method is used to avoid problems with level crossing, and electronic free energy is used as the variational quantity, with the electronic levels occupied according to Fermi statistics corresponding to the temperature of the system. Forces and the stress tensor are calculated using the Hellmann–Feynman theorem (see Ref. [10]). The temperature is controlled using a Nosé thermostat [17]. In the present approach to FPMD, convergence to the ground state at each step is accelerated by extrapolating the wavefunctions and the charge density from previous steps, as described in Ref. [4]. In the present work, we use a modification of the procedure described by Kresse and Furthmüller [10,11]. We represent the charge density $\rho(\mathbf{r})$ as $\rho_{\mathrm{atom}}(t) + \delta\rho(t)$, where ρ_{atom} is a linear superposition of atomic charge densities. The initial value of the small quantity $\delta\rho$ is then obtained for each new step by quadratic extrapolation from the two previous steps. This gives better performance than extrapolation of the full density employed in the standard version of the VASP code [10,11].

All our calculations use ultrasoft pseudopotentials, following the ideas originally proposed by Vanderbilt [18]. The use of such pseudopotentials is particularly crucial for our liquid iron simulations, which would otherwise be computationally prohibitive. The general problem of constructing efficient ultrasoft pseudopotentials has been discussed in detail by Kresse and Hafner [19], and a detailed assessment of the VASP pseudopotentials as applied to transition metals has recently been published by Moroni et al. [20].

3. Illustrative results

3.1. A test case: liquid aluminium

We choose liquid aluminium for our initial tests, because it is a rather simple system for FPMD. The calculations are rapid, and the experimental shear viscosity is well established. The present calculations build directly on our recent work in which first-principles simulations were used to study the melting properties of aluminium [21]. Technical details of the present calculations are as follows: The local density approximation was used for the electronic exchange-correlation energy, and the plane-wave cut-off was 130 eV. The simulations were done on a periodic system with 64 atoms in the cell, using Γ-point sampling. The time step used for integration of the equation of motion was 3 fs, and the self-consistency tolerance on the ground-state energy was 1.5×10^{-8} eV/atom. With this tolerance, the drift in the total energy was ~0.2 meV/atom/ps, which is extremely small. Our longest simulation of l-Al was done at 1000 K (the melting point is 930 K), and a density of 2470 kg m^{-3}, which gives a calculated pressure close to zero; this density is ca. 5% greater than the experimental value at this temperature. We believe the discrepancy is mainly due to the LDA, which generally underestimates equilibrium volumes. The total duration of this simulation was 80 ps.

The average $\phi(t)$ of the five SACFs, normalised by dividing by the value $\phi(0)$, is displayed in Fig. 1. As expected, $\phi(t)$ decays rapidly to zero as $t \to \infty$. We have estimated the statistical error on $\phi(t)$, and we find that it is almost independent of t, having a root-mean-square value of ca. 1.5% of the correlation function at $t = 0$. For t greater than ca. 0.4 ps, the average value of $\phi(t)$ is smaller than this error.

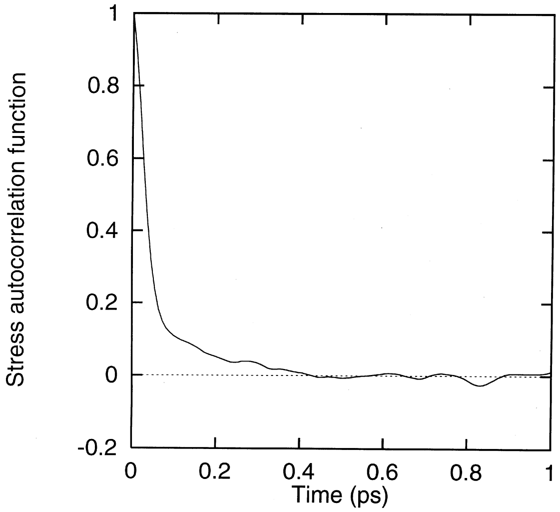

Fig. 1. Average over the five independent components of the autocorrelation function of the traceless stress tensor $\phi(t)$ calculated for liquid Al at 1000 K at the density 2470 kg m^{-3}. Values are normalised by dividing by $\phi(0)$.

Fig. 2 reports the viscosity integral $\int_0^t dt' \phi(t')$ as a function of t, the $t \to \infty$ limit of the integral being the shear viscosity. We have estimated the error in the integral as a function of t using the scatter of the SACFs calculated by breaking the simulation into short, statistically independent intervals. This method is combined with an analytic expression for the error, and the resulting error estimate is also reported in Fig. 2. From the point where $\phi(t)$ falls below the noise, we integrate only the latter, so no further information can be gained. If we assume that $\phi(t)$ is zero for $t > 0.4$ ps, we obtain $\eta = 2.2 \pm 0.1$ mPa s, which should be compared with the experimental value of 1.25 mPa s [22].

The point we wish to stress is that the statistical error on our calculated η is only ca. 5%. This means that the fully first-principles calculation of the viscosity, with an accuracy that is more than enough for most practical purposes, is now feasible.

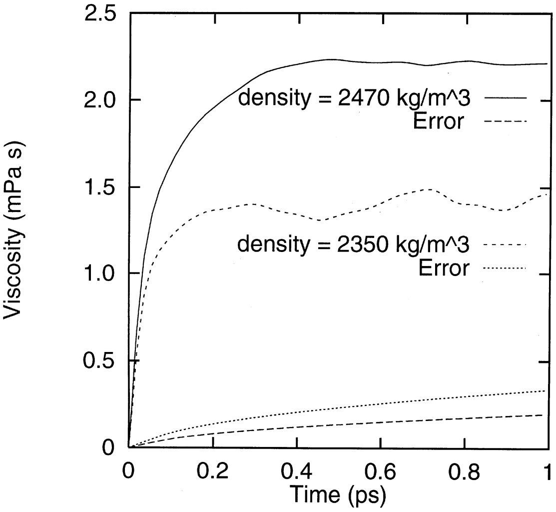

Fig. 2. Viscosity integral of the average stress autocorrelation function and its statistical error as a function of time for liquid Al at 1000 K. Results are shown for the calculated zero-pressure density 2470 kg m^{-3} and the experimental density 2350 kg m^{-3}.

Nevertheless, the agreement with the experimental η is not entirely satisfactory. Our tests suggest that the discrepancy is mainly due to the error in the equilibrium density produced by LDA. To check this, we have performed another simulation under the same conditions, but at the experimental density of 2350 kg m^{-3} (this yields a calculated pressure of −2 GPa). The duration of this simulation was 20 ps. The results for the viscosity integral reported in Fig. 2 give $\eta = 1.4 \pm 0.15$ mPa s, which is in close agreement with the experimental value.

3.2. Liquid iron in the Earth's core

We now turn to a problem of fundamental importance in the Earth sciences: the viscosity of the material in the Earth's outer core. Seismic studies show that the Earth's core consists of a liquid outer part and a solid inner part [23]. Arguments based on the abundance of chemical elements in the Sun and in meteorites lead one to expect a large amount of iron in the core [23]. A combination of seismic and other data gives a fairly accurate profile for the density (and hence pressure) as a function of depth, and the inferred density as a function of pressure is close to that given by laboratory experiments on iron. Nevertheless, the inferred density is about 10% less than that of pure iron [23], so there is little doubt that the core consists of iron alloyed with lighter elements; sulphur, oxygen and silicon are leading candidates [23]. The liquid outer core is in a state of turbulent convection, and this motion drives the dynamo responsible for the generation of the Earth's magnetic field, as well as transporting heat from the inner core to the mantle.

The viscosity of the outer core is one of the most poorly determined quantities in geophysics, with estimates from different sources spanning some 12 orders of magnitude, as reviewed recently by Secco [24]. It is also an important quantity, because if it was as large as some estimates suggest, the nature of the turbulent convection could be radically altered. If the core consisted of pure iron, we should expect the liquid to have a simple close-packed structure not very different from that of a hard-sphere system, and then it would be hard to imagine that the viscosity would be much different from that of normal liquid metals under ambient conditions. But if iron is combined with other elements, perhaps at concentrations greater than 20%, a much larger viscosity cannot be ruled out.

In an effort to improve our understanding of iron in the Earth's core, we have initiated a programme of work in which first-principles calculations are being used to investigate the properties of both solid and liquid iron over a wide range of conditions. We have recently reported VASP calculations on solid and liquid Fe at pressures up to those in the Earth's core [25,26]. We demonstrated that calculations based on ultrasoft pseudopotentials reproduce rather precisely the known properties of solid iron under ambient pressures (see also Moroni et al. [20]), and that they give good agreement with the results of all-electron calculations on the zero-temperature solid at high pressures. Our FPMD simulations of l-Fe at several thermodynamic states relevant to the outer core showed the close-packed structure expected under these conditions. We made viscosity estimates based on the value of the diffusion coefficient, and these indicated low values in the region of 13 mPa s.

We present here some results from our current work on a liquid Fe/S alloy in which we have calculated the viscosity directly from the Green–Kubo formula. The S mole fraction was taken to be 18.75%, in line with maximum estimates for S abundance in the core [23], the temperature was 6000 K, and the density was 12 330 kg m^{-3} (the inferred density of the liquid at the inner-core boundary is ca. 12000 kg m^{-3}). The simulations were performed on a system of 64 atoms per repeated cell (52 Fe and 12 S), with the generalised gradient approximation for exchange-correlation energy [27], a plane-wave cut-off of 350 eV, a time step of 1 fs and a self-consistency threshold of 1.5×10^{-7} eV/atom. The total duration of the simulation was 10 ps.

The viscosity integral $\int_0^t \mathrm{d}t' \phi(t')$ from this simulation is reported in Fig. 3, together with the error estimated as for the l-Al case. The SACF itself appears to have gone to zero after ca. 0.2 ps, and our estimate of η from these results is 9 ± 2 mPa s. Clearly the statistical error is substantial, because the run is relatively short, but given the uncertainties faced by earth scientists, the result is still valuable. It is similar to our earlier estimate for pure l-Fe under core conditions, and fully confirms that the viscosity is not much greater than that of typical liquid metals at ambient pressures (recall the η of 1.4 mPa s for l-Al).

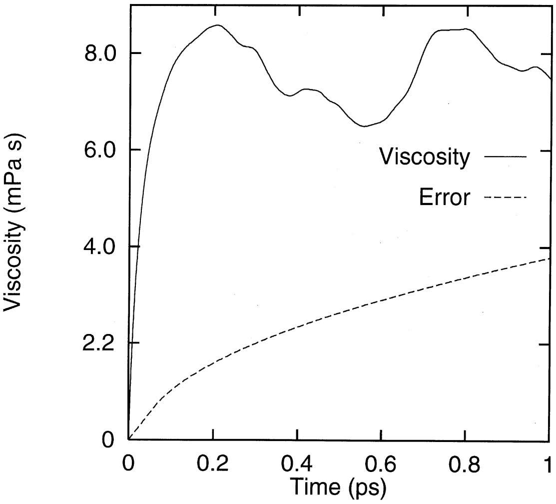

Fig. 3. Viscosity integral of the average stress autocorrelation function and its statistical error as a function of time for liquid Fe/S under Earth's core conditions.

We are currently engaged in similar calculations on the l-Fe/alloy, which are giving even smaller viscosities. So even at this preliminary stage, we have evidence against the much larger η values that have sometimes been suggested on the basis of seismic and other data.

3.3. Structure and dynamics of liquid selenium

Liquid Se is an unusual and much studied system. In the trigonal crystal structure of the solid, the atoms form infinite chains, with strong covalent bonds between neighbouring atoms within the chains, but rather weak bonds between different chains. This chain structure survives essentially unchanged when the system melts ($T_{\mathrm{m}} = 490$ K), and diffraction measurements show that the coordination number in the liquid is almost exactly equal to 2 [28]. Just above the melting point, the viscosity is exceptionally high, with a value of ~5 Pa s [29], i.e. about 3000 times that of l-Al. With increasing temperature, the viscosity decreases rapidly, reaching values of ~4 mPa s at 1000 K [29]. This decrease indicates that the Se chains become more and more disrupted as the temperature increases, though diffraction measurements [28,30] indicate that the average coordination number remains close to 2 even at high temperatures. Experimental measurements using nuclear magnetic resonance (NMR) and other techniques have been used to derive the average chain length (number of atoms per chain), and reported values go from ~10^4 at the melting point to ~10 at 1600 K [31,29].

There has been a considerable amount of simulation work on l-Se, using both first principles [6,32–34] and tight-binding [35] methods. The FPMD simulations we shall present here are an extension of the simulations reported recently by Kirchhoff et al. [6]. A detailed analysis of these simulations to extract chain lengths and defect concentrations has been made by Kresse et al. [36]. The structure factors and radial distribution functions produced by the recent FPMD simulations [6,34] agree fairly closely with diffraction data. However, it has become clear that the simultaneous presence of weak and strong bonds poses non-trivial problems for DFT, and that the LDA is much less satisfactory than GGA [6]. The chain lengths calculated even from the most recent FPMD simulations do not appear to agree very well with experimental estimates, particularly at temperatures near the melting point. In our recent analysis [36], we found chain lengths of 62 and 23 at 870 and 1370 K, respectively, compared with NMR values of ~1000 and ~20 at these two temperatures. This indicates quite good agreement at high temperatures but a difference of at least an order of magnitude at 870 K.

Because of the relationship between chain length and viscosity, it is clear that a calculation of viscosity can help to show whether the disagreement about chain lengths is pointing to a real deficiency in the simulations, rather than, for example, a problem with the interpretation of the experimental data. We have calculated the viscosity of l-Se from FPMD simulations at 870 and 1370 K. The simulation techniques and details of the pseudopotentials are exactly the same as in our recent work [6]. As before, there are 69 atoms in the repeating cell. The present simulations represent continuations of the previous ones, and our viscosity results are calculated from runs of 14 ps duration at both temperatures.

The viscosity integrals are shown in Fig. 4, together with the estimated errors. From the asymptotic values we estimate viscosities of 0.52 ± 0.04 and 0.30 ± 0.04 mPa s at 870 and 1370 K, respectively. We compare these with the values of 6.0 mPa s and 0.55 mPa s at 870 and 1370 K, respectively, given by the measurements of Perron et al. [29]. (The value at 870 K is taken directly from their Fig. 1, but the 1370 K value is our extrapolation of their results, which extend only to 1000 K.) Our results therefore agree moderately well with experiment at high temperature, but there is a substantial disagreement at 870 K. It seems likely that this disagreement is related to the disagreement about chain lengths. Since the chain length in the simulated system appears to be too short by about an order of magnitude at 870 K, it is intuitively reasonable that the viscosity should be too small by a similar amount. Our viscosity calculations for l-Se therefore suggest rather strongly that the disagreement about chain lengths is due to some kind of deficiency in the FPMD simulations.

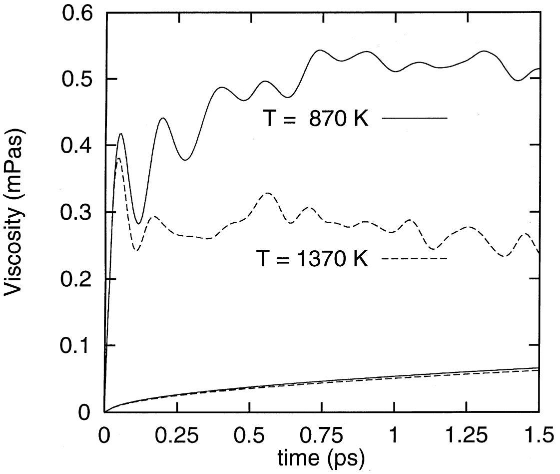

Fig. 4. Viscosity integral of the average stress autocorrelation function and its statistical error as a function of time for liquid Se at the temperatures 870 and 1370 K.

It seems possible that this problem may be due to the small size of our simulated system. To investigate this further, we are now performing molecular dynamics simulations using an order-N tight-binding technique, which should allow us to go to systems of at least 1000 atoms. Even though the use of the tight-binding approximation entails a loss of absolute accuracy, this approach should be perfectly adequate to discover whether size effects are important for this type of problem.

4. Discussion

The results we have presented on liquid aluminium leave little doubt that transport coefficients such as viscosity can now be calculated entirely from first principles, without any need for empirical modelling or adjustable parameters. Given the well established accuracy of first-principles methods for many kinds of system, the reliability of calculated transport coefficients raises two main issues: statistical accuracy, and size effects. The statistical accuracy depends on the duration of the simulation, and for a collective quantity such as viscosity is generally almost independent of the size of the simulated system. Our demonstration that the purely statistical errors on the calculated viscosity for l-Al are of order 5% shows that, at least for this simple type of metal, this source of error can be brought under control. However, the question of size effects is more subtle and more interesting.

For simple model systems, such as the hard-sphere and Lennard-Jones liquids, the influence of size effects on transport coefficients calculated by classical molecular dynamics has been exhaustively studied by many authors. For example, Schoen and Hoheisel [37] studied the viscosity for Lennard–Jonesium using system sizes ranging from 32 atoms to 2048 atoms. They found that even a system as small as 32 atoms gave quite respectable values of the viscosity. The system-size error is known to depend quite strongly on thermodynamic state, but near the triple point we expect this kind of error for a system of $\sim$64 atoms to be in the region of 10%. Clearly size errors cannot simply be ignored, and first-principles calculations on larger systems are desirable, but for simple liquids this kind of error does not appear to be a major issue. Liquid iron and its alloys with sulphur and oxygen under Earth's core conditions should count as 'simple' in this sense, because of their close-packed structure, whereas selenium may well not be 'simple'. Indeed, the case of selenium shows that for some liquids there are still problems. Although the calculated viscosity is essentially correct at high temperatures, it becomes definitely incorrect at lower temperatures. The origin of this problem needs further investigation.

Although we have focused entirely on the shear viscosity in this paper, we emphasise that other transport coefficients such as thermal and electrical conductivity are also extremely important. But for metals we cannot simply apply the present methods to calculate these quantities, because electronic degrees of freedom play a crucial role. The essential distinction here is that in calculating the viscosity it is correct to assume that the electrons follow the nuclei adiabatically (the Born–Oppenheimer principle). So provided the motion of the nuclei is correctly described the viscosity will be correct. But for thermal and electrical conductivities transport due to electronic degrees of freedom is of the essence. There have already been approximate first-principles calculations of the electrical conductivity of liquid metals, based on Kubo–Greenwood theory [38,39]. (This is related to the Green–Kubo theory used in the present work, but applies to transport of electrons.) However, we suggest that what is now needed for a full treatment of electronic transport in liquid metals is a many-body analysis based perhaps on the GW approximation. The calculation of electronic response functions by computational many-body theory is a rapidly developing field, and calculations of this kind should soon become feasible.

5. Conclusions

We have demonstrated that the first-principles calculation of the viscosity of liquid metals is now feasible, and that it is capable of delivering accurate and reliable results. The potential importance of being able to do this has been illustrated by calculations on liquid iron and its alloys under Earth's core conditions. However, we have shown that liquid selenium is an unusual case where the calculated viscosity agrees less well with experiment, and where deeper study is needed.

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