Physics – Uspekhi **62** (6) 623 – 629 (2019)

METHODOLOGICAL NOTES

PACS numbers: 64.70.P –, 65.20.De, 66.20.Cy

Can glassforming liquids be ‘simple’?

V V Brazhkin

DOI: https://doi.org/10.3367/UFNe.2018.06.038382

Contents

1. Glass-forming and non-glass-forming liquids 623
2. Nonergodicity of the glasslike state 624
3. Simple liquids, scaling, and isomorphous states 625
4. Viscosity of liquids and the effective potential of interparticle interaction 626
References 628

Abstract. **The tendency of various types of liquids to vitrify at moderate cooling rates is discussed. Good glass-forming liquids — covalent melts, polymer and organic liquids — feature high viscosity values of $10^{-2} - 10^{7}$ Pa s at temperatures close to the melting point. The glasses obtained by cooling such liquids are nonergodic systems, i.e., their properties are not unambiguously defined by external parameters. At the same time, many glass-forming molecular liquids are usually considered to be ‘simple’ systems described by an effective pair central potential of interaction between particles. In particular, the scaling of thermodynamic and transport characteristics for varying temperature and density and behavior under pressure of the melting temperature and the bulk modulus of molecular liquids are well described by the parameters of a simple effective pair potential. It is shown that the values of the viscosity of glassy molecular liquids in no way correspond to the effective-potential parameters (in contrast to the viscosity of true ‘simple’ fluids, such as liquefied inert gases). Due to the complex structure of the molecules of such liquids, the effective-potential parameters heavily depend on the distance between particles. A complex set of intermolecular and interatomic chemical bonding emerges when such liquids are vitrified. Thus, glass-forming molecular liquids can only be considered ‘simple’ from the point of view of their thermodynamic properties, while the polyatomic structure of their molecules results in a ‘complex’ behavior of transport characteristics and anomalously high viscosity values.**

Keywords: liquids, vitrification, ergodicity, viscosity, scaling, intermolecular interaction

1. Glass-forming and non-glass-forming liquids

The tendency of different liquids to glass formation is a quantitative rather than a qualitative characteristic. In liquids at temperatures lower than the melting temperature T_{m}, crystalline nuclei form and grow, and the maximum crystallization rate upon homogeneous nucleation is achieved at a definite supercooling ($\Delta T = 0.2 - 0.3 T_{\mathrm{m}}$) (Fig. 1). If the crystallization upon cooling in this temperature range does not have time to occur, then the further temperature decrease leads to a retardation of the processes of crystallization and to an increase in the viscosity of the liquid. At values of the viscosity at the level of 10^{13} Pa s, the characteristic relaxation times in the liquid (actually, the times a ‘settled’ life of an atom or a molecule) are several minutes and it is assumed that the substance passes into the state of a solid glass. In this paper, we will not concern ourselves with the problem of an ultrarapid increase in the viscosity in the specific temperature range close to the temperature of glass formation T_{g} and different models of the vitrification of liquid (the contemporary state of this problem is described in recent review [1]).

Melts are usually considered as the easily vitrifying liquids for which the critical rate of cooling necessary for obtaining a glasslike state (avoiding crystallization) does not exceed 100 K s^{-1} [2]. At these rates of cooling, it is possible to obtain macrosized samples of glasses — centimeter-sized and larger. Such liquids include many covalent melts, polymeric liquids,

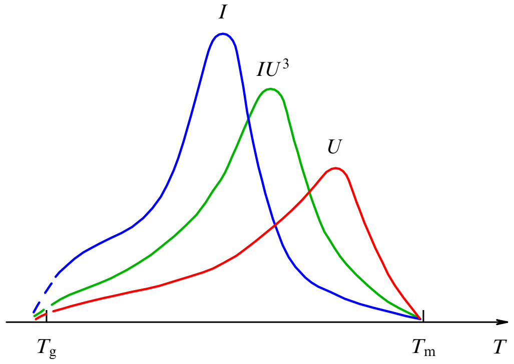

Figure 1. Temperature dependences of the frequency of the formation of nuclei of a crystalline phase I and of the rate of growth of crystals U. The intensity of the process of crystallization in the rough approximation is determined by the quantity IU^3. T_{m} and T_{g} are the melting point and the temperature of vitrification, respectively.

V V Brazhkin Vereshchagin Institute of High Pressure Physics,
Russian Academy of Sciences,
Kaluzhskoe shosse 14, 108840 Troitsk, Moscow, Russian Federation
E-mail: brazhkin@hppi.troitsk.ru

Received 5 April 2018, revised 27 May 2018
Uspekhi Fizicheskikh Nauk **189** (6) 665 – 672 (2019)
DOI: https://doi.org/10.3367/UFNr.2018.06.038382
Translated by S N Gorin

and some molecular organic melts. Among elementary substances, the only 'good' glass-former is selenium. For many covalent melts, e.g., B_2O_3, SiO_2, or As_2S_3, the critical rate of cooling is so small ($10^{-5}-10^{-3}$ K s^{-1}) that the problem lies in growing crystals rather than in obtaining glasses. Metallic melts and simple molecular liquids are considered difficult vitrifying systems: the cooling rates necessary for obtaining glasses are 10^5-10^{13} K s^{-1}, although for a number of multicomponent metallic melts the critical rate of cooling is substantially lower.

The maximum rates of cooling accessible experimentally (10^9-10^{10} K s^{-1}) are insufficient for obtaining the glasslike state of liquified inert gases, simple molecular elements, and many elementary metals. At the same time, with computer simulation, the effective rate of cooling is almost unlimited. At rates of cooling equal to 10^{14} K s^{-1}, in computer experiments, such simple substances as argon, water, and elementary metals can be obtained in the glasslike state comparatively easily.

Thus, at first glance, all liquids can be vitrified and there is no qualitative difference between the different classes of substances. However, this is not entirely true. In condensed media, there is a characteristic scale of time, namely, the period of oscillations of particles τ, on the order of the inverse Debye frequency, which is 10^{-12} to 10^{-13} s. As a result, in the case of vitrification of quite badly vitrified substances, the time of transition of the liquid through the temperature interval of intense crystallization should not exceed several periods or several dozen periods of oscillations of the particles (atoms, molecules) ($\approx 10\,\tau$) , and for good glass-forming substances this time can be up to $10^{18}\tau$. Consequently, as a qualitative criterion characteristic of a good glass-forming liquid, we can assume that at any temperature for the formation of a crystal nucleus in such a liquid a time $t \gg \tau$ is required (what should be taken as the criterion for 'much more' is the problem of a convention). Moreover, for systems with Lennard-Jones-type simple interparticle potentials, even at temperatures much lower than the temperature of vitrification (e.g., $T = (0.05-0.10)T_g$), nanocrystalline clusters start to form in a relatively short time ($100-1000\,\tau$) [3]. This means that some systems fundamentally cannot be vitrified: nucleation in the liquid and in the glass does not slow down exponentially with the decrease in temperature, contrary to how this occurs in the majority of substances.

There is a completely natural correlation between the tendency toward glass formation and the viscosity of liquids at temperatures close to T_m. Easily vitrifying covalent melts, and polymeric and complex organic liquids at $T \sim T_m$ have moderate or high values of viscosity of 10^{-2} to 10^7 Pa s, while for liquid metals, molecular substances, and liquified inert gases, the viscosity at T near T_m, as a rule, lies within the limits of 10^{-3} to 10^{-4} Pa s. The problem of the connection between the absolute value of viscosity and the type of liquid will be discussed below.

At the same time, it should be noted that easily vitrifying covalent melts refer, according to the classification of C Angel, to 'strong' liquids with an almost Arrhenius dependence of viscosity on temperature. Furthermore, easily vitrifying polymeric melts, especially relatively simple molecular melts (glycerin, propylene carbonate, propylene glycol, etc.), according to this classification, refer to 'soft' (fragile) liquids with a strongly non-Arrhenius dependence of viscosity on temperature (the effective activation energy increases rapidly with a decrease in the temperature). Liquids with a Lennard-Jones potential are record 'soft'. In other words, even very low values of the viscosity at temperatures close to T_m do not formally forbid the anomalously rapid growth of viscosity and vitrification in the supercooled region.

For the majority of easily vitrifying systems, such as covalent melts and polymeric liquids, the mechanism that is most important and most complex for the description of the processes of diffusion and vitrification during cooling is the mechanism of the formation of chemical bonds and of structural organization. The interparticle interaction in such liquids is a phenomenon that is extremely complex for the description. Several hundred studies have been devoted to this question. At the same time, for a number of easily vitrifying molecular liquids (glycerin, propylene carbonate, propylene glycol, etc.), the interaction is frequently described with the aid of simple central pair potentials of interaction (Lennard-Jones type). The purpose of this paper is to analyze the vitrification of such liquids, which conditionally are referred to 'simple' liquids.

2. Nonergodicity of the glasslike state

The theory of ergodicity, strictly speaking, more likely refers to mathematical physics, and upon the application of this concept to real systems one should be careful. We will use this concept in the simplest and intuitive (upon analyzing experimental data) sense. Liquids and gases are ergodic systems: the averaging of their characteristics over time is equivalent to averaging over an ensemble of particles, and their properties at not-too-short times of measurement are uniquely determined by the external parameters. Crystals, according to N N Bogolyubov's classification, are conditionally ergodic systems: relaxation to the state of equilibrium occurs very rapidly within the framework of a given crystal lattice, but there are additional minima in the configuration space which correspond to other crystal lattices, separated from the equilibrium minimum by very large energy barriers. A metastable crystalline state can exist without relaxation for an extremely long time. A brilliant example is diamond under standard conditions. Conditionally ergodic metastable systems also comprise many molecular substances and all organic compounds: their properties on the accessible levels of time change reversibly and unambiguously only in a specific range of temperatures and pressures [4, 5].

Glasses are a good example of metastable nonergodic systems. In glasses, a change can occur in the properties in the course of time at fixed external parameters (annealing or aging of glasses) [1]. In contrast to the existence of only several energy minima in the configuration space in the case of metastable crystalline phases, in glasses there is a continuum of such minima and, correspondingly, a continuous spectrum of relaxation times. The reason for the existence of a diffuse spectrum of relaxation times in glasses is the existence of a wide distribution of the parameters of the structure of short-range and intermediate order. The most important manifestation of the nonergodicity of glasses in the context of this article is the fact that their properties depend not only on external macroparameters P and T, but also on their thermobaric history [6, 7]. The different ways and times of obtaining glasses in $P-T$ coordinates affect their structure and physical characteristics. Thus, glasses obtained from liquids at different rates of cooling have different microstructures and densities [8, 9]. The history of a thermobaric

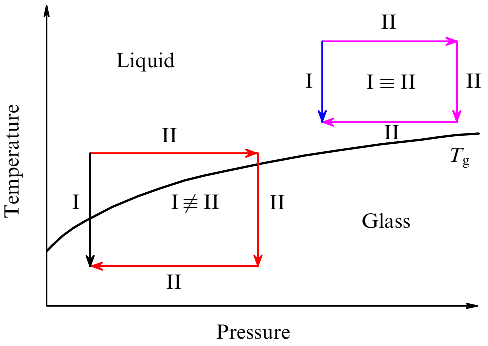

Figure 2. Difference in the behavior of liquids and glasses along a closed trajectory in the $P-T$ phase diagram. In the liquid state, the properties of the substance are uniquely determined by the external parameters (in this case, by the temperature and pressure). In the glasslike state, the properties depend on the prehistory and on the path in the phase diagram.

treatment also influences the structure, glass hardness [10, 11], and temperature of vitrification T_g [12, 13].

Vitrification is sometimes considered an analog of a second-order phase transition. For the usual second-order phase transitions, the Prigogine–Defay condition follows from Ehrenfest's relationship:

$$\Pi = \frac{\Delta C_p \Delta \kappa_T}{T_g V_g (\Delta \alpha)^2} = 1 \, ,$$

where ΔC_p, $\Delta \kappa_T$, and $\Delta \alpha$ are, correspondingly, the jumps of the heat capacity, compressibility, and thermal expansion coefficient upon transition, and T_g and V_g are the temperature of the transition and the specific volume, respectively. This equation is valid when for the description of the system it is sufficient to use one order parameter apart from the pressure and temperature [14]. Upon the transition of a liquid into glass, it is necessary to use several order parameters, and the Davis–Jones inequality $\Pi > 1$ should be fulfilled [15]. This inequality means that the glass state is *determined by pressure and temperature ambiguously and, after a closed cycle on the* $T-P$ *plane, the structure and properties of the glass can change substantially* (Fig. 2). This is manifested most clearly when a part of this cycle passes through the region of the liquid state. Glasses obtained by cooling the liquid at high pressures have a higher density and a different structure (of an intermediate and sometimes even short-range order) in comparison with those of glasses compressed to the same pressures at low temperatures. The phenomenon of residual densification of glasses after treatment by pressure is observed experimentally for all investigated substances. At the same time, according to the results of computer simulations, in many systems described by pair interparticle potentials of interaction, no such densification is observed in the limits of the error of calculations, i.e., in simulations, many glasses behave like ergodic systems with one order parameter, and the condition $\Pi = 1$ is satisfied in them [16–18]. This also leads to questions about the applicability of the usual concepts of vitrification to many model systems. Finally, note that for glasses, just as for other metastable systems, an important factor is the time of observation or measurement. In the limit of infinite times, discussion of the nonergodicity of glasses and of their metastability is meaningless: they will be crystallized. However, in many instances the corresponding times of crystallization are much more than the lifetime of the Universe; therefore, the need to describe the problem of the vitrification and properties of glasses is retained.

3. Simple liquids, scaling, and isomorphous states

The term 'simple liquids' is also conditional to a considerable extent. Usually, substances refer to simple liquids in which the effective interparticle interaction is described sufficiently well by a central pair potential (Lennard-Jones, Morse, and other types) (Fig. 3, curve *1*). Such potentials, in particular, describe liquid inert gases, simple molecular liquids, and ionic melts. The maximally simple cases are systems with a uniform potential of interaction between the particles, for example, with a power-law-repulsion potential (potential of 'soft' spheres) (see Fig. 3, curve *2*).

A system of 'soft spheres,' together a the system of 'solid spheres,' is one of the most studied, simplest, and most convenient for computer simulation model objects in the statistical physics of many particles. The interaction of particles in such a system is reduced to their repulsion according to the power law $U(r) \sim \varepsilon(\sigma/r)^n$ (ε is the characteristic interaction energy, σ is the characteristic spatial scale of interaction); therefore, this system can exist only at a positive external pressure. The potential of interaction in question is a uniform function, and for this system there are valid scaling relationships connected with the fact that the imperfect part of the statistical sum and, correspondingly, the thermodynamic properties do not depend separately on the volume and temperature, but are functions of a combined variable $\Gamma = \rho^{n/3}/T$, where ρ is the bulk density [19, 20].

The phase diagram of a system of 'soft spheres' is very simple: one crystalline phase and a fluid are present in it. The type of crystal is determined by the power index n: for $n > 6$, a face-centered cubic (fcc) lattice is stable; at smaller values of n, a body-centered cubic (bcc) lattice is stable [21]. The melting point T_m of the crystal of 'soft spheres' is expressed as $T_m \sim \rho^{n/3} \sim P^{n/(n+3)}$; the coefficients of proportionality are determined only by the index n [19]. For a system of soft spheres, not only the thermodynamic but also the kinetic properties are single-valued functions of the variable Γ. This is connected with the circumstance that the kinetic energy of particles is also a second-order uniform function of their momenta. A rigorous study of this problem with the attraction of the appropriate Lagrangian and Hamiltonian of the system was carried out by Hiwatari et al. [22], and then by Zhakhovskii [23]. The basic idea of the analysis is that,

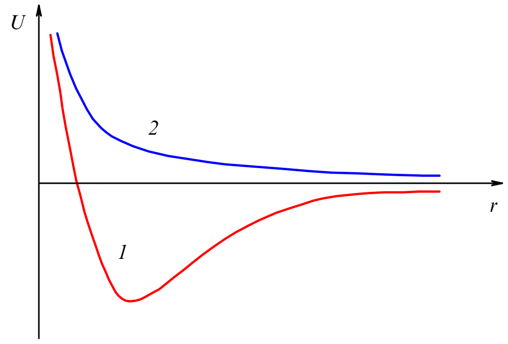

Figure 3. Typical Lennard-Jones pair potential (curve *1*) and the 'soft-spheres' potential (curve *2*).

upon scaling, identical values of Γ correspond to identical sets of the phase trajectories of the particles; in particular, along the line of melting the two-phase system (crystal–liquid) passes into an analogous two-phase system. Along the lines with a constant value of Γ, the viscosity of the liquid η changes as $\eta \sim T^{1/2+2/n} \sim T^{1/2}\rho^{2/3}$; i.e., the quantity $\eta T^{-1/2}\rho^{-2/3}$ is kept constant. The states of the system that correspond to constant values of Γ are called isomorphous.

Certainly, interaction in real substances does not reduce to repulsion according to a power law. Nevertheless, in many instances, the attracting part of the potential can be ignored, especially at high pressures; for example, the melting point of rare gases is described well by the expression $T_{\mathrm{m}} \sim \rho^{n/3}$, where the value of n is close to 9–14 [24]. It was experimentally established that for many molecular liquids in a wide range of temperatures and densities both thermodynamic and dynamic scaling can be fulfilled, although the effective values of n for the isomorphous states determined from measurements of the viscosity and of the melting point coincide only for liquid rare gases and for simple molecular fluids [25, 26]. For many molecular liquids based on large complex molecules, the values of n for the dynamic isomorphous states are noticeably larger than for the thermodynamic states [26], i.e., the dynamics are more sensitive to density changes than the melting point is. There are also reverse examples for a number of liquids with hydrogen bonds (for example, glycerin) [27].

The values of the effective index n do not remain strictly constant upon a change in the temperature and pressure, and for liquids of some classes (for example, with strong hydrogen bonds), the concept of isomorphous states proves to be completely inapplicable. In order to quantitatively characterize the degree of the 'similarity' of the behavior of liquid to the behavior of the fluid of 'soft spheres,' researchers in J Dyre's group developed a concept of the 'degree of simplicity' of liquids [28–30]. The key idea in this approach is a comparison of the values of the fluctuations of the potential energy with the virial, and also the calculation of the degree of their correlation [28]. For the fluid of 'soft spheres,' the potential energy coincides with the virial and the degree of the correlation of their fluctuations is, naturally, equal to 100%. The degree of the correlation of fluctuations was calculated by the method of molecular dynamics for systems with different effective interparticle potential over a wide range of densities and temperatures [16, 29–31]. As the criterion of the 'Roskilde simplicity' (Roskilde, Denmark, is the place where Dyre's group works) the value of the correlation of fluctuations equal to 80–90% was conditionally accepted. It turns out that at low pressures and high temperatures (for example, near the critical point) no 'simple' liquids exist according to this criterion. At high pressures, near the melting line many classes of liquids prove to be 'simple' with well correlated fluctuations, e.g., simple molecular liquids, liquid rare gases, or liquid metals. Certainly, even in the case of rare gases or ionic substances, there are no physical grounds for the repulsive part of the potential to be described by a power-law function. In reality, the repulsion is connected with the overlap of the internal electron shells of the ionic cores and is described by a complex combination of exponents. However, the exponential repulsion is close to the power-law repulsion in a wide region of densities, and systems with an exponential potential of repulsion are also 'simple' with well correlated fluctuations [31]. At the same time, according to the criterion of 'correlated fluctuations,' the covalent network melts and liquids with strong hydrogen bonds are not 'simple' even at high pressures.

It was established by experimental studies that 'simple' (according to computer simulation) liquids indeed have isomorphous states [25, 26, 33, 34]. Moreover, isomorphous states are observed even for the dynamic properties of many liquids with hydrogen bonds, which have low values of correlations. This is possibly connected with the small range of densities at which the measurements were conducted. According to the data of computer simulations, the lower the degree of 'correlation' between the liquids, the greater the value of the Prigogine–Defay parameter Π and the greater the effects of the residual densification of the glass after cycling at high pressures [16–18]. However, for a number of 'simple' liquids, the simulation gives a value of $\Pi = 1$ even in the absence of the effects of densification of glasses within the error limits of calculations, while in the experiment the effects of a densification of glasses and of changes in their properties depending on the method used to obtain them are observed for absolutely all studied glass-forming liquids, including such relatively 'simple' liquids without strong hydrogen bonds as propylene carbonate [35] and tetramethyl tetrafenyl trisiloxane (DC704) [36]. On this basis, in [36] a conclusion was reached that the concept of 'simple liquids' requires revision. Moreover, it is incomprehensible how at all the 'simple' organic liquids described by 'simple' potentials of interparticle interaction can generally have high values of viscosity and easily be vitrified upon cooling. In other words: what 'nonsimple' liquids are hidden in 'simple' liquids?

4. Viscosity of liquids and the effective potential of interparticle interaction

Upon analyzing scaling for viscosity at different temperatures and densities, the reduced viscosity $\eta^* = \eta T^{-1/2}\rho^{-2/3}M^{-1/2}$, where M is the mass of particles, is used as a rule. Many simple pair potentials (such as 'soft-sphere,' Lennard-Jones, Morse, and other potentials) are described using two characteristic parameters: an energy parameter ε (in many cases connected with the depth of the effective potential well) and a spatial parameter σ (assigning the radius of the interaction). Through these parameters of the potential, it is also possible to introduce an effective quantity having the dimensionality of viscosity: $\eta_0 = \varepsilon^{1/2}M^{1/2}\sigma^{-2}$. It is obvious that the viscosity of fluids described by an identical type of interparticle interaction, when referred to η_0, should be identical at the equivalent points of the phase diagram, similar to how the dimensionless viscosity η^* is constant along the isomorphs. Thus, in the case of a Lennard-Jones system, the viscosity of the liquid near the triple point in the phase diagram is $\eta \approx 3\eta_0$ [37]. Along the melting line at moderate pressures, the viscosity changes only weakly, and for substances with a Lennard-Jones potential, the relationship $\eta \approx 3\eta_0$ must be fulfilled near the line of melting.

Thus, at first glance, all liquids with an interparticle interaction close to the Lennard-Jones type must have at temperatures close to T_{m} at a normal pressure a viscosity $\eta \approx 3\eta_0 = 3\varepsilon^{1/2}M^{1/2}\sigma^{-2}$. Note that the value of η_0 for different substances described by a Lennard-Jones potential changes within sufficiently narrow limits: from $(0.5-1.0)\times 10^{-4}$ Pa s for inert gases and simple molecular substances to $(1-3)\times 10^{-4}$ Pa s for organic molecular substances with large molecules. Thus, near the melting point, the viscosity of *all* fluids with an interparticle interac-

Table. Viscosity values at temperatures close to the melting point.

Substance	Viscosity, Pa s	Viscosity in the approximation of Lennard-Jones interparticle interaction, Pa s
Argon Ar	3×10^{-4}	2.8×10^{-4}
Neon Ne	1.5×10^{-4}	1.6×10^{-4}
Krypton Kr	4.5×10^{-4}	4.3×10^{-4}
Xenon Xe	5.1×10^{-4}	4.8×10^{-4}
Nitrogen N_2	3×10^{-4}	1.6×10^{-4}
Oxygen O_2	9×10^{-4}	2.3×10^{-4}
Methane CH_4	2×10^{-4}	1.6×10^{-4}
Carbon dioxide CO_2	2.5×10^{-4}	2.7×10^{-4}
Ethylene C_2H_4	6.8×10^{-4}	2.2×10^{-4}
Ethane C_2H_6	1.3×10^{-3}	2×10^{-4}
Propane C_3H_8	1.1×10^{-2}	1.9×10^{-4}
Propylene carbonate $C_4H_6O_3$	5×10^{-2}	1.7×10^{-4}
Glycerin $C_3H_8O_3$	2	8×10^{-4}
Propylene glycol $C_3H_8O_2$	200	6×10^{-4}

tion described by a Lennard-Jones potential must lie in a narrow range, $10^{-4} - 10^{-3}$ Pa s.

Experimental data for the viscosity of liquified inert gases near the triple point [38] indeed confirm this assumption (see Table). For argon, krypton, and xenon, $\eta = 3.2 - 3.3\,\eta_0$; for neon, $\eta = 2.8\eta_0$ (the data on the effective values of ε and σ are borrowed from [39]). Close relationships also take place for fluid CO_2 ($\eta = 2.9\eta_0$) and for methane CH_4 ($\eta = 4\eta_0$). However, for other molecular substances, this assumption is not fulfilled. Thus, the experimental values of the viscosity are $\eta \approx 6\eta_0$ for fluid nitrogen N_2; $\eta \approx 12\eta_0$ for oxygen O_2; $\eta \approx 10\eta_0$ for ethylene C_2H_4; $\eta \approx 20\eta_0$ for ethane C_2H_6; $\eta \approx 180\eta_0$ (!) for propane C_3H_8 ($\eta_0 = 0.6 \times 10^{-4}$ Pa s, $\eta = 1.1 \times 10^{-2}$ Pa s) (see Table).

An even more striking discrepancy between the viscosity of a liquid in the state close to the melting point and estimations of η_0 based on data on the parameters for the effective Lennard-Jones potential is observed for glass-forming molecular liquids. According to the criterion of ‘correlation of fluctuations,’ many of these liquids are ‘simple’ [16–18], and the behavior of many of them upon compression is described well by a Lennard-Jones potential [27]. These are such liquids, notably, as propylene carbonate, propylene glycol, and glycerin. For these liquids, just as for liquified inert gases, the derivative of the bulk shear modulus with respect to pressure is $B'_P \approx 8$, which indeed should be observed for a system of particles with a Lennard-Jones interaction potential [27]. In propylene carbonate there are also no hydrogen bonds, and its melt is considered a ‘standard’ simple liquid.

Estimations of the parameters of the corresponding Lennard-Jones potentials ε and σ for these substances were taken from data on the density and energy of cohesion. As a result, it can be estimated that for propylene carbonate ($C_4H_6O_3$), $\eta \approx 300\eta_0$ (!) ($\eta_0 = 1.7 \times 10^{-4}$ Pa s, $\eta = 5 \times 10^{-2}$ Pa s). Consequently, the ‘standard simple liquid’ — propylene carbonate — has near the melting point a viscosity that is 100 times greater than it must have on the basis of the parameters of intermolecular interaction. For liquids with hydrogen bonds, the discrepancy between the experimental and calculated values of viscosity is colossal. For glycerin ($C_3H_8O_3$), $\eta \approx 10^4\eta_0$ (!!), while for propylene glycol ($C_3H_8O_2$), $\eta \approx 10^6\eta_0$ (!!!). Thus, for glass-forming liquids, the viscosity at temperatures close to T_m is many orders of magnitude greater than the values evaluated from the parameters of interparticle interaction (see Table). This means that the ‘softness’ of these liquids according to the Angel classification and the strongly non-Arrhenius behavior of the viscosity in the supercooled region are not sufficient for the low critical rates of cooling ($10^{-1} - 10^3$ K s^{-1}) necessary for vitrification. Let us recall that the critical rates necessary for the vitrification of systems of Lennard-Jones particles are $10^{11} - 10^{14}$ K s^{-1}. It is surprising that this (to a certain degree ‘trivial’) fact was not previously noted.

Thus, for many glass-forming melts, a simple effective pair potential well describes the thermodynamic characteristics of liquids and absolutely inadequately describes their transport properties. The reason for this is, obviously, connected with the complex structure of the molecules of glass-forming liquids. In the equilibrium state, the molecules are located at large distances from each other, and their effective interaction can be described with the aid of a simple pair potential. This potential of interaction between conditional point-like centers well describes the phase diagram of the system (the lines of melting and boiling, the parameters of the triple point) and the compressibility of liquid. At the same time, the diffusion processes in a liquid are connected with the activation-related ‘jumps’ of atoms or molecules from their nearest environment. In this case, at the moment of the ‘jump’ the particle in a fraction of a picosecond converges with the neighbors to anomalously small distances. In the case of atomic liquids, this does not substantially influence the effective potential of interaction (Fig. 4). However, for molecular liquids, this is not the case. At short distances, organic molecules no longer interact as point centers; the structure and composition of the molecules become critically important factors (Fig. 5). In this case, at the moment of the jump, it is necessary to take into account the interaction of all adjacent atoms (ions). The complex structure of the molecules leads to an anomalously strong dependence of the parameters of interaction on the intermolecular distance.

Earlier, in [26] it was noted that the high sensitivity of the dynamics of liquids to density changes can be explained by the growth of the effective steepness of the potential. For atomic fluids such as liquified inert gases, the activation energy of diffusion (in fact, the value of the energy barrier for the ‘jump’) is determined by the same parameters, ε and σ, as in the case of thermodynamic properties. However, in molecular organic liquids, the value of the activation barriers for the diffusion jumps is not determined by the parameters of the effective pair potential for the equilibrium volume. It should be noted that the growth of the effective barrier by a factor of only 2–3 corresponds to a decrease in the diffusion mobility by several orders of magnitude. A conclusion about the need to examine the structure of molecules at close distances is to a certain degree natural. For ‘classical’ glass-formers, it was well known long ago that to explain the processes of vitrification, it is necessary to consider the formation of chemical bonds and of the structural configurations [40].

Thus, the reason for the anomalously high viscosity of glass-forming organic liquids at temperatures close to the

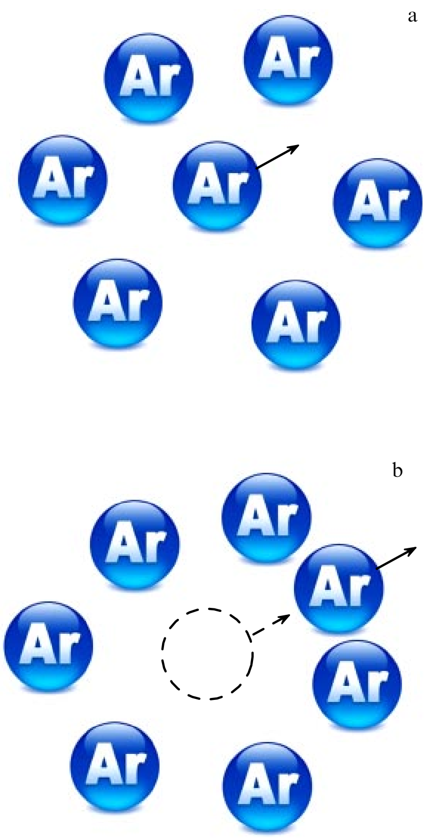

Figure 4. (a) Initial arrangement of Ar atoms. (b) Diffusion jump of an Ar atom into an adjacent cell. The Lennard-Jones interaction between the atoms occurs at all stages of the jump.

melting point is connected with a strong modification of the interaction of large molecules at short distances: individual atoms from different molecules begin 'to feel' each other; the form of the molecules can cause steric limitations upon their convergence. All this leads to a considerable growth of the effective energy barriers for the diffusion jumps of molecules.

Note that all simple potentials based on the pair central potential with small additions cannot adequately describe the absolute values of the viscosity of vitrified molecular liquids. When using more complex effective potentials of interaction with several characteristic energy and scale parameters, it is possible to describe the growth of viscosity at temperatures close to the melting point by 1–2 orders of magnitude, which cannot be achieved with the aid of simple pair potentials. At the same time, the growth of viscosity by 4–6 orders of magnitude in comparison with the 'Lennard-Jones' values for glycerin and propylene glycol cannot be described at all with the use of empirical effective intermolecular potentials. This is connected with an abrupt change in the type of interparticle interaction in the process of jumps of molecules.

As a result, many organic glass-forming liquids can be considered 'simple,' described by 'simple' potentials of interparticle interaction, from the viewpoint of thermodynamics, but these liquids are 'complex' from the viewpoint of transport characteristics. Upon vitrification of such liquids, a complex set of chemical bonds appears in them, as in 'classical' glass-formers [40]. At the same time, the simple liquids described by the simple pair potential of interaction (such as liquified inert gases) prove to be fundamentally 'non-glass-forming'. A 'quasi-glass' state obtained in such systems upon ultra-rapid cooling is ergodic and is crystallized for relatively short times at any low temperature.

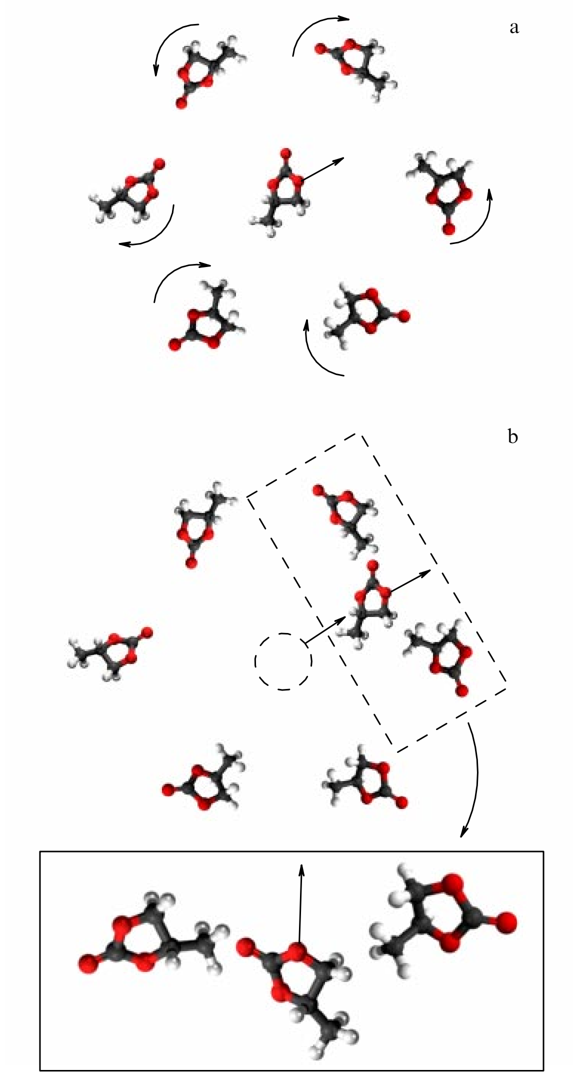

Figure 5. (Color online.) Demonstration of a diffusion jump of a molecule of propylene carbonate $C_4H_6O_3$. (a) The initial arrangement of the molecules (carbon atoms are shown in black; oxygen in red; hydrogen in light grey). (b) Effective interaction between molecules radically changes in the process of the jump. At short distances, details of the structure of the molecules and the interaction between each of the atoms (ions) are important.

Acknowledgments
The author is grateful to V N Ryzhov, A G Lyapin, Yu D Fomin, S M Stishov, and S M Roland for discussions of the work; and also to I V Danilov for help in the preparation of the article. This study was supported by the Russian Scientific Foundation (grant 14-22-00093).

References

1. Tropin T V, Schmelzer Ju W P, Aksenov V L *Phys. Usp.* **59** 42 (2016); *Usp. Fiz. Nauk* **186** 47 (2016)
2. Feltz A *Amorphe und glasartige anorganische Festkörper* (Berlin: Akademie-Verlag, 1983); Translated into English: *Amorphous Inorganic Materials and Glasses* (Weinheim: VCH, 1993); Translated into Russian: *Amorfnye i Stekloobraznye Neorganicheskie Tverdye Tela* (Moscow: Mir, 1986)

3. Mokshin A V, Galimzyanov B N *J. Chem. Phys.* **142** 104502 (2015)
4. Brazhkin V V *Phys. Usp.* **49** 719 (2006); *Usp. Fiz. Nauk* **176** 745 (2006)
5. Brazhkin V V *J. Phys. Condens. Matter* **18** 9643 (2006)
6. Gupta P K, Mauro J C *J. Chem. Phys.* **126** 224504 (2007)
7. Mauro J C, Loucks R J, Gupta P K *J. Am. Ceram. Soc.* **92** 75 (2009)
8. Levelut C et al. *J. Non-Cryst. Solids* **352** 4495 (2006)
9. Ruta B et al. *Nature Commun.* **5** 3939 (2014)
10. Smedskjaer M M et al. *Sci. Rep.* **4** 3770 (2014)
11. Smedskjaer M M et al. *J. Chem. Phys.* **143** 164505 (2015)
12. Wondraczek L et al. *Phys. Rev. B* **76** 014202 (2007)
13. Wondraczek L et al. *J. Am. Ceram. Soc.* **90** 1556 (2007)
14. Prigogine I, Defay R *Chemical Thermodynamics* (London: Longmans, 1954)
15. Davies R O, Jones G O *Adv. Phys.* **2** 370 (1953)
16. Fragiadakis D, Roland C M *J. Chem. Phys.* **147** 084508 (2017)
17. Gundermann D et al. *Nature Phys.* **7** 816 (2011)
18. Gnan N et al. *Phys. Rev. Lett.* **104** 125902 (2010)
19. Stishov S M *Sov. Phys. Usp.* **18** 625 (1975); *Usp. Fiz. Nauk* **114** 3 (1974)
20. Hoover W G, Gray S G, Johnson K W *J. Chem. Phys.* **55** 1128 (1971)
21. Agrawal R, Kofke D A *Phys. Rev. Lett.* **74** 122 (1995)
22. Hiwatari Y et al. *Prog. Theor. Phys.* **52** 1105 (1974)
23. Zhakhovskii V V *JETP* **78** 871 (1994); *Zh. Eksp. Teor. Fiz.* **105** 1615 (1994)
24. Stishov S M *JETP* **103** 241 (2006); *Zh. Eksp. Teor. Fiz.* **130** 276 (2006)
25. Roland C M et al. *Rep. Prog. Phys.* **68** 1405 (2005)
26. Fragiadakis D, Roland C M *Phys. Rev. E* **83** 031504 (2011)
27. Lyapin A G, Gromnitskaya E L, Danilov I V, Brazhkin V V *RSC Adv.* **7** 33278 (2017)
28. Bailey N P et al. *J. Chem. Phys.* **129** 184507 (2008)
29. Gnan N et al. *J. Chem. Phys.* **131** 234504 (2009)
30. Ingebrigtsen T S, Schröder T B, Dyre J C *Phys. Rev. X* **2** 011011 (2012)
31. Coslovich D, Roland C M *J. Non-Cryst. Solids* **357** 397 (2011)
32. Dyre J C *J. Phys. Condens. Matter* **28** 323001 (2016)
33. Grzybowski A et al. *J. Phys. Chem. B* **114** 11544 (2010)
34. Bøhling L et al. *New J. Phys.* **14** 113035 (2012)
35. Danilov I V, Gromnitskaya E L, Brazhkin V V *J. Phys. Chem. B* **120** 7593 (2016)
36. Casalini R, Roland C M *J. Non-Cryst. Solids* **475** 25 (2017)
37. Meier K “Computer simulation and interpretation of the transport coefficients of the Lennard-Jones model fluid”, PhD Thesis (Hamburg: Helmut Schmidt Univ., 2002)
38. NIST Chemistry WebBook, https://webbook.nist.gov/chemistry/
39. Mourits F M, Rummens F H A *Can. J. Chem.* **55** 3007 (1977)
40. Dembovskii S A, Chechetkina E A *Stekloobrazovanie* (Moscow: Nauka, 1990)