Can high pressure experiments shed light on the puzzles of glass transition? The problem of extrapolation

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V V Brazhkin

Institute for High Pressure Physics, Troitsk 142190 Moscow region, Russia

E-mail: brazhkin@hppi.troitsk.ru

Abstract
The issues of the extrapolation to multi-GPa pressures of the experimental data obtained at moderate pressures are considered for different classes of glass-forming substances. For covalent glass-forming substances, the phase transitions and structural changes are major factors that hamper extrapolation. Organic glass-forming liquids are not ground thermodynamic states of matter; under high pressures they transform to polymeric substances and then to mixtures of simple inorganic compounds. Therefore, extrapolation of the data obtained at moderate pressures is hardly possible for this class either. Metallic melts and rare gas liquids are the only substances whose properties can be extrapolated into the megabar region. However, such an extrapolation is highly uncertain due to the low viscosity and weak pressure dependences of the properties of these liquids. New experimental studies of rare gas and metallic liquids in the pressure region of tens of GPa are urgently needed for the extrapolation to be reliable.

The problem of glass transition is currently regarded as one of the hottest topics of condensed matter physics [1]. The area adjacent to this problem is the experimental study and theoretical description of the viscosity behavior of liquids and corresponding relaxation times under changes of P, T-parameters. However, the overwhelming majority of experimental and fundamental studies are carried out at atmospheric pressure, which may be taken as zero pressure in terms of the pressure impact on the glass-transition processes. At the same time, a considerable increase in the viscosity of the liquid and the transition of the liquid to a glassy state can be achieved not only on isobaric cooling of the melt but also at isothermal compression. It is also known that for many glass-forming molecular liquids the viscosity rises with pressure exponentially at the beginning; then, as the glass-transition pressure is approached, critical behavior is observed [2–4]. The pressure dependence of the glass-transition temperature T_g prescribes the glass-transition line $T_g(p)$ on the T, P plane and in so doing, the glass-transition line has a positive slope, as a rule. In recent years, the relaxation and glass-transition processes in a number of molecular melts have been investigated under changes of both temperature and pressure [5–7], making it possible, in particular, to separate the effects of liquid density change from 'pure temperature'

effects. Such kinds of experiments are presently conducted at pressures up to ~1 GPa. At the same time it is evident that at sufficiently high compression values, the role of an attractive term of the inter-particle potential is reduced and a specific universal behavior of both the viscosity and glass-transition temperature ought to be observed [8]. The work in [9] has theoretically demonstrated that the glass transition of molecular liquids at super-high pressures is bound to be similar to a jamming-like glass transition in colloids. In the process, a qualitative change in the behavior of the glass-transition line $T_g(p)$ should be observed [9]. The estimated pressures needed for such qualitative changes for many organic molecular liquids are about 10 GPa, which is a pressure range accessible not only for diamond-anvil high pressure apparatus but also for large-volume high pressure devices, i.e. for those of toroid, belt, and multi-anvil type.

So, at first glance the situation looks promising: studies on glass-forming melts at already available pressures of 5–20 GPa are expected to crack many fundamental puzzles of the glass transition. However, such a study is unlikely to succeed.

The purpose of this paper is to point out the 'pitfalls' on the way for those exploring the glass transition of melts at $P \sim 10$ GPa and to outline potentially promising directions
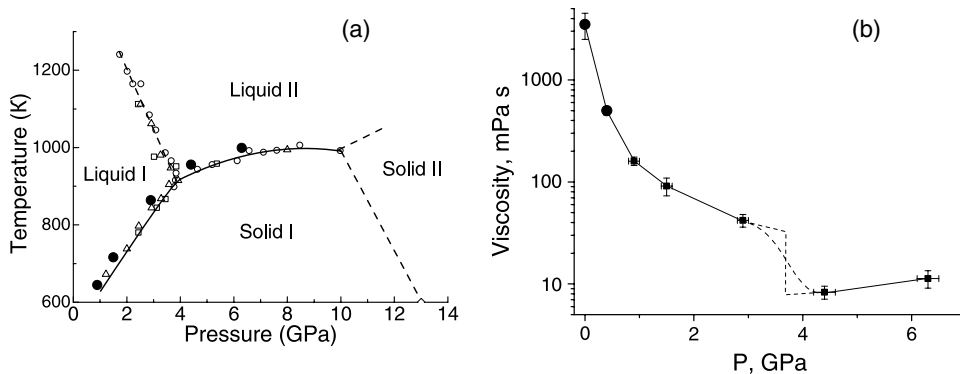
Figure 1. (a) Experimental conditions (closed circles) mapped onto the P, T-phase diagram of Se from open symbols onto the phase diagram correspond to the anomalies of electrical resistance, density and heat observed at the line of the metallization of melt. (b) The viscosity–pressure dependence of liquid selenium along the melting curve from [15]. The dashed parts of the line are guides to the eye near the semiconductor-to-metal transition in the melt.
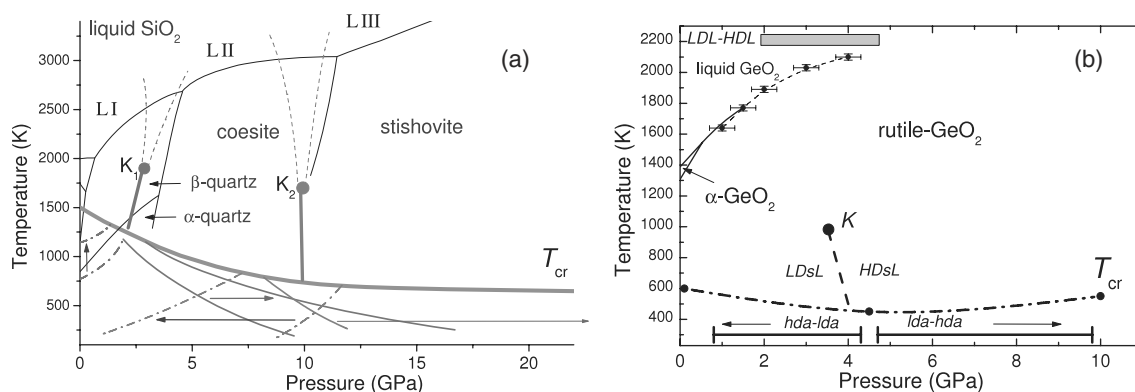

Figure 2. (a) The generalized P, T-phase diagram of SiO_2 including phase transformations in liquid and glassy states. (b) The generalized P, T-phase diagram of GeO_2 including phase transformation in liquid and glassy states.

of possible experimental research at even higher pressures of about 100 GPa.

In what follows we shall be discussing separately the behavior under pressure of different classes of substances varying in the type of inter-atomic or inter-molecular interaction. Easily glass-forming liquids with high viscosity include many oxide melts with covalent bonding (SiO_2, GeO_2, B_2O_3), halogenide and chalcogenide melts with covalent–ionic interaction (BeF_2, $ZnCl_2$, As_2S_3), and many molecular organic liquids with molecular (van der Waals) interactions between large molecules. The melts of substances with the Lennard-Jones interaction like rare gas liquids and with a metallic type of bonding like elementary metallic melts have very low viscosity of $\sim 10^{-4}$–10^{-2} Pa s near the melting temperature. The glass transition of such substances may be observed only at ultra-high cooling rates. As a consequence, the behavior of such liquids in the viscous region near their respective glass-transition temperatures has virtually been unexplored even at atmospheric pressure.

The properties of glass-forming covalent and ion-covalent melts, such as SiO_2, GeO_2, Se, and $ZnCl_2$, have been studied, including under pressure, fairly well. As it was found out, the behavior of the properties of these substances under pressure does not follow any simple laws and the data obtained at

moderate pressures up to 1 GPa cannot be extrapolated to higher pressures in principle. Thus, for many oxide melts, including liquid GeO_2 and SiO_2, an uncommon nonmonotonic behavior of the viscosity with pressure is observed [10–13]. The decrease of the viscosity with pressure is also observed for the S melt [14]. A record fall in the viscosity along the melting curve has been recently found for the Se melt: the viscosity value dropped by 500 times with the pressure rise up to 4 GPa [15] (see figure 1). The reasons for such an 'irregular' behavior of the viscosity have to do with a significant change in the nature of the inter-particle interactions, as well as with the modification of the short-range order structure of covalent and ion-covalent melts under pressure [16–19]. Thus, in the oxide and chalcogenide melts at compression, broad and sharp structural phase transformations are observed (see figures 2 and 3). In this case, the transition to the states with higher atomic coordination numbers occurs, accompanied by the corresponding modifications of all properties of the melt, including viscosity. The S and Se melt structures undergo drastic changes too. First the average length of molecular chains severely decreases under pressure followed by the transition from a molecular semiconductor to an atomic metal (see figure 1(a)). These structural changes bring about a radical viscosity decrease along the melting curve in the
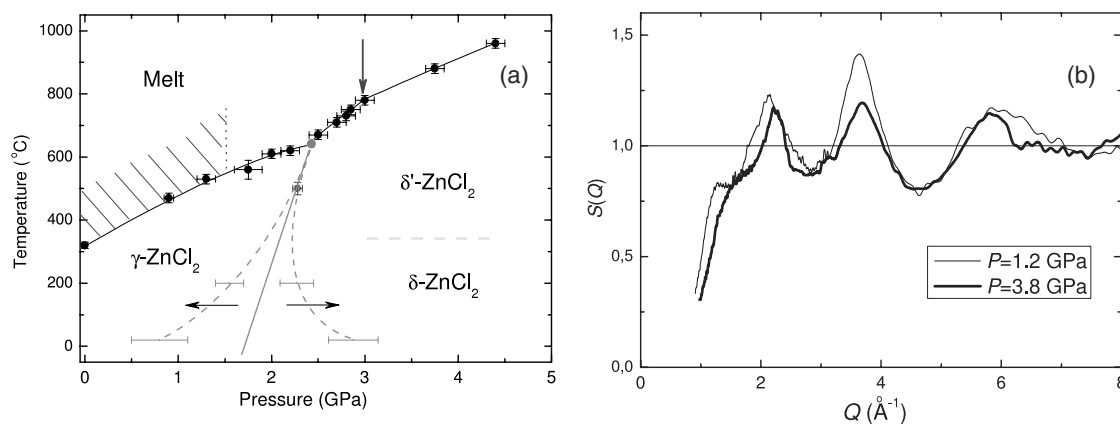
Figure 3. (a) The generalized P, T-phase diagram of $ZnCl_2$ including phase transformation in the liquid state from [23]. (b) Structure factors of the molecular-network and ionic states of $ZnCl_2$ liquid state from [23].

semiconductor region and an additional sharp viscosity fall at melt metallization.

As a result, many covalent glass-forming melts cease to be viscous at high pressures. Thus, the cooling of the Se melt with the rate of 10^2–10^3 K s^{-1} does not lead to its transition to glass at pressures $P > 1.5$ GPa [20]; the SiO_2 melt is not subject to glass transition with the experimental cooling rates at $P > 6.5$ GPa [21]. It has been recently found that the cooling of such glass-forming melts as B_2O_3 and $ZnCl_2$ under pressure results in their crystallization, not glass transition [22, 23]. Critical pressures are 0.5 GPa for $ZnCl_2$ [23] and 6 GPa for B_2O_3 [22].

It is evident that, similarly to Se, many other glass-forming chalcogenide melts, for example, As_2S_3, will undergo metallization under pressure [24], which should inevitably lead to an abrupt decrease in viscosity and a rise in the critical cooling rate necessary for glass transition.

Some melts at compression even exhibit several phase transformations, resulting in a very non-trivial viscosity behavior. Thus, the AsS melt at 2 GPa pressure first undergoes the transition from a quasi-molecular to a covalent net fluid followed at $P \sim 5$ GPa by the transition to the metallic state of the melt [24]. In this case, the AsS melt at $P < 2$ GPa and $P > 5$ GPa has low viscosity and crystallizes at the experimental cooling rates whereas in the 2–4 GPa range the melt is apparently very viscous as its cooling results in the formation of glass [25].

The general conclusion about the behavior under pressure of glass-forming covalent and ionic-covalent melts is that the short-range order structure and effective inter-particle interaction of the melts in strong compression conditions are subject to drastic changes. As a consequence, a universal rapid increase in the viscosity with pressure is not observed for these liquids and the data obtained at moderate pressures cannot be extrapolated to higher pressures.

A separate discussion should be given to the behavior under very high pressures of glass-forming molecular organic fluids, such as glycerol, alcohols, and the like. Because of their low melting and glass-transition temperatures (near to room conditions) and chemical inactivity, these substances are

intensely studied, including at pressures up to 1–3 GPa or even higher [5–7, 26, 27]. However, pressure dependences of the viscosity and glass-transition temperature of these fluids cannot be extrapolated to higher pressures of $P \geqslant 10$ GPa either. Moreover, most of these substances do not exist at very high pressures! The point is that the overwhelming majority of condensed phases based on carbon, hydrogen, and nitrogen atoms are not thermodynamically equilibrium states for a given chemical composition [28, 29]. Thus, all hydrocarbons, including ethylene, acetylene, benzene, and others, are metastable in relation to the transition to a mixture of methane and graphite [29]. Similarly, glass-forming organic fluids, such as spirits, glycerol, and others, are metastable in relation to the decomposition into simple compounds H_2O, CH_4, CO_2, NH_3, and elemental substances [28, 29].

Metastability of organic molecular compounds is provided for by the existence of an energy barrier in the way of the chemical decomposition into a more energy-beneficial mixture of simple compounds. In the moderate pressure and temperature region, these energy barriers are so high that the decomposition does not happen during any reasonable experimental times and the glass-forming molecular substances can be regarded as stable compounds. However, very high pressures of 10 GPa significantly lower the barrier for the transformation of the molecular substances in question (figure 4(a)). In the beginning, the irreversible transformations of molecular substances into various polymerized states occur; on further increase of pressure and temperature the transition to a mixture of high pressure phases of simple compounds take place [28, 29]. As a result, transitional P, T phase diagrams for the majority of molecular substances may conditionally be divided into three zones (figure 4(b)). We again emphasize that the transformation to polymeric phases and the decomposition into simple compounds occur with energy decrease and represent irreversible processes.

It should be pointed out again that both ionic-covalent substances and organic molecular compounds at high pressures $P \geqslant 10$ GPa experience a change of the inter-molecular interaction type. When considering molecular substances, the very possibility of separating
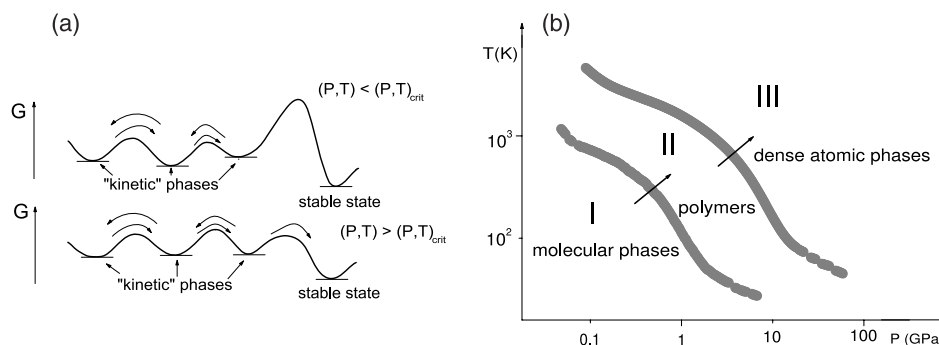
Figure 4. (a) Energy minima in the configuration space. At threshold P, T-parameters the irreversible transitions from the 'kinetic' phases to the stable modifications occur for the experimental times. (b) General kind of transitional P, T-phase diagram of molecular organic compounds. The transitions from zone I to zone II and zone III are non-equilibrium irreversible transformations.

molecules as independent structural units is associated with a considerable, by a hundred times, difference in intra-molecular (covalent) and inter-molecular (van der Waals) interaction energies. At compression, the weak inter-molecular interaction is modified. When the distance between the atoms of neighboring molecules becomes comparable with intra-molecular distances, the molecules can no longer be regarded as invariable structural units: the polymerization of the molecules or their decomposition into simple chemical compounds takes place. The appropriate pressures for most molecular organic compounds fall within the 2–20 GPa range [28, 29]. In the case of ionic-covalent substances, the separation of the molecules as independent structural units is conditional even at zero pressures. An interaction hierarchy, however, exists even for this particular class of substances, although in this case the intra- and inter-molecular energies differ by times, not by a hundred times as with molecular substances. At higher pressure, the covalent and ionic-covalent substances reveal either the disappearance of molecular units, as, for instance, with Se metallization, or a change of the type of inter-particle potential and molecular packing, as with SiO_2. In all cases, the effective inter-particle interaction for glass-forming classes of substances at pressures $P > 10$ GPa dramatically changes, making any extrapolations impossible.

Let us now consider those classes of substances whose effective inter-atomic interaction does not change up to $\sim$100 GPa and above. These substances in the first place include rare gas solids and liquids and some close packed metals. It may be thought for rare gas solids and liquids that the inter-particle interaction is primarily estimated by the Lennard-Jones potential up to pressures of about 10^2 GPa, and for As and Ne up to 10^3 GPa [30]. The bonding in metals cannot be described by introducing a simple effective paired inter-atomic potential since the interaction has fundamentally many-body character. However, for many close packed metals like Au, Ag, Pt, Pb, etc the effective interaction and close atomic packing do not change significantly with pressure. The viscosity and glass-transition temperature data obtained at pressures of 1–10 GPa for such substances as rare gas liquids and close packed liquid metals can apparently be extrapolated to pressures of $\sim$100 GPa and above. Unfortunately, these substances at moderate pressures have very low viscosity and do not belong

to the glass-forming systems. As a result, the behavior of these types of liquids in the supercooled region near glass transition remains, in fact, unexplored. Some studies, though few in number, have been done into the viscosity of rare gas liquids and liquid metals under pressure in the stable region above the melting point, see [8] and references therein [31–33].

There are two empirical approaches to the description of the viscosity behavior of simple liquids under simultaneous changes of temperature and pressure. The first approach goes back to Bridgman's works [34] and suggests that the viscosity of the liquid is nearly constant along the isochors. The other and currently more widespread approach was formulated by Pourier [35]. It is based on the presumption that the viscosity of the melts is invariable along the melting curve. The experimental data analysis shows that both 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 melting line and the isochor slopes [8] (figure 5). As a consequence, the viscosity of simple melts along the melting curve increases and this increase can be extrapolated to megabar pressures [8]. However, this extrapolation is in effect difficult because of the rather small viscosity variation in the covered range [36]. For example, the viscosity of the Fe melt grows along the melting curve by several times with the pressure increase to 10–15 GPa [33, 36]. However, the obtained data do not permit drawing any conclusions with regard to the character of this growth; various analytic models equally closely descriptive of the studied baric dependences give different extrapolation results. In consequence, different equations employed in the extrapolation of the Fe melt viscosity to pressures of 1.4–3.1 Mbar, corresponding to the conditions existing in the outer earth's core, provide data that differ by 10–20 orders of magnitude [36] (figure 6). The same goes with other 'simple' melts like liquid Ar. Thus, it is presently impossible to draw inferences about how high the viscosity can grow along the melting curve for the given melts with pressure increase to about 100–1000 GPa. If the viscosity growth is minor, the liquid metals and rare gas liquids will remain very bad glass formers at megabar pressures. In the event that the viscosity growth along the melting curve amounts to several orders of magnitude, the liquid metals and rare gas liquids become viscous glass-forming systems. In this
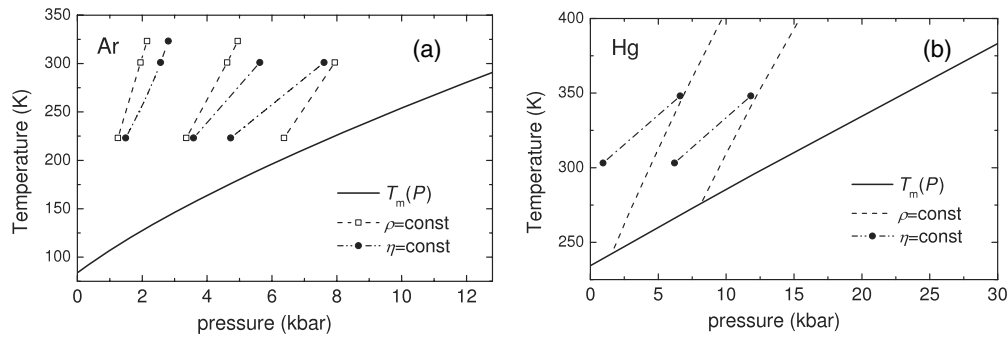
Figure 5. Melting line, lines of constant liquid density, and lines of constant liquid viscosity on the P, T-plane of Ar. (b) Melting line, lines of constant liquid density, and lines of constant liquid viscosity on the P, T-plane of Hg.
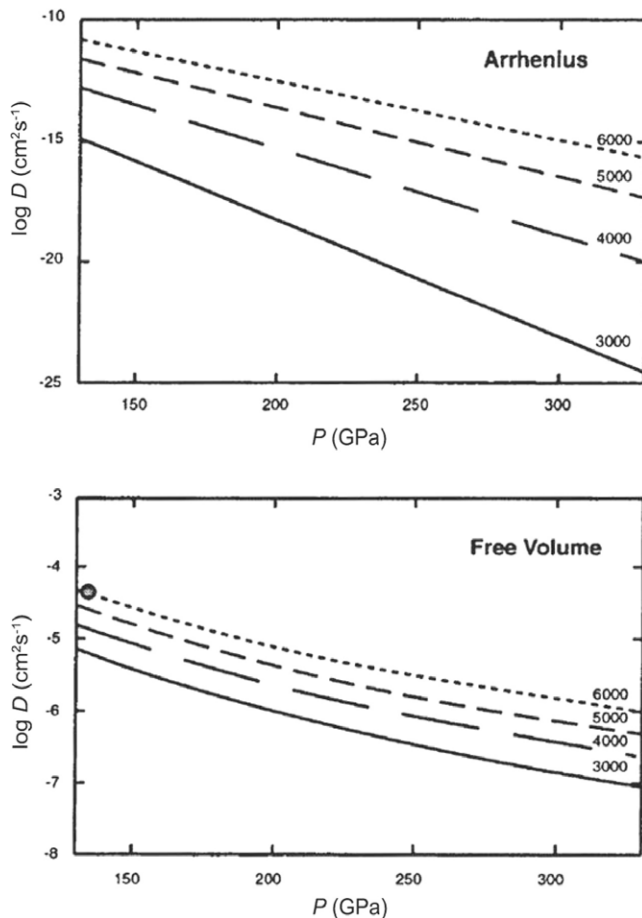

Figure 6. Predicted Fe-self-diffusivity along the isotherms from [36]. The Arrhenius extrapolation yields diffusivities 10–20 orders of magnitude lower than the free volume model. The picture is presented with the kind permission of Dobson.

case, the glass transition of the given melts in the megabar range should be similar to the jamming of soft spheres.

Conclusions

Thus, the extrapolation of the viscosity and glass-transition temperature from pressures of 1–10 GPa to the megabar range is presently impossible for either class of liquids. For ionic-covalent and molecular melts, these extrapolations are impossible in principle, while the only problem for metallic melts and rare gas liquids is that the studied temperature and pressure range is not yet sufficient for extrapolation. Hopefully, the studied pressure range for the viscosity of rare gas liquids can be extended up to 10 GPa and for the viscosity of the metals up to 25–30 GPa in the near future. Furthermore, of interest are experiments on quenching the melts of some metals (Pb, Ag, In, and others) and rare gas liquids in a diamond-anvil high pressure apparatus in the megabar pressure range and subsequent *in situ* examination of the structure of the corresponding solid after quenching at high pressure. If the viscosity of the melt is high, the quenching of the latter should result in glass transition instead of crystallization. These investigations can be conducted in the near future, too. They will give us the answer to the question of whether there is universal growth of the viscosity of melts at megabar pressures [8] and universal change of the glass-transition condition [9].

Acknowledgments

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