Properties of liquid iron along the melting line up to Earth-core pressures

Yu D Fomin\textsuperscript{1}, V N Ryzhov\textsuperscript{1,2} and V V Brazhkin\textsuperscript{1,2}

\textsuperscript{1} Institute for High Pressure Physics, Russian Academy of Sciences, Troitsk 142190, Moscow, Russia
\textsuperscript{2} Moscow Institute of Physics and Technology, 141700 Moscow, Russia

E-mail: fomin314@gmail.com

Received 13 February 2013, in final form 8 April 2013
Published 12 June 2013
Online at stacks.iop.org/JPhysCM/25/285104

Abstract

We report a molecular dynamics study of the transport coefficients and the infinite frequency shear modulus of liquid iron at high temperatures and high pressures. We observe a simultaneous rise of both the shear viscosity and the diffusion coefficient along the melting line and estimate whether liquid iron can vitrify under Earth-core conditions. We show that in the conditions of the model studied in our work iron demonstrates a moderate increase of viscosity along the melting line. It is also demonstrated that at the limit of high temperatures and high pressures the liquid iron behaves similarly to the soft sphere system with exponent \( n \approx 4.6 \).

(Some figures may appear in colour only in the online journal)

1. Introduction

The behavior of iron at Earth-core pressure–temperature conditions has been a topic of hot debate for many decades. It is apparent that the behavior of iron is of great importance for an understanding of the phenomena occurring in the inner and outer core. However, it appears to be very difficult to find any unambiguous information about iron in such extreme conditions. The problem is clear: it is impossible to carry out direct experiments at such high temperatures. Therefore one has to use extrapolation of lower temperature results. This leads to great uncertainty in the principal data. Even the location of the melting line of iron at high pressures is not clear: the results from diamond anvil experiments give the melting temperature as approximately one half of that found in shock wave experiments (a possible explanation of this discrepancy was proposed in [1]).

The situation with the transport properties of iron at high pressure is even worse. A difference of \( 10^{14} \) between viscosities is obtained by the use of different methods [2]. Secco classified iron viscosity estimates in three groups [3]. Those from geodesic measurements and seismological investigations give an Earth-core viscosity of up to \( 10^{11} \) Pa s. The viscosities obtained from the Earth's magnetic field are of the order of \( 2.7 \times 10^7 \) Pa s. Finally, theoretical predictions give iron viscosities from \( 2.5 \times 10^{-3} \) up to 50 Pa s [3]. One can see from these data that the disparity between the estimates from different methods reaches as much as \( 10^{14} \), which is obviously not acceptable.

One of the possible sources of errors in high pressure iron viscosity estimation can originate from the extrapolation of low pressure data far beyond the range of pressures where we have experimental data. In this respect it is desirable to find a system which we can study with reasonable precision in a wide range of pressures and temperatures. The most obvious way to implement this idea is to employ some model of iron in molecular dynamics (MD).

Several authors have carried out MD simulations of iron at Earth-core conditions with different empirical potentials or by means of the density functional theory method. In [4, 5] the authors use the same parametrization of the embedded atom potential (EAM) for iron as that proposed by Sutton and Chen [6]. The authors of [4] and [5] have chosen different density–temperature points, which makes it more difficult to compare their results. However, the viscosity data from both articles look to be consistent with each other. The viscosities in Earth-core conditions obtained in both cited papers are of the order of magnitude of 0.01 Pa s. In [5] the viscosities are also compared to the \textit{ab initio} calculations of Alfe et al [7] (table I of [7]). One can see from this comparison that the data from classical MD calculations and from \textit{ab initio} MD are close to each other and that there is no systematic deviation of EAM data from the \textit{ab initio} ones.

A lot of information about iron at high pressure was recently obtained by \textit{ab initio} simulations. It includes melting...
This we simulate a system of 3456 iron atoms in the (P, T) phase diagram with dT = 0.0002 ps. The diffusion coefficient increases just 1%. The viscosity rise is especially dramatic: at the highest temperatures studied (8000 K) it is 2%. The viscosity and the diffusion coefficient increase with increasing pressure along the melting line. However, even if these model liquids can be used as rough models to analyze the most general trends in liquids, the simplicity of these models can result in large qualitative errors at high pressures and high temperatures compared to the experimental liquids. In this respect the present work is aimed at understanding the high pressure–high temperature behavior of an example of real liquid. We choose the particular case of liquid iron due to its importance in geophysical investigations.

Figure 1(a) shows the melting line of iron [11] and Figure 1(b) demonstrates the liquid branch of the melting line in the density–temperature plane. This line was obtained by performing NPT simulations at the PT data points from [11]. As expected the density of the liquid quickly rises along the melting curve.

Figures 2(a) and (b) represent the diffusion coefficient and the shear viscosity of liquid iron along the melting line. As in simple models, both the diffusion coefficient and the viscosity rapidly increase with increasing temperature. The viscosity rise is especially dramatic: at the highest temperature studied (8000 K) it is 2.5 times higher than at the lowest temperature (2500 K). At the same time the diffusion coefficient increases just 1.5 times. However, the liquid becomes more viscous and more diffusive at the same time.

## 3. Results and discussion

As mentioned in the introduction we are interested in the behavior of the transport coefficients of liquid iron along the melting line. In our previous publications we analyzed the behavior of simple liquids along the melting curve [14, 15]. Two simple models were studied: soft spheres (Φ(r) = ε(σ/r)n with n = 12) and Lennard-Jones (Φ(r) = ε · ((σ/r)n − (σ/r)n)2)) liquids. It was shown that in these models both the shear viscosity and the diffusion coefficient increase with increasing pressure along the melting line. However, even if these model liquids can be used as rough models to analyze the most general trends in liquids, the simplicity of these models can result in large qualitative errors at high pressures and high temperatures compared to the experimental liquids. In this respect the present work is aimed at understanding the high temperature–high pressure behavior of an example of real liquid. We choose the particular case of liquid iron due to its importance in geophysical investigations.

Table 1. Fitting coefficients from equations (2) to (5).

| P, GPa | a | b |
|--------|---|---|
| 1.329 × 10⁻⁴ | 1.5657 | 13.110 |
| G_{\text{ad}}, GPa | 7.045 × 10⁻⁶ | 0.1957 |
| D/10⁸, m² s⁻¹ | 0.0576 | 0.2811 |
| η, mPa s | 2.8526 × 10⁻³ | 0.9378 |

The off-diagonal pressure component. The diffusion coefficient is computed from the slope of the mean square displacement of the particles via the Einstein relation.

One of the central quantities of our analysis is the shear viscosity of liquid iron along the melting line. In order to compute the viscosity we employ the reverse non-equilibrium MD method also known as the Müller-Plathe method [12]. In this method an artificial momentum flux is imposed in the system which results in a linear velocity profile of particles. The viscosity coefficient can be calculated from the slope of the velocity profile and the momentum transferred to the system [12]. For the viscosity calculation the system was simulated for 2 × 10⁶ time steps with dt = 0.0002 ps. The momentum transfer was undertaken every 10 steps. The temperature was held by coupling to a Berendsen thermostat with time constant τ_b = 10 · dt. The first half of the simulation was used for equilibration while during the second half the velocity distribution was written in the file every 100 steps. All of these distributions written to the file were used to estimate the viscosity.

All simulations reported in this work were done in the LAMMPS simulation package [13].
Figure 1. (a) The iron melting line as obtained in [11] in $P-T$ coordinates. (b) The liquid branch of the melting line. Squares—MD data, continuous line—soft sphere-like approximation (see the text).

The question of a simultaneous increase in diffusion coefficient and shear viscosity was raised in our previous publication [15]. This question is interesting when considered in conjunction with glass transition. The most common criterion of glass transition states that the liquid experiences glass transition when its viscosity reaches a very high value. A typical convention is that the viscosity of glass transition is $10^{13}$ Poise. However, it is implicitly assumed that the liquid loses its diffusivity as viscosity grows. However, in cases of high temperatures and high pressures both viscosity and diffusivity increase, so one comes to a contradiction to the usual and common view on glass transition.

In order to solve this contradiction we proposed in [15] to use one more criterion of glass transition: the liquid undergoes the glass transition if the relaxation time becomes as long as the typical time of experiments. Different publications propose to use 100 s or 1000 s as the glass transition relaxation time. Following this definition one needs to see the behavior of the relaxation time in order to understand if the liquid vitrifies following the melting line up to extremely high temperature–high pressure limits.

The relaxation time can be computed via the Maxwell relation [16]
\[
\tau = \frac{\eta}{G_{\text{inf}}},
\]
where $\eta$ is the viscosity of the liquid and $G_{\text{inf}}$ the infinite frequency shear modulus. In the majority of experimental situations it is supposed that the viscosity changes much faster then $G_{\text{inf}}$ and the relaxation time is mainly determined by the viscosity behavior. In this case the viscosity criterion of glass...
transition becomes equivalent to the relaxation time criterion. However, as was shown in [15] the infinite frequency shear modulus of liquid can dramatically grow along the melting line.

Figure 3(a) shows the infinite frequency shear modulus of iron along the melting line. One can see that $G_{\text{inf}}$ drastically increases with increasing temperature. The ratio of $G_{\text{inf}}$ at the highest and the lowest temperatures is approximately 10, while for the viscosity it is 2.5. As a result in spite of the rise of viscosity the relaxation time still decreases (figure 3(b)).

From the results presented above one can see that the qualitative behavior of liquid iron at high temperatures–high pressures is equivalent to the behavior of simple liquids such as soft spheres and Lennard-Jones ones. The soft sphere model is especially simple since it demonstrates a set of scaling properties along the melting line [17–20]. The scaling relations for all quantities presented here are given in [14, 15]. Here we repeat them for the sake of completeness,

$$P \sim T^{1+3/n},$$  \hspace{1cm} (2)

$$D \sim T^{1/2-1/n},$$ \hspace{1cm} (3)

$$\eta \sim T^{1/2+2/n},$$ \hspace{1cm} (4)

$$G_{\text{inf}} \sim T^{1+3/n}.$$ \hspace{1cm} (5)

In order to see the relations between the simplest model studied and the current liquid iron system we fit all the quantities above ($D$, $\eta$, $P$ and $G_{\text{inf}}$) to the relations of the form $X = a \cdot T^\alpha + b$, where $X$ is the quantity of interest and $\alpha$ is the correspondent exponent from equations (2)–(5). In order to ensure all of the exponents are consistent with the case of soft spheres all quantities are fitted simultaneously. The results of such fitting are given in figures 1–3 and the fitting coefficients are given in table 1. The exponent coefficient $n$ is found to be equal to $n = 4.568$. One can see that except the melting pressure all of the quantities are well represented by the soft sphere-like scaling relations. In the case of pressure the deviation does not exceed 12% in the whole range of temperatures considered in this work. However, the slopes $dP/dT$ from the scaling formula and from the MD data are very different which means that the melting line itself is poorly represented by the scaling law. At the same time the transport coefficients and elastic properties ($G_{\text{inf}}$) are well described by the soft sphere-like model.

It is well known that the structure of liquid metals can be well approximated by a simple hard sphere model [21]. In [22] experimental measurements of liquid iron structure factors were reported and comparisons of experimental curves with the hard sphere model were performed. As it follows from figure 3 of [22] the structure factors of iron can be sufficiently well represented by hard spheres, which proves that the main contribution into the liquid structure comes from the repulsive part of the interaction. It is well known that the structure of liquid is closely related to its transport properties. Therefore one can expect that simple purely repulsive models of liquid can reproduce the diffusion and shear viscosity of iron sufficiently well.

At the same time melting line is strongly affected by the presence of attractive terms in the interparticle interaction potential [23] which means that a purely repulsive model such as soft spheres should fail to reproduce the melting curve of a system with both repulsive and attractive interactions.

In [25] it was proposed that the viscosity of a liquid is constant along the melting line (Poirier statement). Later on this statement was checked for liquid iron in [24]. The authors of this paper measured the viscosity of iron at the temperature $T = 2050$ K and compared it to the magnitude of viscosity at the melting temperature at normal pressure. They found that the viscosities at these two temperatures are very close and concluded that the statement of [25] is correct. From our results we see that this is just partially true. The viscosity change along the melting line is not fast: it increases 2.5 times on a 3.2-fold temperature change. However, we observe the systematic rise of viscosity along
the melting line, so one cannot claim that it is constant: if one measures the viscosities along the melting line for large enough temperature intervals one will clearly see the rise of viscosity. However, the temperatures studied in our work range from 2500 up to 8000 K, which exceeds the range of temperatures reported in most experimental works. This means that in the range of temperatures explored in experiments the viscosity change can be small enough to use the Poirier statement with sufficient accuracy.

4. Conclusions

This article represents a molecular dynamics study of the transport coefficients and glass transition of liquid iron at the limit of high temperatures–high pressures along the melting line. We show that both the shear viscosity and the diffusion coefficient increase along the melting line. However, in spite of increasing viscosity the relaxation time rapidly decreases with increasing temperature. This means that liquid iron becomes harder to vitrify at high temperatures and high pressures.

It is worth noting that the magnitudes of viscosities we obtain are consistent with other simulations of liquid iron at high temperatures and high pressures [4, 5, 7]. However, it appears that all simulations of iron in such extreme conditions significantly underestimate the shear viscosity.

Surprisingly, the behavior of liquid iron at Earth-core like temperatures and pressures can be sufficiently well qualitatively described by the soft sphere model which is one of the simplest models of liquids. By fitting the MD data to the soft sphere scaling relation we find that liquid iron is qualitatively similar to the soft spheres with the exponent $n = 4.568$.

The most important difference between the soft spheres and liquid iron represented by the EAM potential [11] is in the collective nature of the later. It is well known that at the limit of high pressures the particles come very close to each other and the system is dominated by the repulsive excluded volume effects, and the collective effects can become negligible. Our simulations confirm this speculation and propose that the exact results for soft spheres reported in our previous work [15] can be extrapolated to the high temperature–high pressure limit of liquids in general.

Acknowledgments

YF is grateful to A B Belonoshko (Theoretical Physics KTH, Sweden) for sharing his results for the iron melting line and V V Stegailov (JIHT RAS) for his help with simulations. YF also thanks the Joint Supercomputing Center of the Russian Academy of Sciences and the Russian Scientific Center Kurchatov Institute for computational facilities. The work was supported in part by the Russian Foundation for Basic Research (Grants Nos 13-02-00579, 13-02-00913, 11-02-00341-a and 11-02-00303), the Ministry of Education and Science of the Russian Federation, projects 8370, 8512 and a Russian President grant for Young Candidates MK-2099.2013.2.

References

[1] Starikov S V and Stegailov V V 2009 Phys. Rev. B 80 220104
[2] Smylie D E, Brazhkin V V and Palmer A 2009 Usp. Fiz. Nauk 179 91
[3] Secco R A 1995 Viscosity of the outer core Mineral Physics and Crystallography: A Handbook of Physical Constants (AGU Reference Shelf vol 2) ed T J Ahrens (Washington, DC: American Geophysical Union) p 218
[4] Zhang Y, Guo G and Nie G 2000 Phys. Chem. Min. 27 164
[5] Desgranges C and Delhommelle J 2007 Phys. Rev. B 76 172102
[6] Sutton A P and Chen S 1990 Phil. Mag. Lett. 61 139
[7] Alfe D, Kresse G and Gillan M J 2000 Phys. Rev. B 61 132
[8] Alfe D, Price G D and Gillan M J 2002 Phys. Rev. B 65 165118
[9] Alfe D 2010 Iron at Earth’s Core Conditions from First Principles Calculations (Book Series: Reviews in Minearology and Geochemistry) vol 107 pp 337–54
[10] Pozzo M, Davies Ch, Gubbins D and Alfe D 2013 Phys. Rev. B 87 014110
[11] Belonoshko A B, Ahuja R and Johansson B 2000 Phys. Rev. Lett. 84 3638
[12] Muller-Plathe F 1999 Phys. Rev. E 59 4894
[13] Plimpton S 1995 Fast parallel algorithms for short-range molecular dynamics J. Comput. Phys. 117 1 (http://lammps.sandia.gov/)
[14] Fomin Yu D, Brazhkin V V and Ryzhov V N 2012 J. Phys. Condens. Matter 25 (2013) 285104 Yu D Fomin et al