



Experimental verification of the Stokes–Einstein relation in liquid Fe–FeS at 5 GPa

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Experiments have been performed at 5 GPa on liquid Fe–FeS in order to determine Fe and S self-diffusivity as a function of temperature. The viscosity of the sample was then obtained using the Stokes–Einstein relation. The results are in excellent agreement with previous experiments where the viscosity of a material of the same composition under similar conditions was measured directly. These results support high, near-metallic, values of diffusivity and low viscosity in liquid Fe–S up to a few hundred K above the eutectic temperature, in contrast with some previous studies. Moreover, these results fully confirm the validity of the Stokes–Einstein relation between viscosity and diffusion coefficients for Fe_{0.61}S_{0.39}.

1. Introduction

Convection within the liquid portions of planetary cores is the source of their self-sustaining magnetic fields. Although viscosity is a fundamental parameter for geodynamo models, it is extremely difficult to constrain. Geophysical estimates of the viscosity of the Earth's outer core, for instance, span some 13 orders of magnitude [1, 2]. Within the Earth, chemical diffusivity is likely to be important, since chemical buoyancy from inner core crystallization will be larger and persist for longer than thermal buoyancy [3].

Iron–sulphur alloys are important potential planetary core materials. The sulphur content of chondrite meteorites, thought to represent primary undifferentiated planetary material, is in the range 2.0–5.8 at% ([4] and references therein). Because sulphur is highly siderophilic, it is expected to strongly partition into planetary cores, and has been suggested as the light element in the cores of Earth, Mars and Ganymede [5–7]. Some small planetary bodies, such as Ganymede, have a magnetic field indicative of a liquid metallic core, despite their small heat budgets. The exceptionally low iron–iron sulphide eutectic temperatures (1263 K at 5 GPa) make it an ideal candidate liquid core material for these satellites. Additionally, the low melting temperatures make liquid Fe–S alloys experimentally acces-

sible to relatively high pressures for physical property measurements [7–12].

The viscosity of liquid Fe–S alloys is currently the subject of some experimental debate. Laboratory measurements at relatively modest pressures to 5 GPa disagree by up to 4 orders of magnitude. Using a Stokes–rising sphere method, with electro-detection of the passage of insulating ceramic spheres past a reference position, Secco and coworkers [8, 9] found eutectic Fe–S compositions to have a high viscosity (10–10³ Pa s), with a high activation energy and a large activation volume. They attributed these high viscosities to the presence of large sulphur structural units. By contrast, Dobson *et al.* [12] used a Stokes–falling sphere method with synchrotron-based X-radiography to directly image the passage of dense, high absorption spheres in real time. They found that the viscosity of near-eutectic compositions and end-member Fe_xS was close to normal metallic values, with a systematic variation of activation energy and viscosity with sulphur content and a negligible pressure dependence. These results suggest that liquids in the Fe–FeS system contain dissociated species, or at the most small structural units.

The Stokes–Einstein relation has proven to be an effective link between viscosity and diffusivity in monatomic liquids:

$$\eta_i^* = \frac{k_B T}{D_i \lambda_i}, \quad (1)$$

where η_i^* is the viscosity predicted from species i , D_i and λ_i are the diffusivity and jump distance (taken to be the

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interatomic distance) of species i , T is absolute temperature and k_B is the Boltzmann constant. Dissociated liquid metals and liquid salts all closely obey the Stokes–Einstein relation [1], as do the monatomic ionic components of polymerized silicate melts [13]. Large structural units, however, such as liquid Se_4 and the polymerized components of liquid silicates do not obey the relationship. The Stokes–Einstein relation is therefore a strong test for polymerization in liquids. We present results here of iron and sulphur self-diffusion measurements in liquid Fe–S eutectic at 5 GPa. Using atomic bond-lengths derived from simulations results we relate the diffusivity to viscosity measurements via the Stokes–Einstein relation, and find these data to be entirely consistent with recent viscosity measurements [12, 14].

2. Experimental

2.1. Materials and methods

High pressure tracer diffusion experiments were performed in a Walker-type multi-anvil press at UCL using the technique described in [11]. Details of high pressure techniques are given elsewhere [15, 16]. Samples of $\text{Fe}_{0.61}\text{S}_{0.39}$ were prepared as follows. Powders of Fe and FeS were ground together under acetone in eutectic proportions. ^{34}S enriched FeS was prepared from a stoichiometric mixture of Fe and S by fusion at 2 GPa and 1050 °C. The recovered sample was found to be entirely pyrrhotite (Fe_7S_8) by powder X-ray diffraction. Thin (40 μm) discs of $\text{Fe}_{0.61}\text{S}_{0.39}$, enriched in ^{34}S and ^{57}Fe , were prepared and placed on the end of 2–3 mm long cylinders with natural isotopic abundances. The whole was then compacted in a pellet press under a 0.5 ton load to produce a solid cylinder of 0.8 mm diameter and 2 mm length, which was loaded into the capsule. Double encapsulation, with inner Al_2O_3 and outer Fe capsules, was used to chemically isolate the sample and, in particular, minimize oxygen contamination. The filled capsule was placed centrally in a horizontal cylindrical graphite furnace, but just above the furnace axis. This ensured that the sample experienced a gravitationally stable thermal gradient, inhibiting convection. Experiments were performed by compressing the sample to 5 GPa at room temperature. The sample was then heated at a rate of 300 K min^{-1} to the experimental temperature, upon which power was cut to the furnace, resulting in quench rates in excess of 500 K s^{-1} .

2.2. Analytical

Polished sections of recovered samples were analysed by electron microprobe for oxygen content and by secondary ion mass spectrometry (SIMS) for ^{57}Fe , ^{54}Fe , ^{32}S and ^{34}S . Electron probe standards consisted of pure Fe, FeS_2 pyrite and fayalite for Fe, S and O, respectively,

with an accelerating voltage of 15 kV. Quench textures were averaged by rastering the 1 μm beam over an area of 300 μm^2 . SIMS analyses were performed under the following conditions: a 20 mA O^- primary beam was used with secondary acceleration of 5 kV. Burns of 60 s were followed by 5 s collecting on each mass. Relative ion yield for the tracer ions was obtained from the ratios of ^{57}Fe to ^{54}Fe and of ^{34}S to ^{32}S . The mass resolving power in the low mass resolution mode was 2000 for ^{32}S , which was sufficient to resolve between ^{32}S and $^{16}\text{O}_2$ interferences using a 100 V offset on the secondary accelerating voltage.

3. Results

Figure 1 shows measured ^{57}Fe and ^{34}S diffusion profiles for one experiment and the profile fitted according to the tracer equation [17]

$$C/C_0 = \exp\left(-x^2/4Z\right), \quad (2)$$

where C is the concentration a distance x from x_0 , C_0 is the concentration at x_0 , and Z is the diffusivity D integrated over time t :

$$Z = \int_0^t D(t) dt. \quad (3)$$

The small positive errors for low x arise from the finite thickness of the ‘tracer’ source and are negligible for values of x more than 10 times the tracer thickness. This small deviation from true tracer behaviour has negligible effect on the calculated diffusivities. For longer durations, the profile reflects at the sample ends, which act as impermeable boundaries; this is treated in the normal way [11].

In experiments where heating is a negligible proportion of the duration, D is constant, $Z = Dt$ and equation (2) becomes the standard tracer equation. However, because diffusion in these experiments occurred during increasing temperature, the diffusivity varied with time. Samples quenched from different temperatures during constant heating rate experiments sample different values of Z , everything else being constant. Experimentally determined values of Z were integrated assuming an Arrhenius dependence of D on temperature:

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

where T is a linear function of t , to give values of D at each experimental temperature. The preexponential D_0 and apparent activation energy Q_D were treated as parameters for fitting, and errors were minimized by an iterative least-squares process. Measured Fe and S self-diffusion coefficients at 5 GPa and high temperature are presented in table 1.

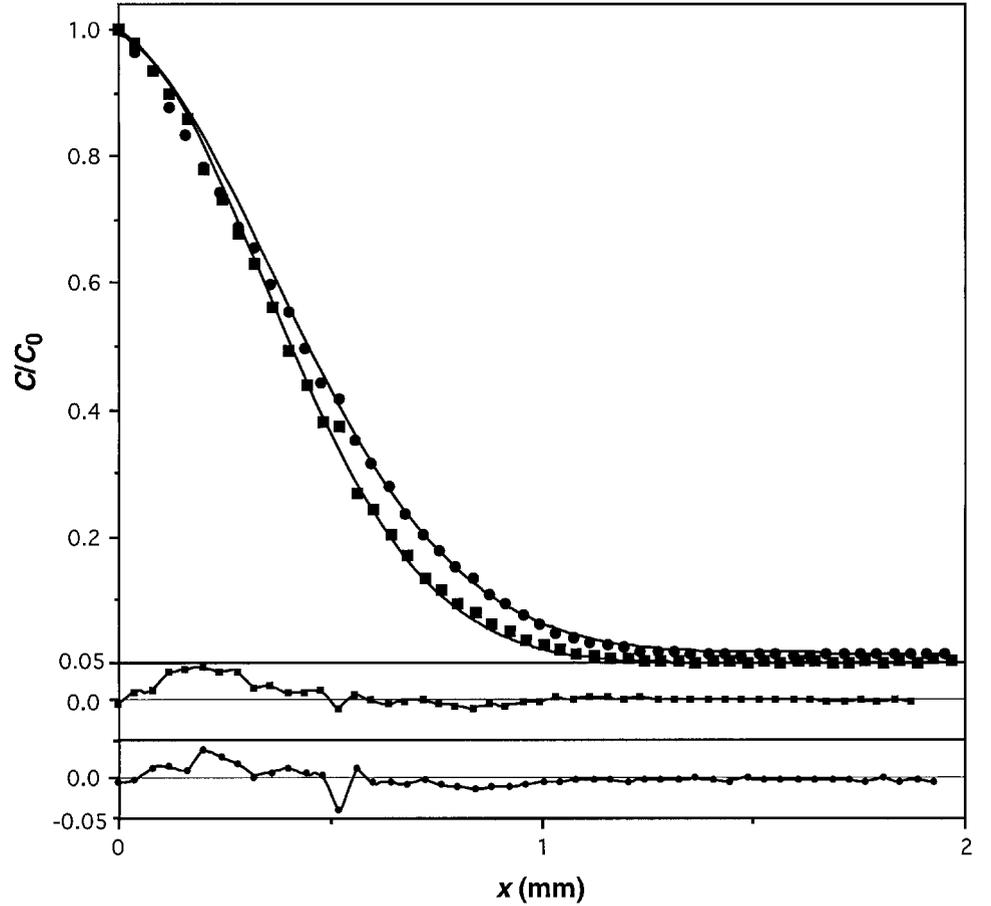


Figure 1. Concentration profiles of tracer isotopes ^{57}Fe (circles) and ^{34}S (squares) for one experiment on liquid $\text{Fe}_{0.61}\text{S}_{0.39}$ at 5 GPa. Lines are the fits to the data. Lower lines show the fitting errors.

Table 1. Measured Fe and S self-diffusivities and Arrhenius parameters for liquid $\text{Fe}_{0.61}\text{S}_{0.39}$.^a

T/K	$Z_{\text{Fe}}/\text{mm}^2$	$D_{\text{Fe}}/\text{cm}^2 \text{s}^{-1}$	Z_{S}/mm^2	$D_{\text{S}}/\text{cm}^2 \text{s}^{-1}$
1293	$0.95 \pm 0.04 \times 10^{-1}$	$1.05 \pm 0.1 \times 10^{-5}$	$0.77 \pm 0.03 \times 10^{-1}$	$0.80 \pm 0.1 \times 10^{-5}$
1423	$1.88 \pm 0.04 \times 10^{-1}$	$2.29 \pm 0.01 \times 10^{-5}$	$1.29 \pm 0.03 \times 10^{-1}$	$1.64 \pm 0.1 \times 10^{-5}$
1473	$2.91 \pm 0.04 \times 10^{-1}$	$2.97 \pm 0.01 \times 10^{-5}$	$2.17 \pm 0.08 \times 10^{-1}$	$2.09 \pm 0.05 \times 10^{-5}$
$Q_{\text{D}}/\text{kJmol}^{-1}$		91 ± 4		84 ± 10
$D_0/\text{cm}^2 \text{s}^{-1}$		$5.20 \pm 0.10 \times 10^{-2}$		$1.98 \pm 0.14 \times 10^{-2}$

^a Errors quoted are one standard error.

4. Stokes–Einstein treatment

Vočadlo *et al.* [18] performed *ab initio* simulations of Fe–FeS eutectic melt at 5 GPa and 1300 K and 1500 K. Their Fe–S partial radial distribution function (PRDF) first peak at 1500 K ($\sim 2.2 \text{ \AA}$) is consistent with the experimental value for Fe_xS at 5 GPa and 1873 K (2.35 \AA) [10]. Using the first peaks of the Fe–Fe PRDF and S–S PRDF from [18] for λ_{Fe} and λ_{S} , respectively, and diffusion values from table 1 in equation (1), two independent estimates of viscosity are obtained for the Fe and S species. The predicted viscosities are given in table 2 and compared with previously determined values for the same composition in figure 2. The predicted

viscosities from sulphur and iron diffusivities are indistinguishable and the data agree with measured viscosities within two standard errors.

5. Discussion

The accuracy of the Stokes–Einstein relation for liquid $\text{Fe}_{0.61}\text{S}_{0.39}$ suggests that this is a strongly dissociated liquid, consistent with previous structural studies [10] and *ab initio* simulation results [18]. Furthermore, the excellent agreement between η_{Fe}^* and η_{S}^* strongly implies that large sulphur structural units are not affecting melt properties; indeed the difference between

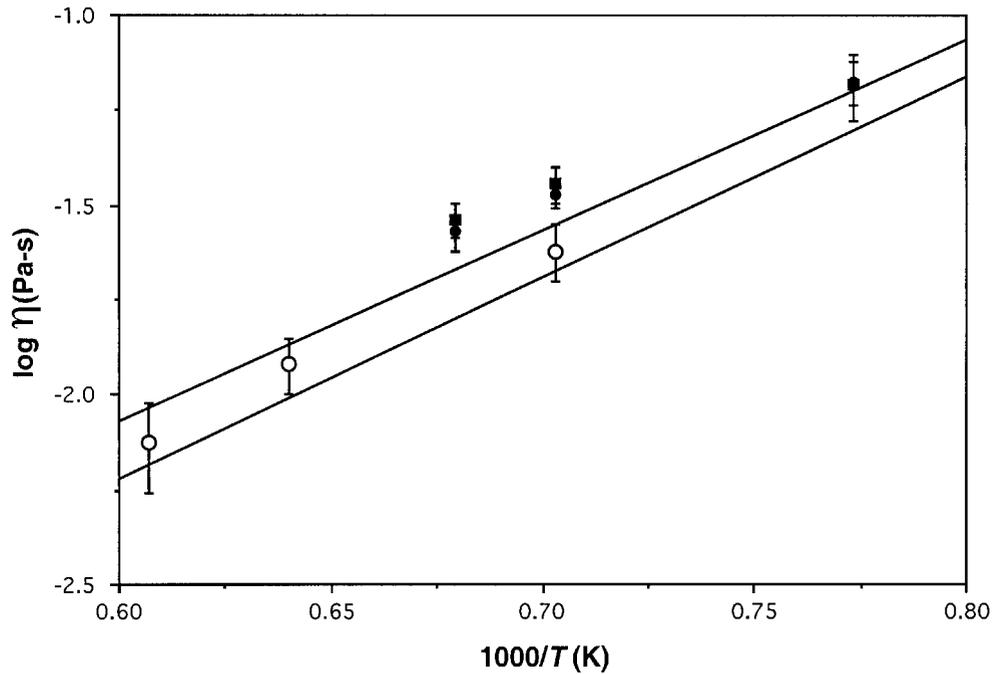


Figure 2. Predicted viscosity η_i^* for Fe and S self-diffusion (solid circles and squares), using simulated atomic sizes from Vočadlo *et al.* (2000), and measured viscosity (open circles) (Dobson *et al.* 2000). Errors are one standard error for η_i^* and upper and lower error bounds for measured viscosity; solid lines represent the viscosity range extrapolated from the measured values. The predicted and measured values are consistent at a 95% confidence level.

Table 2. Measured and predicted viscosity in liquid $\text{Fe}_{0.61}\text{S}_{0.39}$.^a

T/K	$\eta_{\text{Fe}}^*/\text{Pa s}$	$\eta_{\text{S}}^*/\text{Pa s}$	$\eta_{\text{meas}}/\text{Pa s}$
1293	0.067 ± 0.009	0.066 ± 0.013	
1423	0.034 ± 0.003	0.036 ± 0.004	0.024 ± 0.004
1473	0.027 ± 0.003	0.029 ± 0.003	
1563			0.012 ± 0.002
1647			0.0075 ± 0.002

^a η_{Fe}^* , η_{S}^* and η_{meas} are the predicted viscosities from Fe and S diffusivity, and the directly measured viscosity from [12], respectively.

D_{S} and D_{Fe} can be attributed entirely to the difference in atomic size between the two species.

Eyring's activated state theory of liquids [19] relates viscosity to diffusivity via an equation of Stokes–Einstein form. Additionally, it predicts that, along the melting path, viscosity should be independent of pressure. As noted in [1], such homologous behaviour would be highly useful for geophysicists since the melting temperature viscosity at ambient pressure would be equal to the viscosity at the solid inner-liquid outer core boundary. We have previously [12] tested the homologous behaviour of an $\text{Fe}_{0.83}\text{S}_{0.17}$ liquid and find this assumption to be consistent with low pressure experimental and simulation results, and simulation results at 330 GPa, the pressure of the outer–inner core boundary [20]. The present results imply that it would, in principle, be possible to estimate chemical diffusivity of liquid planetary cores from geophysical estimates of

viscosity and density. The large scatter in geophysically determined outer core viscosity suggests, however, that many of these measurements sample the eddy viscosity, which can be many times larger than the molecular viscosity and therefore are not appropriate for such a treatment.

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