

First principles calculations on the diffusivity and viscosity of liquid Fe–S at experimentally accessible conditions

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Abstract

Ab initio molecular dynamics calculations, based upon density functional theory within the generalised gradient approximation (GGA) using ultrasoft non-norm conserving Vanderbilt pseudopotentials, have been used to predict the transport properties of liquid Fe–S. In order to compare our simulations with experimental data, the simulations were performed for the eutectic composition of Fe–S at the experimentally accessible conditions of 5 GPa and of 1300 and 1500 K. Our results give values for Fe and S diffusion of a few times $10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Our calculated viscosities, obtained directly from the simulations, are 11 ± 5 and $4 \pm 1 \text{ mPa s}$ at 1300 and 1500 K, respectively. Our calculated diffusion and viscosity coefficients agree well with recent experiments at similar pressures and temperatures, supporting a high diffusivity and low viscosity in liquid Fe–S at temperatures up to a few hundred Kelvin above the eutectic temperature. Furthermore, an extensive study of the liquid structure shows no evidence for sulphur polymerisation or the existence of any large viscous flow units. These results are in direct conflict with the previously reported experimental results of Le Blanc and Secco [LeBlanc, G.E., Secco, R.A., 1996. Viscosity of an Fe–S liquid up to 1300°C and 5 GPa, *Geophys. Res. Lett.*, 23, 213–216.]. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The Earth's outer core is thought to be made predominantly of liquid iron with some 6–10 wt.% light element inferred from the seismologically observed reduced density. Several candidates of alloy elements have been proposed (see Poirier, 1994, for review), including sulphur. However, our knowledge of the properties of iron alloys at core conditions,

particularly viscosity and diffusion, is limited. Determination of the transport properties of the Earth's outer core provides inconclusive results; geophysical viscosity estimates span no less than 12 orders of magnitude (see, e.g., Poirier, 1988; Secco, 1995) and because of the extreme conditions of pressure and temperature involved ($\sim 6000 \text{ K}$, $\sim 360 \text{ GPa}$), experimental determination of transport properties at core conditions is currently prohibitively difficult. Recent experiments on the viscosity of Fe–S (LeBlanc and Secco, 1996; Brazhkin, 1998; Dobson et al., 2000a; Urakawa, 2000) and diffusion measure-

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ments on Fe in Fe–FeS liquids (Dobson, 2000b) have been limited to just a few GPa, but even at these modest conditions, there are conflicting, and sometimes startling, results. Using a Stoke's law rising sphere technique, LeBlanc and Secco (1996) have measured the viscosity of Fe–S liquid with a eutectic composition (27 wt.%, 39 atm.% S), at 2–5 GPa and 1373–1573 K. Their results indicate that the viscosity of this phase is three orders of magnitude higher than the ambient pressure value, and two to three orders of magnitude higher than that for pure iron. They suggest that the enhanced viscosity may be due to the polymerisation tendency of S atoms in the melt, inhibiting diffusion. In contrast, using a Stoke's law *falling* sphere technique, Dobson et al. (2000a) have measured the viscosity of $[\text{Fe–S}]_{\text{eut}}$ at $\sim 1450 \pm 50$ K and ~ 2.5 GPa to be $\sim 10^{-2}$ Pa s, approximately twice the ambient pressure value. Using a similar technique, Urakawa (2000) has measured the viscosity of $[\text{Fe–S}]_{\text{eut}}$ (with ~ 1 atm.% oxygen contamination) at 5–7 GPa and ~ 1350 K and also obtains a value of $\sim 10^{-2}$ Pa s. More recently, experiments have been performed on the diffusion of Fe (Dobson, 2000b) and S (Dobson, 2000c) in liquid $[\text{Fe–S}]_{\text{eut}}$. At conditions of 2–5 GPa and up to 150 K above the solidus, these experiments yield results for diffusivities similar to those of pure metals in each case (10^{-4} to 10^{-5} cm² s⁻¹), but with an unexpectedly high activation energy for Fe diffusion of ~ 250 kJ mol⁻¹.

A possible method for assessing the reliability of these experimental results is provided by the Stokes–Einstein equation, which gives a relationship between diffusion and viscosity of the form:

$$D\eta = \frac{k_{\text{B}}T}{2\pi a}, \quad (1)$$

where a is an atomic diameter, T is the temperature, k_{B} is the Boltzmann constant and D and η are the diffusion and viscosity coefficients, respectively. However, it is first necessary to establish the validity of this equation before using it to assess whether or not the various experiments are giving reliable results for D and η ; computer simulation provides a possible route by which this may be done.

Computer simulations are extremely useful in both underpinning experimental results and predicting material properties beyond the range of experimentally

accessible conditions. In particular, first principles calculations have already proved to be remarkably reliable when predicting the properties of iron and iron alloys. We have already been able to accurately reproduce the magnetic and elastic behaviour of the body-centred cubic (bcc) phase of iron, the bcc to hexagonal close-packed (hcp) phase transition, including its transition pressure, the compressibility of both bcc- and hcp-Fe, the phonon dispersion, density of states and thermodynamic properties of bcc and hcp-Fe as a function of pressure, and the structural properties of FeSi (Vočadlo et al., 1997, 1999a, 1999b; Alfè and Gillan, 1998a; Alfè et al., 1999; Mao et al., 2000). In particular, we have also proved the reliability of these methods in predicting the viscosity of liquid aluminium at ambient conditions (de Wijs et al., 1998a), and in three previous papers (Alfè and Gillan, 1998a; Alfè et al., 2000; de Wijs et al., 1998b), we have determined the behaviour of both pure Fe and Fe–S (12 wt.%) liquid at outer core conditions. These calculations on Fe and Fe–S showed that at core conditions, (i) the viscosity of pure Fe (~ 8 – 15 mPa s) is approximately twice that at ambient conditions (~ 6 mPa s), (ii) the viscosity and diffusion coefficients of Fe–S (12 wt.%) are very similar to that of pure iron, and (iii) despite the considerable effort made to encourage sulphur polymerisation by initially forcing the S atoms to stay together. In *all* cases, the Fe and S atoms became randomly mixed almost immediately, with S–S bond lengths that were considerably longer than those of either Fe–S or Fe–Fe.

It could be argued, however, that comparing the results from calculations on Fe–S with 12 wt.% S at core temperatures and pressures with those of experiments on $[\text{Fe–S}]_{\text{eut}}$ at much lower temperatures and pressures is not necessarily valid. Moreover, the experimental results themselves are not consistent results. The purpose of this paper, therefore, is to address the problem of conflicting experimental data and, in doing so, help decide what are the true transport properties of liquid $[\text{Fe–S}]_{\text{eut}}$ at experimentally accessible pressures and temperatures. After a short description of the methodology used in these calculations, we present our results where we initially focus on the structure of liquid $[\text{Fe–S}]_{\text{eut}}$, establishing whether or not it is at all possible for diffusion to be inhibited by sulphur polymerisation;

we then present the results for our calculated diffusion and viscosity coefficients, comparing them with the available experimental data. Finally, we test the validity of the Stokes–Einstein equation and, therefore, determine the reliability of the experimentally determined viscosity data by establishing whether or not they give credible diffusivities for this system.

2. Calculation methodology

The calculations we present here are based on density-functional theory (DFT), which is a widely employed general scheme for using electronic structure calculations to obtain the total energy of a system as a function of atomic positions. More specifically, we use the pseudopotential approach in which only valence electrons are treated explicitly, with the interactions between these electrons and the ionic cores being described by a pseudopotential. This approach allows calculations to be as accurate as all-electron methods while being computationally much less demanding (Alfè et al., 2000). We treat electronic exchange-correlation energy using the generalised gradient approximation (GGA), coupled with non-norm-conserving ultrasoft Vanderbilt pseudopotentials (Vanderbilt, 1990) as implemented in the Vienna Ab initio Simulation Package (VASP) code (Kresse and Furthmüller, 1996). The results presented here were obtained using a plane-wave basis set with a cutoff of 350 eV, which gives total energies converged to within a few tens of meV/atom. For the Fe pseudopotential, all electron states up to $3p$ are treated as core states, i.e., with an $[Ar]$ frozen core, and for the S pseudopotential all electron states up to $2p$ are treated as core states, i.e., with a $[Ne]$ frozen core. As mentioned earlier, the excellent quality of our pseudopotential DFT calculations has already been demonstrated for both pure iron and a number of iron alloys, including Fe–S (12 wt.%) (e.g., Alfè and Gillan, 1998a; Alfè et al., 2000; de Wijs et al., 1998b).

To simulate the liquid, we have used finite temperature ab initio molecular dynamics with a Nosé thermostat. The forces between the atoms are calculated quantum mechanically, with the total energy of the system calculated exactly at each time-step. Newton's laws of motion are then solved to give an evolving trajectory over a period of time for all the

particles in the system. Periodic boundary conditions are applied to the system to simulate the required infinite system. In our simulations, we have used a 64-atom supercell containing 40 Fe atoms and 24 S atoms, approximately equivalent to a eutectic composition of 39 atm.%. The influence of the size of the simulated system on calculated transport coefficients has been studied in detail for liquid Fe (Alfè et al., 2000), and it is known that a 64-atom cell gives results for diffusion coefficients and viscosity to within $\sim 20\%$.

We performed two simulations at $\sim 5 \pm 0.1$ GPa and at two temperatures: the first, at 1500 K, was run for 10.70 ps; and the second, at 1300 K, was run for 24.01 ps. In each case, the timestep between successive configurations for the first half of the simulation was 1 fs and for the second half of the simulations was 2 fs. The simulation times were necessarily long in order to obtain good statistics. The results are presented using the latter half of each simulation, allowing a considerable equilibration time for each of the 1500 and 1300 K simulation (5 and 12.5 ps, respectively).

3. Results

3.1. Structural properties

The structural properties of our system were investigated by analysing the partial radial distribution functions (RDFs), $g_{\text{FeFe}}(r)$, $g_{\text{FeS}}(r)$ and $g_{\text{SS}}(r)$. The partial RDFs, $g_{\alpha\beta}(r)$, are defined in such a way that, by considering an atom of the species α , the probability of finding an atom of the species β in a spherical shell (r , $r + dr$) is $\rho_{\beta} 4\pi r^2 g_{\alpha\beta}(r) dr$, where $\rho_{\beta} = x_{\beta}/V$, is the number density of the species β with mole fraction x_{β} , and V is the volume per atom.

As mentioned earlier, it has been suggested that the high viscosity observed in experiments (LeBlanc and Secco, 1996) could be due to the polymerisation tendency of sulphur atoms or the existence of large viscous flow units impeding atomic diffusion. Therefore, we initially carried out a series of test simulations in order to establish the structure of the eutectic Fe–S liquid and to see if we could observe any such sulphur polymerisation. We used a starting configuration in which all the S atoms were artificially

forced into a cluster, giving them every opportunity to remain together. By observing the evolution of both the atomic positions and the RDF's with time, we found that after only a very short time (< 2 ps) the sulphur atoms readily dissociated and had become thoroughly mixed (in agreement with the high pressure calculations of Alfè and Gillan, 1998a). Moreover, after ~ 2 ps, the average S–S bond length was considerably longer than both the Fe–S and Fe–Fe bond lengths indicating an S–S repulsion. Despite the considerable effort that was made to encourage the clustering of S atoms, we found no evidence for sulphur polymerisation whatsoever and, therefore, carried out all subsequent calculations with a random starting configuration.

We then performed two calculations at 5 GPa and 1300 K, and at 5 GPa and 1500 K, with simulation times of 24.01 and 10.70 ps, respectively. Fig. 1 shows the RDFs calculated over the latter half of each simulation in blocks of 2.5 ps. The fact that the RDFs do not change from one block to the next confirms that the system is well equilibrated and that no systematic changes are occurring. We also note that each $g_{\alpha\beta}$ is essentially the same at the two temperatures so that there is no indication of any significant dependence of structure on temperature in this temperature range. The nearest neighbour distance is that between Fe and S with a bondlength of ~ 2.2 Å compared to the considerably longer S–S bondlength of ~ 3.3 Å. The relative positions of the peaks are comparable to those previously calculated at much higher pressures and temperatures (~ 330 GPa, ~ 6000 K) (Alfè and Gillan, 1998a). However, there are two notable differences: (i) the absolute positions of the peaks calculated in this work are at slightly longer lengths than the previous high P/T work due to the considerably lower pressures involved, and (ii) the previous high P/T simulations did not show any well defined S–S peak due to the significantly increased iron content. However, the results of both these and our previous calculations do indicate that the structure of Fe–S liquid is unlikely to radically alter with either increased temperature, pressure or iron content. Moreover, the sulphur atoms are not only behaving differently from the iron atoms, but are definitely not undergoing the polymerisation proposed by LeBlanc and Secco (1996). Indeed, in all cases, our results suggest an S–S repulsion.

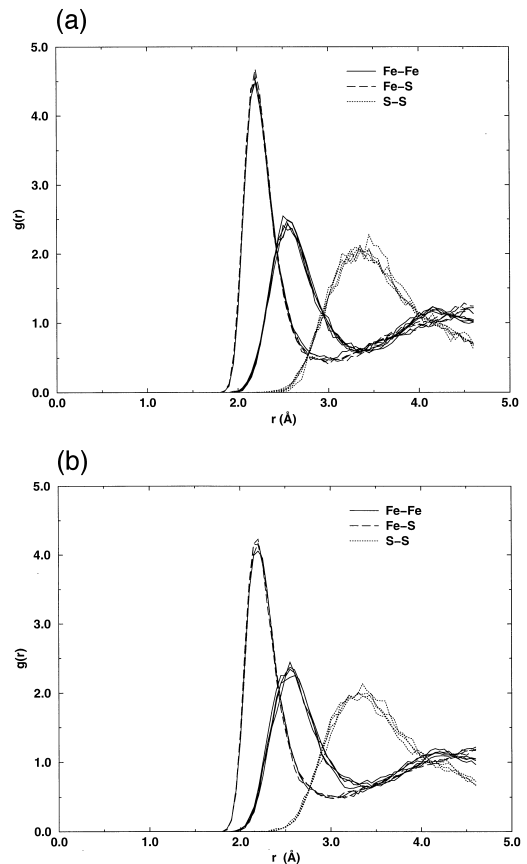


Fig. 1. Radial distribution functions at ~ 5 GPa and (a) 1300 K and (b) 1500 K calculated by averaging over 2.5-ps time windows throughout the latter half of each simulation. The consistent overlap indicates that the RDFs do not vary significantly with time.

3.2. Diffusion

The self-diffusion coefficient, D_α , of each species α can be obtained from the time-dependent mean-square displacement (MSD) $\langle \Delta r_\alpha(t)^2 \rangle$, which is defined as:

$$\langle \Delta r_\alpha(t)^2 \rangle = \left\langle \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} |r_{\alpha i}(t_0 + t) - r_{\alpha i}(t_0)|^2 \right\rangle, \quad (2)$$

where $r_{\alpha i}(t)$ is the vector position at time t of the i th atom of species α , N_α is the number of atoms of species α in the cell, and the angular brackets

indicate time average over t_0 . In the long time limit, $|t| \rightarrow \infty$, the MSD has the asymptotic form:

$$\lim_{t \rightarrow \infty} \langle \Delta r_\alpha(t)^2 \rangle = B_\alpha + 6D_\alpha|t|, \quad (3)$$

where B_α is a constant. Our results for $\langle \Delta r_\alpha(t)^2 \rangle$ are displayed in Fig. 2. The linear nature of $\langle \Delta r_\alpha(t)^2 \rangle$ with t for large t confirms that our system is, indeed, a liquid. This is also corroborated by the static structure factors, $S_{\alpha\beta}(k)$, not reported here. If any incipient crystallisation were occurring, the main peaks in $S_{\alpha\beta}(k)$ would increase drastically, and we do not observe this.

The self-diffusion coefficient for each species and at each temperature was calculated using Eq. 3. At ~ 5 GPa, the calculated self-diffusion coefficients for both Fe and S are a few times 10^{-5} cm² s⁻¹

with that of Fe being somewhat higher ($D_{\text{Fe}} \sim 2.5 \times 10^{-5}$ cm² s⁻¹ and $D_{\text{S}} \sim 1.1 \times 10^{-5}$ cm² s⁻¹ at 1300 K and $D_{\text{Fe}} \sim 3.5 \times 10^{-5}$ cm² s⁻¹ and $D_{\text{S}} \sim 2.0 \times 10^{-5}$ cm² s⁻¹ at 1500 K). These results are close to the values previously calculated at core pressures and temperatures (although with 12 wt.% S) of $4\text{--}6 \times 10^{-5}$ cm² s⁻¹ for each species (Alfè and Gillan, 1998a). In Fig. 3, we compare our calculated diffusion coefficients with the experimental values of Dobson (2000b,c) in the form of an Arrhenius plot. We note that if the diffusion coefficients showed strict Arrhenius behaviour:

$$D = D_0 \exp\left(\frac{-\Delta Q}{RT}\right), \quad (4)$$

then the activation energy, ΔQ , would be proportional to the negative slope of the results on this plot. We see that our results for both Fe and S diffusion are numerically very similar to those of Dobson (2000b,c). We also note that the Arrhenius slope of his experimental results for D_{Fe} is considerably higher than ours. In fact, the statistical error bars on our values are too large for us to obtain accurate values for ΔQ , but we obtain rough estimates for ΔQ of a few tens of kJ mol⁻¹ for both Fe and S. Dobson (2000b) claimed very small error bars on his experimental results for D_{Fe} and reported a ΔQ of 252 kJ mol⁻¹. However, we would suggest that further investigation may be needed before this very high value of ΔQ is accepted. If D_{Fe} showed strict Arrhenius behaviour with such a large ΔQ , it would reach physically impossible values in the region of 10^{-3} cm² s⁻¹ at rather modest temperatures of ~ 3000 K. The apparent conflict between the Arrhenius slopes from experiment and simulation would be resolved if one assumed that the experimental values, and the ΔQ deduced from them, were somewhat less precise than they were claimed to be.

We, therefore, believe that the good agreement between experimental and simulation values of D_{Fe} and D_{S} is very significant. However, further work is probably needed before a reliable comparison of activation energies can be made.

3.3. Viscosity

The viscosity, η , of the liquid may be calculated directly from the autocorrelation function of the fluctuating stress, as shown by Alfè and Gillan (1998b).

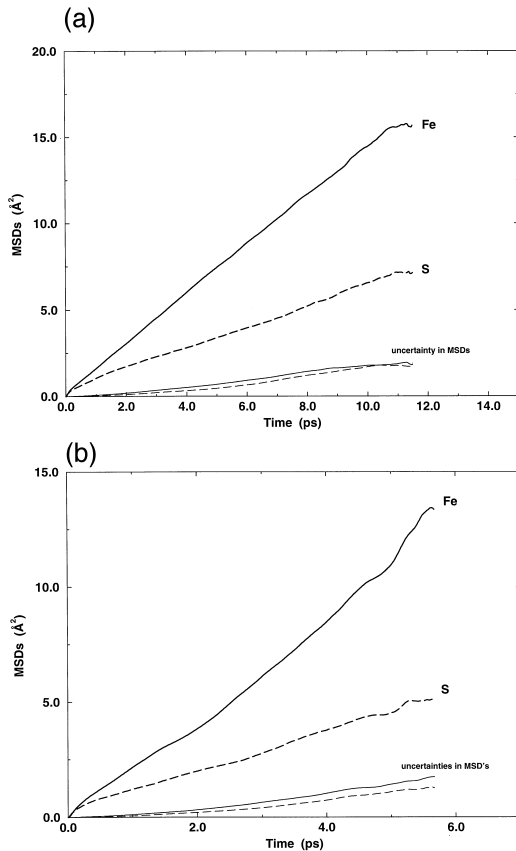


Fig. 2. Mean-square displacements at ~ 5 GPa and (a) 1300 K and (b) 1500 K; the continuous increase of the MSDs for each species at each temperature indicates that the system has retained its liquid structure.

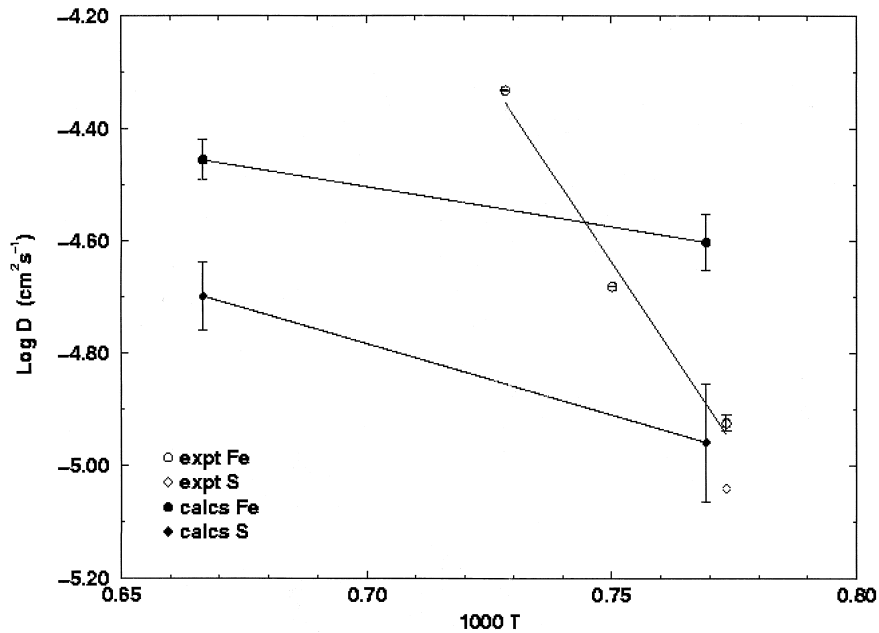


Fig. 3. An Arrhenius plot for diffusion at ~ 5 GPa comparing the calculated diffusion parameters with those of recent experiments (Dobson, 2000b).

This general approach to the calculation of viscosity relies on the rigorous Green–Kubo relation (see, e.g., Allen and Tildesley, 1987), which expresses η as:

$$\eta = \frac{V}{k_B T} \int_0^\infty dt \varphi(t), \quad (5)$$

where V is the volume of the system, and $\varphi(t)$ is the autocorrelation function for the off-diagonal stress:

$$\varphi(t) = \langle P_{xy}(t+t_0) P_{xy}(t_0) \rangle. \quad (6)$$

Here, the angular brackets denote a thermal average over time origins, t_0 , and $P_{\alpha\beta}$ are the elements of the stress tensor, with α, β Cartesian components. The calculation of the elements $P_{\alpha\beta}$ at any instant of time during an ab initio simulation is standard. In practical calculations, the statistical accuracy can be greatly improved by noting that equivalent but statistically independent results for $\varphi(t)$ can be obtained from autocorrelation functions of the four other traceless parts of the stress, namely $P_{yz}, P_{zx}, (P_{xx} - P_{yy})$ and $(2P_{zz} - P_{xx} - P_{yy})$, as explained by Alfè and Gillan (1998b).

Our results for $\varphi(t)$ and the time integral $(V/k_B T) \int_0^t dt' \varphi(t')$ calculated from our simulations at 1300 and 1500 K are displayed in Figs. 4 and 5. The viscosity is obtained from the asymptotic long-time value of the time integral. Also shown in Fig. 5 are the statistical errors on the time integral, estimated using the scatter of the stress autocorrelation functions calculated by splitting the simulation into many short intervals and then combining this estimate with an analytical expression for the error. The statistical error on the time integral grows with t , since one integrates long-time statistical noise in $\varphi(t)$, and the asymptotic value of the time integral is estimated as its value in the region of t at which the signal $\varphi(t)$ becomes comparable with the noise, as explained by Alfè and Gillan (1998b).

This procedure gives η values of $\sim 10.8 \pm 5$ and $\sim 4.2 \pm 1$ mPa s at 1300 and 1500 K, respectively. These values are close to those of ~ 10 mPa s from the experiments of Dobson et al. (2000a) at 1450 ± 50 K and 2.5 GPa and of ~ 10 mPa s from the experiments of Urakawa (2000) at ~ 1350 K and 5–7 GPa. These theoretical and experimental values all conflict with the values due to LeBlanc and Secco

(1996), which are three to four orders of magnitude higher.

We can assess the implications of the very high η favoured by LeBlanc and Secco (1996) by referring to the Stokes–Einstein equation mentioned earlier (Eq. 1). With our calculated diffusion coefficients, the Stokes–Einstein equation can be used to estimate a viscosity, which may then compared with that obtained directly from the calculations. Firstly, however, we must give some attention to the atomic diameter, a , in Eq. 1. The Stokes–Einstein relation is exact for the Brownian motion of a macroscopic particle of diameter a in a liquid with a viscosity of η . However, the relation is necessarily approximate when applied to atoms, since the choice of a is somewhat arbitrary. In this case, this arbitrariness is even larger because there are two atomic species and

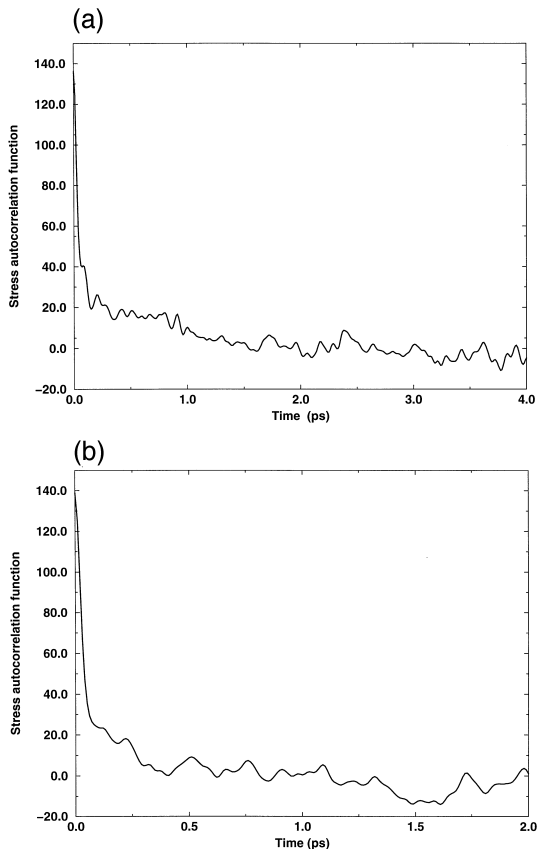


Fig. 4. Average over the five independent components of the autocorrelation function of the traceless stress tensor, $\varphi(t)$, calculated at ~ 5 GPa and (a) 1300 K and (b) 1500 K. Values of $\varphi(t)$ are normalised by dividing by $\varphi(0)$.

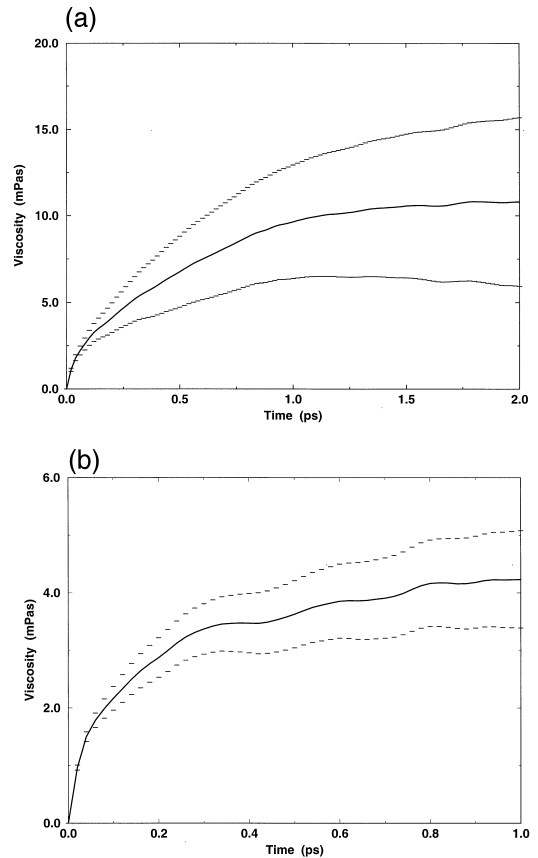


Fig. 5. Viscosity integral of the average traceless stress autocorrelation function (solid line) and its statistical error (dashes) as a function of time at ~ 5 GPa and (a) 1300 K and (b) 1500 K.

it is not obvious what the atomic diameter for each species should be. However, at $T = 1300$ K, if we use the iron diffusion coefficient, D_{Fe} , and the position of the first peak of the Fe–Fe RDF (in Fig. 1) as the effective atomic diameter, we obtain an estimate for the viscosity of ~ 5 mPa s; using the equivalent sulphur parameters, we obtain an estimate for the viscosity of ~ 8 mPa s. At 1500 K, we obtain values of ~ 5 and ~ 4.3 mPa s for Fe and S, respectively. The estimates of viscosity obtained from the Stokes–Einstein relation are in remarkably good agreement with those determined from the more rigorous Green–Kubo relation. Therefore, the Stokes–Einstein equation is valid for this system, which implies that the high viscosities obtained by LeBlanc and Secco require the system to have far

smaller diffusion coefficients than those measured by Dobson (2000b) and Dobson et al. (2000a).

4. Conclusions

We have used first principles calculations to investigate the structure, diffusivity and viscosity of an Fe–S eutectic melt under experimentally accessible conditions. We find that our calculated diffusion coefficients and viscosities agree well with the latest experiments at similar pressures and temperatures (Dobson, 2000b; Dobson et al., 2000a; Urakawa, 2000). Our results, therefore, support a high diffusivity and low viscosity in liquid $[\text{Fe–S}]_{\text{eut}}$ at temperatures up to a few hundred Kelvin above the eutectic temperature, in conflict with the experimental results of LeBlanc and Secco (1996). Furthermore, a study of the structure of liquid $[\text{Fe–S}]_{\text{eut}}$ gives strong evidence against sulphur polymerisation or the existence of any other large viscous unit. We, therefore, find nothing to support the reason proposed by LeBlanc and Secco (1996) for their observed high viscosity. Moreover, we find no significant variation of liquid structure as a function of temperature, and comparisons with our earlier work (Alfè and Gillan, 1998a) suggest that the structure also changes little with pressure and composition. Our calculations also fully confirm the validity of the Stokes–Einstein relation between viscosity and diffusion coefficients for liquid $[\text{Fe–S}]_{\text{eut}}$. A diffusivity of a few $\times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ implies a viscosity of a few mPa s and, therefore, a diffusivity of this order is incompatible with a much higher viscosity.

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