Isoviscosity lines and the liquid-glass transition in simple liquids

Yu. D. Fomin, V. V. Brazhkin, and V. N. Ryzhov

Institute for High Pressure Physics, Russian Academy of Sciences, Troitsk 142190, Moscow Region, Russia

This article presents the study of the generic behavior of viscosity of liquids based on some simple theoretical models, the soft-spheres and Lennard-Jones systems. The use of these simple models allows us to investigate in detail the viscosity behavior in a wide range of temperatures and pressures including the high-temperature–high-pressure limits. Based on the simulation results, we discuss the shape of isoviscosity lines and analyze the glass transition at high temperatures and high pressures. Despite the fact that the viscosity drastically increases in the limit of high temperatures and high pressures along the melting line, the relaxation time rapidly decreases in this region, and the system becomes further from the glass transition.

I. INTRODUCTION

Knowledge of the transport coefficients is extremely important for characterizing the properties of a liquid. They allow one to characterize the speed of the dynamics of the liquid. Because of this, transport coefficients are intensively studied experimentally, theoretically, and in simulations. The most important transport property for the experimental study is viscosity. Viscosity can be easily measured with a number of techniques. Nevertheless, many questions concerning the behavior of viscosity as a function of pressure and temperature still remain unsolved. Some of them are considered in the present article.

It is well known that the viscosity of most liquids grows exponentially with increasing pressure at constant temperature and demonstrates very fast growth in the vicinity of the glass transition line. Such behavior is typical for supercooled liquids, but the behavior of viscosity close to the melting line is not clear.

As was discussed in Ref. [1], there are two empirical approaches to the description of the viscosity behavior of simple liquids under simultaneous changes in temperature and pressure. In one approach, Bridgman [2] suggests that the viscosity of liquid is nearly constant along isochores. The other, currently more widespread approach was formulated by Poirier [3] based on the assumption that the viscosity of melts is invariable along the melting curve. The analysis of experimental data shows that both of the approaches are incorrect: The constant viscosity lines for rare gas liquids, as well as for liquid metals, have a slope that is intermediate between the slopes of the melting line and the isochore (Ref. [4], Fig. 5). As a consequence, the viscosity of simple melts along the melting curve increases, and this increase can be extrapolated to megabar pressures [4]. However, this extrapolation is difficult because of the small viscosity variation in the covered range [5]. For example, the viscosity of the Fe melt grows along the melting curve several times with increase in pressure of 10–15 GPa [5,6]. However, the obtained data do not permit any conclusions with regard to the character of this growth; various analytic models that equally describe the studied baric dependencies give different extrapolation results. As a consequence, different equations employed for the extrapolation of the Fe melt viscosity to pressures of 1.4–3.1 Mbar, corresponding to the conditions

existing in the Earth's outer core, provide data that vary within 10–20 orders of magnitude (Ref. [5], Fig. 6). The same is valid for other simple melts such as liquid Ar.

Thus, it is at present impossible to infer how high the viscosity can grow along the melting curve for given melts with pressure increase to about 100–1000 GPa. If the viscosity growth is minor, liquid metals and rare gas liquids will remain very poor glass formers at megabar pressures. On the other hand, the viscosity growth along the melting curve amounts to several orders of magnitude, so the question arises of whether liquid metals and rare gas liquids become viscous glass-forming systems under increasing pressure. In this case, the glass transition of given melts in the megabar range should be similar to the jamming of soft spheres.

The main purpose of this paper is to carry out a computer simulation study of the behavior of the transport coefficients of some simple model systems in a wide range of temperatures and pressures. Although the systems used in this work (soft-spheres and Lennard-Jones systems) cannot be used to describe liquid metals, these system can give some hints about the high-pressure–high-temperature behavior of liquids.

Note that most of previous studies of the transport coefficients of liquids were, for the most part, devoted to the low-density–low-temperature region, while high-density–high-temperature properties were beyond their consideration. Only few works on the high-density transport properties are available (see, for example, Ref. [7]). In this sense the present work aims to fill this gap.

II. SYSTEMS AND METHODS

Two model systems are studied in this work: the soft-spheres system and the Lennard-Jones (LJ) one. The soft-spheres system is a system of particles interacting via the inverse power potential:

$$\Phi(r) = \varepsilon \left(\frac{\sigma}{r}\right)^n. \qquad (1)$$

In the present work, the softness parameter n was set equal to 12. A detailed description of the soft-spheres simulation was given in our previous publication [8].

Lennard-Jones is the most common system for liquid studies. It is characterized by the potential

$$\Phi(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6], \qquad (2)$$

where ε and σ are the energy and length scales, respectively. In the present article all quantities are expressed in reduced units ($\varepsilon = 1$ and $\sigma = 1$).

One of the focuses of this paper is the behavior of transport coefficients along the melting line. The melting line of soft spheres with $n = 12$ was intensively studied before by a number of authors (see, for example, Ref. [9] and references therein). The principal fact originating from the homogeneity of the soft-spheres potential is that the phase diagram is completely defined by a single parameter. The liquid branch of the melting line corresponds to the condition $\gamma_{melt} = \rho\sigma^3(\frac{\varepsilon}{k_B T})^{3/n} = 1.15$ (for $n = 12$) [10]. Using this relation, one can find the freezing density at arbitrary high temperatures.

The important consequence of this γ invariance of soft spheres is that one can study a system with some ε and σ and then convert the results into the ones for a system with other ε and σ parameters.

In the present study, the energy scale for soft spheres is ε, while for the LJ system it is 4ε. Although this is the usual simulation of these systems, the results cannot be compared directly. For this reason, in some cases [Figs. 4(a) and 4(b)] we plot the results for soft spheres as a function of $4T$, which corresponds to the system with the energy scale 4ε. The melting line of LJ fluid was computed up to very high temperatures in Ref. [11].

Both thermodynamic and kinetic properties of LJ fluid in a vast range of densities and pressures were reported in the literature. As far as we know, the most extensive study is given in Ref. [12]. More then a hundred state points ranging from $T = 0.5$ up to $T = 6.0$ in temperature and from $\rho = 0.01$ up to the density of freezing at the current temperature were reported. In the present study, we use the data from this reference for the low-temperature regime.

The high-temperature data for LJ fluids are not as well reported in previous studies. This induced us to carry out our own simulations of the LJ system for the temperatures from $T = 6.0$ up to $T_{max} = 100$. In our simulations, we use the system of $N = 4000$ particles in a cubic box. The usual cutoff of 2.5σ is applied. The equations of motion are integrated by using the velocity Verlet algorithm. The time step is $dt = 0.001$. The system is equilibrated for 5.0×10^5 steps. After that the averages are computed in the next period of 3.0×10^6 time steps. During the equilibration the temperature is constant because of the velocity rescaling, while in the production run the microcanonical NVE ensemble is used.

In our simulations, we measure the equation of state, radial distribution function, diffusion coefficient, and shear viscosity. The diffusion coefficient is computed from the mean square displacement of particles and the shear viscosity by integrating the stress autocorrelation function (Green-Kubo formula).

III. RESULTS AND DISCUSSION

A. Isoviscosity lines

In our previous publication we discussed the high-pressure–high-temperature behavior of the soft-spheres system [8]. Basing on our extensive simulations, we constructed some fitting functions for the diffusion coefficient and shear viscosity of soft spheres with $n = 12$. It was shown that the combinations

$D\rho/T^{2/3}$ and $\eta/T^{2/3}$ are universal functions of the soft-spheres parameter $\gamma = \rho\sigma^3(\frac{\varepsilon}{k_B T})^{3/n}$. As is mentioned above, the γ parameter of soft spheres is constant along the melting line. It is obvious from this that the viscosity of the soft spheres cannot be constant along the melting line. Instead, it will increase as $T^{(\frac{1}{2}+\frac{2}{n})}$ (i.e., $T^{2/3}$ for the case $n = 12$).

The isochoric behavior of viscosity of soft spheres was widely discussed in our previous publication [8]. It was shown that the viscosity is not constant along isochors. Moreover, the shear viscosity decreases with increasing temperature in the vicinity of the melting line but then passes through a minimum and starts to increase again. This effect is induced by the crossover from the potentially dominated regime to kinetically dominated one [8,13,14]. Recently [13,14], it was shown that the existence of the minima on the temperature dependence of the viscosity is related to the crossover of the dynamic line (Frenkel line), which separates the rigid and nonrigid states of a liquid.

One can clearly see from this consideration that both of the approaches to the constant viscosity lines that we described in the introduction fail even in the case of simple model liquids. Isoviscosity lines definitely should have a more complex shape. In our previous work [8], we proposed some fitting functions for the diffusion coefficient, shear viscosity, and equation of states of soft spheres with $n = 12$. Basing on these approximations, one can easily compute the lines of constant viscosity.

Figures 1(a) and 1(b) show the isoviscosity lines of soft spheres in the P-T and ρ-T planes. In the case of the P-T coordinates, we also plot isochors for comparison (in ρ-T coordinates isochors are just vertical lines). The melting lines are shown in both plots. The isoviscosity demonstrates the positive slope close to the melting line; however, at higher temperatures, it inclines to the left and its slope becomes negative. It is worth noticing that the slopes of the isoviscosity curves close to the melting line lie between the melting line and the isochores, which qualitatively corresponds to the analysis of experimental results reported in Ref. [4].

The same analysis was done for a LJ liquid. Figure 2 shows the viscosity of LJ fluid along the melting line. One can clearly see that the viscosity strongly increases with increasing temperature, which again violates the Poirier proposal [3].

We also calculate the constant viscosity lines of a LJ fluid using the extensive set of data points from Ref. [12] and our own simulations. Based on these data, we construct the lines corresponding to different viscosity values by the linear interpolation.

Figures 3(a) and 3(b) show the isoviscosity lines for the LJ liquid in the P-T and ρ-T planes. One can see that the qualitative behavior of the isoviscosity lines of the LJ system is analogous to the soft-spheres case. Close to the melting line, the isoviscosity lines also have positive slope, which changes to the negative one with increasing temperature. This kind of behavior is related to the minima on the isobaric or isochoric temperature dependences of viscosity, which are attributed to the crossover of the dynamic line (Frenkel line) separating the rigid and nonrigid states of a liquid [13,14].

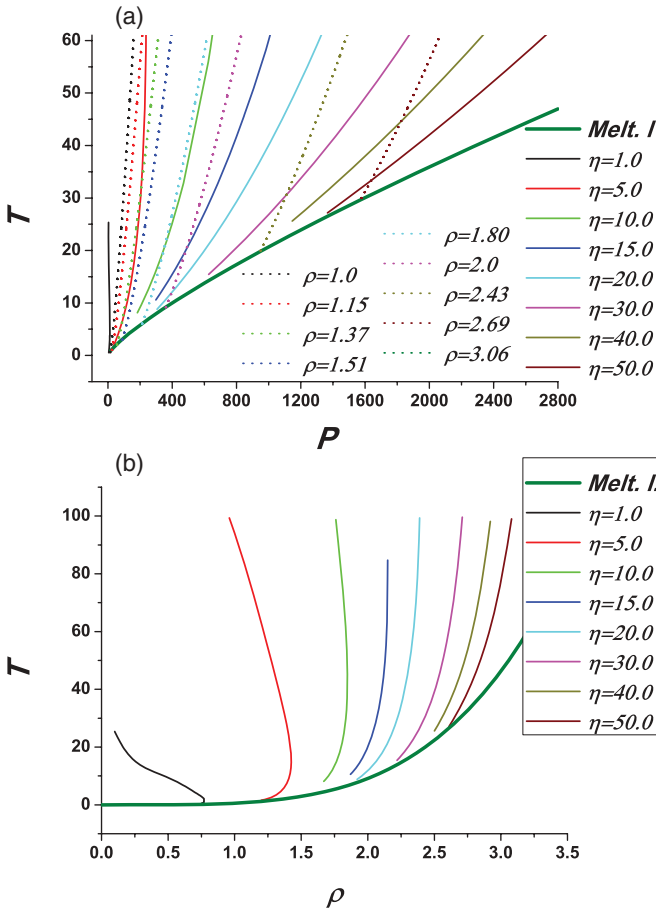One can conclude from the two examples given above that both of the approaches to the isoviscosity lines mentioned

FIG. 1. (Color online) Isoviscosity lines of soft spheres in (a) P-T plane (continuous lines correspond to isoviscosities (from left to right: viscosity=1.0, 5.0, 10.0,15.0, 20.0, 30.0, 40.0, 50.0); dotted lines correspond to densities from 1.0 to 3.06 (from left to right)) and (b) ρ-T plane (continuous lines correspond to isoviscosities (from left to right: viscosity=1.0, 5.0, 10.0,15.0, 20.0, 30.0, 40.0, 50.0)).
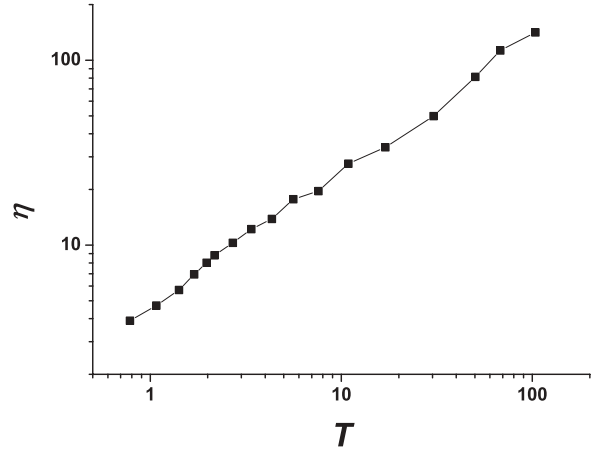

FIG. 2. Viscosity of LJ fluid along the melting line.

viscosity of the liquid reaches 10^{13} P, while in simulations the glass transition temperature is defined as the temperature at which diffusion becomes vanishingly small. One can clearly see that these two criteria contradict each other in the case of the high-temperature–high-pressure limit along the melting line. The liquid is extremely viscous and extremely diffusive
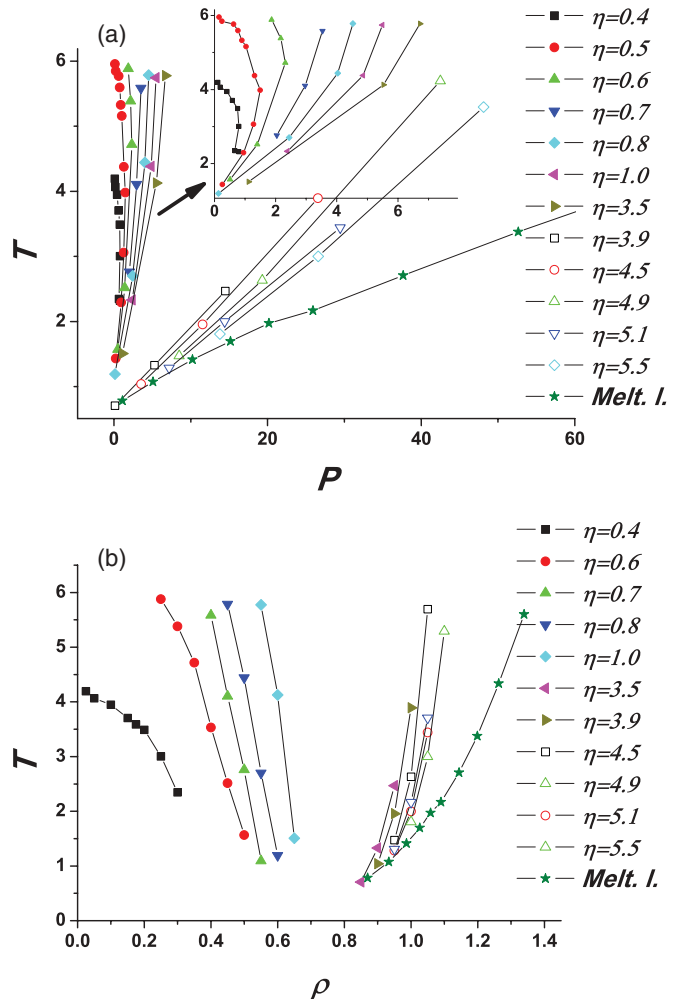
in the introduction fail even for simple liquids. Obviously, they should fail for the experimental systems too. The question concerning constant viscosity lines in both theoretical models and experimental systems undoubtedly requires further investigations and will be addressed in future papers.

It should be also mentioned that the Stokes-Einstein relationship is obeyed along the melting line for the soft spheres, if the Barker diameter is used as a characteristic length scale [15].

B. Glass transition at high temperatures and high pressures

As we saw in the previous subsection, the shear viscosity increases rapidly along the melting line. In the case of the classical simple liquid, the melting curve can be extrapolated to infinitely high temperatures and therefore the viscosity also becomes infinitely high. At the same time the diffusivity of the system also increases along the melting line [8]. Usually it is implicitly assumed that the viscosity increase corresponds to the diffusivity decay. One of the consequences of this assumption is two different criteria of the glass transition used in experimental and simulation works: The experimental criterion says that the glass transition takes place when the

FIG. 3. (Color online) Isoviscosity of the LJ liquid in (a) P-T plane and (b) ρ-T plane. The inset enlarges the low-pressure region.

at the same time. Taking this into account, one can raise the question as to whether the glass transition is approached or becomes more remote, if we move along the melting line.

In order to clarify the question about the glass transition, we recall one more common definition of glass transition point: This is the point where the relaxation time of the liquid becomes as large as 10^3 s. Several elastic models of structural relaxation have been developed (see, for example, Ref. [16]). The main prediction of the elastic models is that the viscosity η and the structural relaxation are activated with energy cost, due to the cage breaking, proportional to an elastic modulus that is explicitly identified with the infinite-frequency shear modulus G_{inf} [16]. The relaxation time is related to the viscosity via the well-known Maxwell relation [17]:

$$\tau = \eta/G_{\mathrm{inf}}, \tag{3}$$

where

$$G_{\mathrm{inf}} = \rho k_B T + \frac{2\pi\rho^2}{15} \int_0^\infty dr\, g(r) \frac{d}{dr}\left(r^4 \frac{d\Phi}{dr}\right) \tag{4}$$

is the infinite-frequency shear modulus [18–20]. Equation (3) may be considered as a microscopic criterion of a glass transition.

Recently it has been reported in the literature that for the correct definition of the relaxation time one has to use not G_{inf} but a finite frequency (or "relaxed") shear modulus for the liquid under investigation [21]. In this paper the evidence is gained that the finite frequency modulus, but not G_{inf}, exhibits strong universal correlations with τ. The use of the infinite frequency shear modulus can overestimate the relaxation time. However, G_{inf} allows us to obtain the correct qualitative behavior of the relaxation time (see, for example, Ref. [19]). Taking into account that our main purpose is to obtain a qualitative explanation of the controversy and G_{inf} can be easily computed via Eq. (3), we use G_{inf} in the present study.

In most experimental situations, G_{inf} changes much more slowly than the viscosity. This means that the relaxation time is determined mostly by the viscosity, and the viscosity and relaxation time criteria become equivalent.

In the case of the soft-spheres system, the behavior of the relaxation time along the melting line can be analyzed from the scaling relations. As shown in our previous publication [8], the shear viscosity along the melting line changes as $\eta \sim T^{(\frac{1}{2}+\frac{2}{n})}$. One can also show that the infinite frequency shear modulus scales as pressure $G_{\mathrm{inf}} \sim T^{(1+\frac{3}{n})}$. Combining these scaling formulas we obtain $\tau \sim T^{(-\frac{1}{2}-\frac{1}{n})}$. It is immediately follows from this relation that even if the viscosity of soft spheres along the melting line rapidly increases, the relaxation time will quickly drop.

Figures 4(a) and 4(b) show the infinite frequency shear modulus G_{inf} and relaxation time τ. Figure 4(a) shows the behavior of G_{inf} of soft spheres and along the melting line. One can see that G_{inf} increases extremely rapidly with increasing temperature. Furthermore, the rate of G_{inf} increase is much higher then the rate of the viscosity growth. This leads to a rapid decrease of the relaxation time of soft spheres along the melting line. As a result, one can conclude that even if the viscosity of the system becomes huge, the system will move further from the glass transition along the melting line.
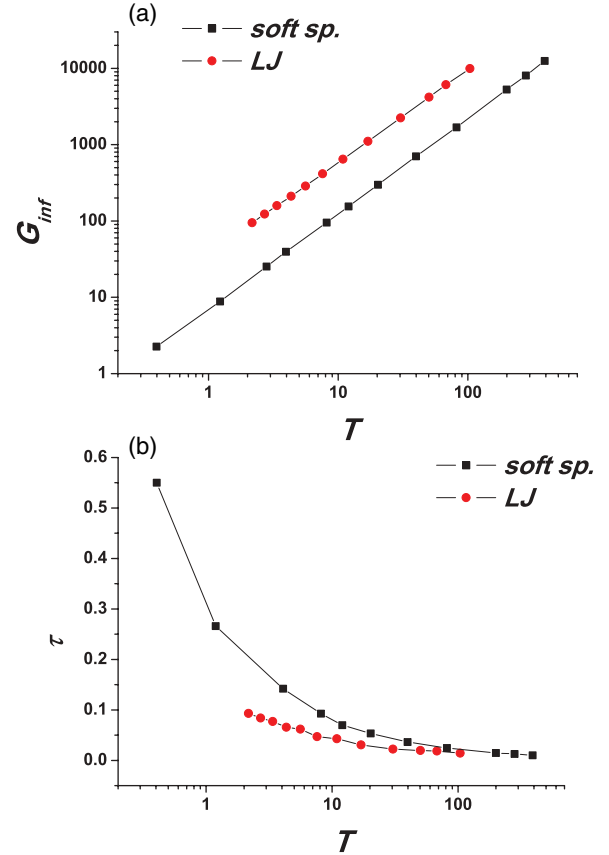

FIG. 4. (Color online) (a) Infinite frequency shear modulus of soft spheres G_{inf} along the melting line. (b) Relaxation time of soft spheres along the melting line. The points for soft spheres are scaled for the system with energy scale 4ε for easier comparison with LJ ones.

The same behavior is observed for the LJ liquid [Figs. 4(a) and 4(b), circles]: Although the viscosity of the LJ liquid greatly increases along the melting line (Fig. 2), the infinite frequency shear modulus increases much more quickly. As a result, the relaxation time rapidly decays along the melting line, which means that the system deviates further from the glasslike behavior. Examination of almost all isotropic potentials found in the literature (see, for example, Refs. [22,23] and references therein) shows that they are approximately positive homogeneous potentials at higher pressures and temperatures, with the degree of homogeneity being controlled by the repulsive part of the potential. Figure 4 shows that after the appropriate scaling of parameters the relaxation time for the soft-spheres and LJ systems converge at high temperatures.

As mentioned above, several criteria of glass transitions of liquids are common in the literature. The above consideration allows us to conclude that the microscopic relaxation time criterion is the most general as it is applicable in all cases, while the viscosity and diffusion coefficient criteria seem to fail in the high-temperature–high-pressure limit along the melting line.

IV. CONCLUSIONS

In conclusion, we studied the viscosity behavior of two model systems, soft spheres and LJ fluids, in a

wide range of temperatures and pressures, particularly the shape of isoviscosity lines and the glass transition in the high-temperature–high-pressure limit. We showed that the isoviscosity lines have quite complex shapes and cannot be described on the basis of the simple approaches known from the literature [2,3]. At the same time, our consideration is in qualitative agrement with experimental results discussed in Ref. [4].

We discuss the glass transition of liquids in the high-temperature–high-pressure limit and the relation between different criteria of glass transition. In spite of the drastic viscosity increase in the limit of high temperatures and high pressures along the melting line, the relaxation time rapidly decreases,

and the system departs further from the glass transition along the melting line. It seems that the microscopic relaxation time criterion is more fundamental then the viscosity one.

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