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Citation:

BLAZHNOV, I. V., MALOMUZH, N. P. and LISHCHUK, S. V. (2004). Temperature dependence of density, thermal expansion coefficient and shear viscosity of supercooled glycerol as a reflection of its structure. *The Journal of Chemical Physics*, 121 (13), 6435-6441. [Article]

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Cite as: J. Chem. Phys. **121**, 6435 (2004); <https://doi.org/10.1063/1.1789474>

Submitted: 14 April 2004 . Accepted: 13 July 2004 . Published Online: 21 September 2004

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Temperature dependence of density, thermal expansion coefficient and shear viscosity of supercooled glycerol as a reflection of its structure

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(Received 14 April 2004; accepted 13 July 2004)

The relationship of the microstructure of supercooled, highly viscous glycerol to the temperature dependence of its density, thermal expansion coefficient, and shear viscosity are discussed. The character of this temperature dependence at the transition from low viscosity state to the solid amorphous state (solidified state without nuclei) is described with help of function ψ , which can be interpreted as the effective number of degrees of freedom responsible for the change of viscosity of glycerol over a broad range; these degrees of freedom are those related to the α -relaxation process. It is shown that the change in effective activation energy of the viscosity is completely determined by the parameter ψ . The change in the shear viscosity of glycerol due to the influence of the solid-phase nuclei is considered. It is shown that the introduction of the parameter φ , equal to the specific volume occupied by the nuclei of the solid phase, together with ψ provides a natural explanation of the temperature dependence of density and thermal expansion coefficients of glycerol in its liquid, solid amorphous, glassy, and crystal states. The peculiarities of the temperature dependence of $\varphi(T)$ and $\psi(T)$ for glycerol and *o*-terphenyl are compared. © 2004 American Institute of Physics. [DOI: 10.1063/1.1789474]

I. INTRODUCTION

The analysis of the experimental data obtained by the molecular light scattering, neutron and x-ray scattering^{1–8} indicates that the structure of glasses is microinhomogeneous. The microinhomogeneous structure of the silicate glass can be also directly seen on the electron microphotographs of its surface.⁹ The existence of microinhomogeneities effectively manifests itself in the following dependence of the integral intensity of molecular light scattering on the wave vector \mathbf{q} :

$$I(\mathbf{q}) \sim \frac{1}{[1 + (qr_c)^2]^p}. \quad (1)$$

The parameter p can take on different values.¹⁰ In particular, $p=1$ corresponds to the Ornstein-Zernike function and $p=2$ to the Debye function. The typical size r_c of microinhomogeneities reaches $10^2 - 10^3$ Å and significantly exceeds the characteristic molecular scale. Note, the quantity r_c does not have meaning of the density fluctuations correlation radius because in the glassy state there is no change of molecular configurations that form the structure of glass.

From the physical point of view the formation of the microstructure of glasses can be caused by the following main reasons.

(1) “Freezing-out” of the orientational configurations corresponding to the α -relaxation (see Refs. 11 and 12 for details).

(2) “Preservation” of the nuclei formed in supercooled states of the liquid phase of the system.

The existence of microinhomogeneities of the first type is the natural prerequisite for self-consistent description of the angular dependence of the polarized and depolarized light scattering in glasses.¹² Here the observable experimental regularities indicate that the size of the microinhomogeneities of this type is of the same order of magnitude as the wavelength of visible light.

The experimental data on the properties of highly viscous liquids suggests that the character of the thermal motion of the molecules in the temperature interval between the melting point T_m and the glassification point T_g ($\Delta T \approx 100$ K for glycerol) undergoes a rather specific change. The density of the system, its dielectric permeability, heat capacity, and other thermodynamic quantities outside this region change in a trivial way; i.e., quasilinearly with the temperature. This also applies to the shear viscosity activation energy.¹³ The listed quantities undergo significant changes only in the temperature interval ΔT . From the physical point of view, this is controlled by the clusterization processes¹⁴ that change the local structure and the orientational motion of the molecules most significantly. It is natural to characterize these changes by the parameter $\psi(T)$ which is interpreted as the effective number of the degrees of freedom responsible for the formation of the high viscosity states.

On the other hand, the nucleation process must take place in supercooled liquid. The supercooled states are metastable states in which the tendency to separation is manifested as nucleation. One should not exclude the possibility

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for the states of the system below glassification temperature to be below the spinodal (liquid-crystal). In this case the homogeneous states are impossible.^{15,16} The dependence of the properties of the system on the cooling rate¹⁷ and the existence of hysteresis in their temperature dependence¹⁸ can be regarded as confirmation of the existence of nucleation processes. The formation of nuclei of the new phase implies concurrent ordering of the positions of the molecular centers of mass, the spatial orientations of nonspherical molecules, the arrangement of H bonds, etc. Strong anisotropy of the intermolecular interaction, inherent to the glasses, at the finite cooling rate impedes the process of full ordering of molecules, thus resulting in the distinction of the nuclei structure and corresponding value of the free volume¹⁹ from that of the crystal phase. Further we will call such nuclei "imperfect." The degree of "imperfection" of nuclei influences the difference in the densities of glass ρ_g and crystal ρ_{cr} at the same temperature. On cooling the system the formation of the stable nuclei takes place in the temperature interval between the melting temperature T_m and the temperature T_s in which the time $\tau_n(T)$ of the formation of the nucleus is equal to the characteristic time τ_e of the experiment: $\tau_n(T_s) = \tau_e$. Therefore one can expect the temperature T_s to be close to the glassification temperature T_g .

The degree of nucleation can be described by the function $\varphi(T)$, which is equal to the specific volume occupied by the nuclei of the new phase.

Thus we come to the conclusion that the supercooled states of the glass-forming liquids are microinhomogeneous. The nuclei of the new phase (or strongly bound clusters^{14,20}), while being an important element of the structure, do not relate directly to the formation of the shear viscosity of the system. The latter is mainly formed by the liquid that surrounds the nuclei. At the same time, the nuclei noticeably affect the behavior of the thermodynamic quantities in an additive way. However, the behavior of the latter is even more determined by the function $\psi(T)$ that describes the behavior of the liquid outside nuclei. In the temperature interval ΔT its viscosity changes by 10–15 orders of magnitude, and the liquid transforms into an amorphous solid state. In the present work we intend to investigate the following.

(A) The relation between the temperature dependence of the shear viscosity and the freezing-out of the orientational degrees of freedom and the changes in the density of the system.

(B) The peculiarities of the behavior of the thermodynamic and kinetic quantities stipulated by the existence of nuclei in the supercooled states of the system.

The approach being developed allows the consistent description of the temperature dependence of all the thermodynamic and kinetic properties of glass-forming liquids. At that, in the temperature interval ΔT the temperature dependence is completely determined by two functions of state, $\varphi(T)$ and $\psi(T)$. In the present work these functions will be determined for glycerol. In future, this should allow them to be used to describe the temperature dependence of other thermodynamic quantities; the heat capacity, the dielectric permeability, the Debye-Waller factor, etc.

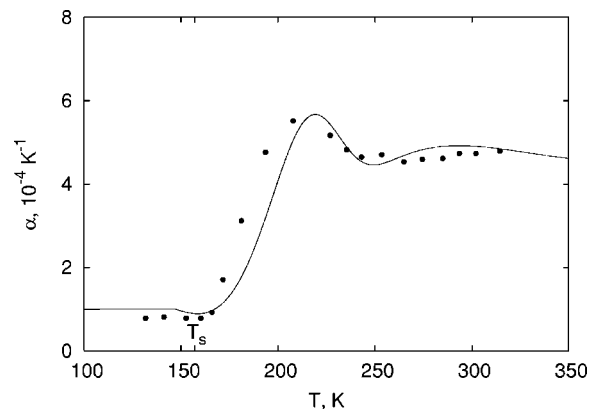


FIG. 1. Temperature dependence of the thermal expansion coefficient of supercooled glycerol. The points represent the experimental data (Ref. 18), the solid line corresponds to the Eq. (25).

II. NUCLEATION IN SUPERCOOLED HIGHLY VISCOUS STATES OF GLASS-FORMING LIQUIDS

In terms of concepts set forth in the Introduction, the density of the supercooled highly viscous liquid $\rho(T)$ can be approximated by the expression

$$\rho(T) = \varphi(T)\rho_n(T) + [1 - \varphi(T)]\rho_l(T), \quad (2)$$

$\rho_n(T)$ being the average density of nuclei (we neglect the variation of density in different nuclei), $\rho_l(T)$ being the density of the surrounding liquid.

The specific volume $\varphi(T)$ and the characteristic size of nuclei essentially depend on the cooling rate and the degree of supercooling of the system.²⁰ For example, the decrease in the density of the boron silicate glass at the increase in the cooling rate of melt observed in²¹ indicates in terms of our approach the decrease in the most slowly changing parameter φ .

In accordance with its physical sense, the parameter $\varphi(T)$ is characterized by the following properties.

(i) It takes on the constant value φ_s at temperatures $T < T_s$. Since the temperature dependence $\rho(T)$ below T_s is linear, the thermal expansion coefficient is constant. The value T_s bounding the region of the constant $\alpha(T)$ (see Fig. 1) appears to be slightly less than the glassification temperature T_g . The quantity φ_s is different for different glass-forming substances and depends both on the cooling rate and the nucleation rate in the system.

(ii) At temperatures $T > T_s$ the value of $\varphi(T)$ monotonously decreases until it reaches zero at the melting point T_m .

In the temperature interval $T_s < T < T_m$, the system is in supercooled states in which the microinhomogeneous structure forms and the rapid increase in the shear viscosity takes place. For the values of $\varphi(T)$ greater than φ_p the nuclei form an infinite percolation cluster. In the assumption of the spherical shape and monodisperse size distribution nuclei we can use the value $\varphi(T) \approx 0.29$ obtained from the Monte Carlo simulation.²² One can expect the temperature T_p , defined by the equation $\varphi(T_p) = \varphi_p$, to be close to the glassification temperature T_g (see also Ref. 14).

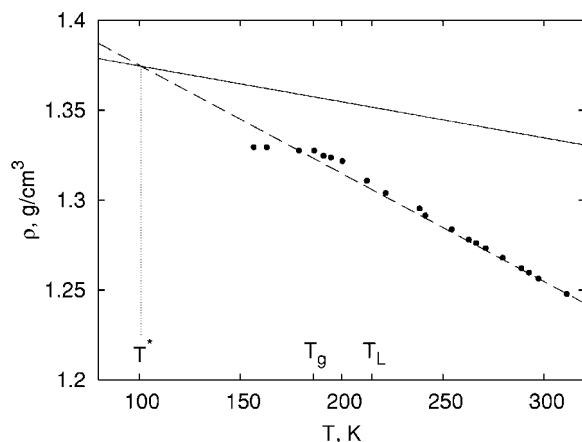


FIG. 2. Temperature dependence of the density of supercooled (points) and crystal (solid line) glycerol (Ref. 18). The dotted line corresponds to the linear approximation for the temperatures $T > T_L$.

To approximate the temperature dependence $\varphi(T)$ we have used the function

$$\varphi(T) = \begin{cases} \varphi_s \times \exp\left[-\left(\frac{T_s - T}{\Delta}\right)^4\right], & T_s < T \\ \varphi_s, & T \leq T_s \end{cases}, \quad (3)$$

which has all the necessary properties listed above. The parameter Δ determines the temperature interval in which the function $\varphi(T)$ undergoes the most significant change. The value of the power index (4) corresponds to the best approximation of the experimental data by the functions of the form $\exp\{-(T_s - T)/\Delta\}^p$.

In terms of our approach, the density of glass ρ_g is determined by the expression

$$\rho_g(T) = \varphi_s \rho_n(T) + (1 - \varphi_s) \rho_l^{(h)}(T), \quad (4)$$

$\rho_l^{(h)}$ being the density of the “solidified” liquid outside nuclei. The values of the parameters φ_s and Δ can be obtained by fitting the experimental data on the temperature dependence of the density and the thermal expansion coefficient.

Let T_L be the temperature below which the temperature dependence of the density of the supercooled liquid becomes different from linear, typical for the vicinity of the melting point (see Fig. 2). In terms of the presented approach this increase has a natural interpretation. Moreover, the radical change in the character of the temperature dependence of the density of the liquid surrounding nuclei in the temperature interval $T_s < T < T_L$ in the vicinity of the glassification point T_g should take place. Note, the absence of change in the character of the thermal motion in liquid would result in its density linearly extrapolated from the low viscosity region at $T < T_0$ (see Fig. 2) being greater than the density of the crystal phase ρ_{cr} which would be unacceptable.

III. CHANGE IN DENSITY OF LIQUID OUTSIDE NUCLEI IN PROCESS OF ITS SOLIDIFICATION

To describe the temperature dependence of the density of liquid $\rho_l(T)$ in the process of its solidification let us introduce the parameter ψ proportional to the number of the degrees of freedom responsible for the formation of highly vis-

cous states and manifested in α relaxation. From the physical point of view, the parameter ψ must have the following asymptotes:

$$\psi = \begin{cases} 1, & \text{in low viscosity states, } T > T_L \\ 0, & \text{in highly viscous states, } T < T_s \end{cases}, \quad (5)$$

gradually changing in the temperature interval between them. Therefore, the component ρ_l of density can be represented as

$$\rho_l = \rho_l^{(l)}(1 - \psi) + \rho_l^{(h)}\psi + \rho_l^{(i)}\psi(1 - \psi) + \dots, \quad (6)$$

where $\rho_l^{(l)}$ and $\rho_l^{(h)}$ should be identified as the values of the density of liquid in low viscosity and highly viscous amorphous states, and $\rho_l^{(i)}$ is the coefficient in the second-order term in the expansion of density in ψ .

The function ψ can be determined by fitting the experimental temperature dependence of the shear viscosity of supercooled glycerol.

IV. INFLUENCE OF NUCLEATION PROCESS ON SHEAR VISCOSITY OF THE SYSTEM

Similar to the increase in the concentration of the admixture particles in suspensions, the formation of nuclei must result in the change in the temperature dependence of the viscosity of liquid. The behavior of the shear viscosity of suspensions was an object of numerous investigations (see Refs. 23 and 24). When the specific volume of admixture particles is not too high the change in the viscosity of the system can be described by the Batchelor formula

$$\bar{\eta} = \eta_l(1 + 2.5\Phi + 6.2\Phi^2), \quad \Phi = \frac{R_0^3}{R_G^3}, \quad (7)$$

$\bar{\eta}$ being the viscosity of the system, η_l being the viscosity of the liquid, Φ being the specific volume of the admixtures in suspension, R_0 being the average radius of suspended particles, and R_G being the average interparticle distance. We can identify Φ with the function φ introduced above.

At $\Phi \geq 0.15$ the validity of the hydrodynamical perturbation theory used to derive the Batchelor formula is not justified. In this case we can employ the expression for the shear viscosity obtained in frames of the cell model²⁵

$$\bar{\eta} = \eta_l F(\gamma), \quad (8)$$

$$F(\gamma) = \frac{\gamma(1 - \gamma)}{\gamma(1 - \gamma) + 1 - \sqrt{1 + 2\gamma^2(1 - \gamma)}}. \quad (9)$$

Here, $\gamma = R_0^3/R^3$ and R is the cell radius determined by the relation

$$R = (\alpha_0 + \alpha_1\Phi + \alpha_2\Phi^2)R_G. \quad (10)$$

The expansion coefficients take on the following values:²⁵ $\alpha_0 = 0.93$, $\alpha_1 = 0.127$, $\alpha_2 = 0.03$, and

$$\gamma = \frac{6\varphi}{\pi(\alpha_0 + \alpha_1\varphi + \alpha_2\varphi^2 + \dots)^3}, \quad (11)$$

where φ is identified with Φ as above. At small Φ Eq. (8) reduces to the Batchelor formula. However, Eq. (9) remains valid for Φ up to the value 0.49 corresponding to the dense random packing of the admixture particles.²⁶

The extension of the applicability region of the hydrodynamic description of the shear viscosity is due to the account of the rotational motion of the admixture particles. This gives the hydrodynamic flows, inside and outside the cell, a symmetry consistent with the spherical symmetry of the cell.

The viscosity of the liquid outside nuclei should be taken as the shear viscosity η_l . The magnitude and the temperature dependence of η_l is discussed in the following section. Here we note in advance that the temperature dependence of η_l plays a crucial role.

V. CHANGE IN SHEAR VISCOSITY OF LIQUID IN PROCESS OF ITS SOLIDIFICATION

The introduction of the parameter ψ proportional to the effective number of the orientational degrees of freedom which “freeze” in the amorphous solid states of the system enables in describing the temperature dependence of the shear viscosity η_l . The viscosity of many liquids consisting of the anisotropic molecules is satisfactorily described by the formula

$$\eta_l = \eta_0 \exp\left(\frac{E_a}{k_B T}\right), \quad (12)$$

E_a being the activation energy. The qualitative reasons in favor of such a representation were given in Refs. 27 and 28. We note that the activation energy determined from isobaric measurement of the viscosity appears to be dependent on temperature due to the effect of the thermal expansion. Therefore, one should use the isochoric viscosity of the system to determine the activation energy E_a (see the Appendix).

Let T_B be the Stickel temperature at which the asymptotes of $\ln \eta$ as a function of $1/T$ in low and highly viscous regions intersect (see Fig. 4). Then far from T_B ($T > T_B$) the temperature dependence of the shear viscosity η_l of the supercooled liquid outside nuclei is described by the formula

$$E_a = E_a^{(l)} + b^{(l)}(T_\eta - T), \quad T > T_\eta, \quad (13)$$

$E_a^{(l)}$ denoting the isochoric value of the activation energy.

Similarly, at temperatures $T < T_B$ far from T_B the activation energy is represented in the form

$$E_a = E_a^{(h)} + b^{(h)}(T_\eta - T). \quad (14)$$

Taking $\eta_0 = 10^{-2}$ Pa s we obtain the following values of the parameters entering Eqs. (13) and (14):

$$\begin{aligned} E_a^{(l)}/k_B T_m &= 11, & E_a^{(h)}/k_B T_m &= 18, \\ b^{(l)} &= 18.4, & b^{(h)} &= 62.3. \end{aligned} \quad (15)$$

For $\eta_0 = 10^{-1}$ Pa s

$$\begin{aligned} E_a^{(l)}/k_B T_m &= 9.5, & E_a^{(h)}/k_B T_m &= 16.5, \\ b^{(l)} &= 20.7, & b^{(h)} &= 64.6. \end{aligned} \quad (16)$$

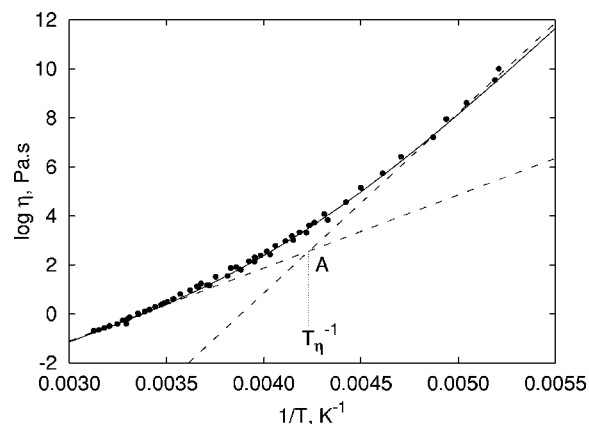


FIG. 3. Temperature dependence of the parameters φ [Eq. (3)] and ψ [Eq. (19)].

Since near T_η the parameter ψ undergoes the most essential changes, the temperature dependence of E_a and b can be approximated by the formulas similar to Eq. (6) for the density

$$E_a(\psi) = E_a^{(l)}(1 - \psi) + E_a^{(h)}\psi + E_a^{(i)}\psi(1 - \psi) + \dots, \quad (17)$$

$$b(\psi) = b^{(l)}(1 - \psi) + b^{(h)}\psi + b^{(i)}\psi(1 - \psi) + \dots. \quad (18)$$

The behavior $\psi(T)$ can be approximated by the function

$$\psi(T) = \begin{cases} 1 - \exp\left[-\left(\frac{T - T_\psi}{\Delta_\psi}\right)^2\right], & T > T_\psi, \\ 0, & T \leq T_\psi \end{cases} \quad (19)$$

with $T_\psi = 147$ K, $\Delta_\psi = 100$ K (see Fig. 3). The inaccuracy in determination of these quantities is 10 K by the order of magnitude.

The results of fitting the experimental data on the shear viscosity with help of Eqs. (12)–(14), (17), and (18) are presented in Fig. 4. The parameters $b^{(i)}$ and $E_a^{(i)}$ do not depend on the value of η_0 and take on the following values:

$$b^{(i)} = 4, \quad E_a^{(i)} \approx 0. \quad (20)$$

It is not difficult to see that $b^{(i)}$ is proportional to the distance between the Stickel point A and the curve $\ln \eta(T)$

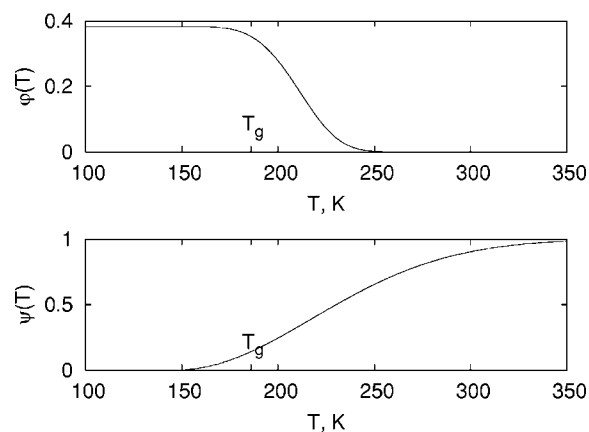


FIG. 4. Temperature dependence of the shear viscosity of supercooled glycerol. Experimental data are taken from Ref. 29.

corresponding to experimental data and therefore takes on large values for the substances that are “fragile” according to the Angell’s classification.³⁰

The fact that the substitution of the parameter ψ obtained from the temperature dependence of the effective activation energy of viscosity into the Eq. (6) enables rather successful reconstruction of the change in the density of the solidifying liquid in the vicinity of T_η , is of particular importance.

VI. DETERMINATION OF NUMERICAL VALUES OF $\varphi(T)$

One can distinguish three different regions in the plot of the temperature dependence of the density: (i) the temperature interval $T > T_L$, where the system under consideration is liquid in a low viscosity state; (ii) the transition region $T_s < T < T_L$ containing the glassification temperature T_g , where the nucleation processes take place; (iii) the temperature interval $T < T_s$ corresponding to glass.

The density $\rho(T)$ in the regions (i) and (iii) is well approximated by the linear dependence

$$\begin{aligned}\rho_g(T) &= \rho_g^{(0)}(1 + \alpha_g T), & 0 < T \leq T_s, \\ \rho_l(T) &= \rho_l^{(0)}(1 + \alpha_l T), & T_L \leq T\end{aligned}\quad (21)$$

with the following numerical values of the coefficients:

$$\begin{aligned}\rho_g^{(0)} &= 1.314 \text{ g/cm}^3, & \alpha_g &= 1.33 \times 10^{-4} \text{ K}^{-1}, \\ \rho_l^{(0)} &= 1.271 \text{ g/cm}^3, & \alpha_l &= 6.01 \times 10^{-4} \text{ K}^{-1}.\end{aligned}\quad (22)$$

We assume that (a) the average density of the substance inside nucleus is greater than the density of liquid ρ_l , but less than that of crystal ρ_{cr} , and (b) the structure of nuclei after their formation does not change. Therefore the density of nuclei $\rho_n(T)$ can be also approximated by the linear dependence

$$\rho_n(T) = \rho_n^{(0)}(1 + \alpha_n T). \quad (23)$$

The first of these assumptions follows from the difference in the degree of ordering in the phases under consideration. Let the density of the system and its derivative with respect to temperature be continuous at T_s ,

$$\begin{cases} \rho_g(T_s) = \varphi_s \rho_n(T_s) + (1 - \varphi_s) \rho_l(T_s) \\ \alpha_g = \varphi_s \alpha_n + (1 - \varphi_s) \alpha_l \end{cases}, \quad (24)$$

where

$$\alpha(T) = -\frac{1}{\rho(T)} \frac{\partial \rho(T)}{\partial T} \quad (25)$$

and the behavior of $\rho_l(T)$ is described by Eq. (6). Then there are five parameters: $\rho_n(T_s)$, $\alpha_n(T_s)$, T_s , φ_s , and Δ to be independently determined from the experimental data. The best fit of the experimental data on the temperature dependence of the density and the thermal expansion coefficient is achieved at

$$\begin{aligned}\rho_n(T_s) &= 1.351 \text{ g/cm}^3, & \alpha_n(T_s) &= 1.33 \times 10^{-4} \text{ K}^{-1}, \\ T_s &= 157 \text{ K}, & \varphi_s &= 0.35, & \Delta &= 43 \text{ K}.\end{aligned}\quad (26)$$

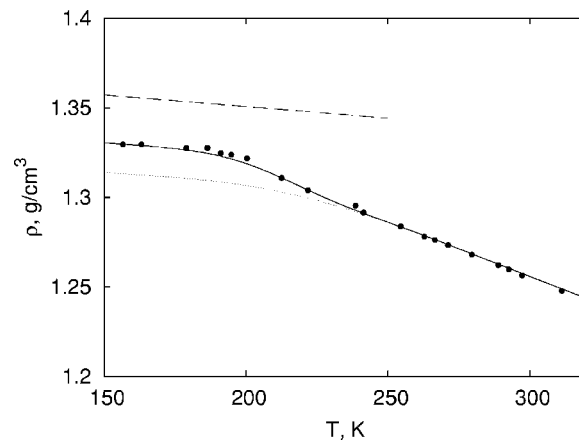


FIG. 5. Extrapolation of the temperature dependence of the density of supercooled glycerol by Eqs. (2), (3), and (23). The lines represent $\rho(T)$ (solid line), $\rho_n(T)$ (dashed line), and $\rho_l(T)$ (dotted line). The points correspond to the experimental data (Ref. 18).

The inaccuracy in the determination of these quantities is different, but it does not exceed 15%. The temperature dependence of the density is presented in Fig. 5.

The thermal expansion coefficients of liquid, crystal, and nucleus satisfy the inequalities similar to that for their densities,

$$\begin{cases} \rho_l < \rho_n < \rho_{cr} \\ \alpha_l < \alpha_n < \alpha_{cr} \end{cases}. \quad (27)$$

VII. CONCLUSION

Main attention in the presented work has been focused upon the peculiarities of the temperature dependence of the shear viscosity, density, and thermal expansion coefficient of glass-forming liquids. It has been shown that the character of the temperature dependence of the stated quantities is determined first of all by (i) the nucleation processes and (ii) the freezing-out of the orientational degrees of freedom in the liquid that surrounds nuclei. The first mechanism enables the natural explanation of the difference in the densities and the thermal expansion coefficients of the system in crystal and glassy states as well as in the liquid surrounding nuclei that gradually goes over to the amorphous solid state. The second assumption, on the freezing-out of the orientational degrees of freedom, is closely related to the α relaxation being the slowest relaxation process in the system. The freezing-out of certain degrees of freedom under cooling must also influence the character of the thermal expansion of the system and the temperature dependence of its density. At the same time, “switching off” a number of the intermediate states of the system results in the increase in the potential barriers separating its available states. This is supported by the character of the temperature dependence of the activation energy.

The thermal motion of molecules in the supercooled liquid can be also characterized by the mean square displacements $\langle \Delta \theta^2 \rangle$ and $\langle \Delta \mathbf{r}^2 \rangle$ of the angular and linear coordinates of molecules from their local equilibrium values. One might expect the following expansion, similar to the expansion for the activation energy, to be valid:

TABLE I. The effective activation energy of nitrogen.

N ₂			
$\rho = \text{const}$		$P = \text{const}$	
ρ (g/cm ³)	$E_{\eta}^{(\rho)}/k_B T_a$	P (atm)	$E_{\eta}^{(P)}/k_B T_a$
0.316	-0.02	250	2
0.746	0.2	500	1.95
0.807	0.42	2000	2.22
0.857	0.54		
1.000	0.76		

$$\langle(\Delta x)^2\rangle = \langle(\Delta x^{(l)})^2\rangle(1 - \psi) + \langle(\Delta x^{(h)})^2\rangle\psi + \dots, \quad (28)$$

where Δx is equal to either $\Delta\theta$ or $\Delta\mathbf{r}$. Consequently, the behavior of the shear viscosity and density turns out to be related to the properties of the second moment $(\Delta x)^2$. The deviation of $\langle\Delta x^2\rangle$ from the linear dependence on $(1/T)$ can also serve as a measure of fragility.

The formulas (12)–(14), (17), and (18) can be also used to fit the experimental data on the temperature dependence of the shear viscosity of *o*-terphenyl.³¹ At $\eta_0 = 10^{-2}$ Pa s the corresponding parameters take values

$$\begin{aligned} E_a^{(l)}/k_B T_m &= 5, & E_a^{(h)}/k_B T_m &= 22, \\ b^{(l)} &= 0.7, & b^{(h)} &= 59.0, \\ b^{(i)} &= 10.5, & E_a^{(i)} &= 0. \end{aligned} \quad (29)$$

According to Angell's classification, *o*-terphenyl is one of the most fragile substances. The equality $b_{\text{OTP}}^{(i)} = 2.34b_{\text{Glycerol}}^{(i)}$ justifies the use of the parameter $b^{(i)}$ as a measure of the fragility.

Note, the temperature dependence of the viscosity of glass-forming liquids was considered previously.^{32–34} The formulas for the temperature dependence of the activation energy proposed therein can be considered as model expressions, first of all, for the function $\psi(T)$.

The advantage of the approach being developed is that the introduction of the functions $\varphi(T)$ and $\psi(T)$ provides natural description of the temperature dependence of different thermodynamic quantities and transport coefficients in the glass transition region. In particular, the use of the functions $\varphi(T)$ and $\psi(T)$ allows the successfully recovery of the behavior of the Debye-Waller factor as a function of temperature and wave vector, the behavior of the heat capacity, dielectric permeability, static sound velocity, and other properties of the highly viscous liquids. These problems will be considered in future publications.

The problem of the physical nature of the temperature dependences of $\varphi(T)$ and $\psi(T)$ is of particular interest.

The number n_H of H bonds per molecule also undergoes an essential change in the supercooled highly viscous region, thus, allowing the identification of the parameter ψ with the quantity $(1 - n_H)$. The detailed analysis of this question is out of the scope of the present paper.

Another important problem that requires separate consideration is the influence of the cooling rate on the function $\varphi(T)$.

TABLE II. The effective activation energy of neon.

Ne			
$\rho = \text{const}$		$P = \text{const}$	
ρ (g/cm ³)	$E_{\eta}^{(\rho)}/k_B T_a$	P (atm)	$E_{\eta}^{(P)}/k_B T_a$
1.160	0.14	300	1.78
1.230	0.239	400	1.78
1.312	0.461	500	1.83
1.340	0.56	750	1.98
1.377	0.752	1000	2.29

APPENDIX: ISOCHORIC AND ISOBARIC VALUES OF ACTIVATION ENERGY

To investigate the influence of the effect of the thermal expansion of the system consider the change in the viscosity of neon and nitrogen on the isochors, isobars, and liquid-gas coexistence line.

The detailed data of this kind for these, as well as for other liquids in a broad region of existence of their states are available.^{35,36} They are typically characterized by the weak linear dependence of the logarithm of viscosity $\ln \eta$ on inverse temperature $1/T$ on the isochors. The corresponding values of the effective activation energy $E_{\eta}^{(\rho)} = d \ln \eta / d(1/T)$ are presented in Tables I and II (T_a denotes the average temperature in the investigated region).

Remarkably, the isochoric values of the activation energy of viscosities are less than the energy of the thermal noise both for Ne and N₂. Moreover, for densities less than the critical density the activation energy appears to be negative. As a matter of fact, this indicates the nonactivation character of the viscous process in simple liquids as well as in more complex molecular liquids.

At the same time, the isobaric values of the activation energy are about two times greater than the thermal noise. Furthermore, the dependence of $\ln \eta$ on $1/T$ on the isobars is noticeably nonlinear. This is the consequence of the influence of the thermal expansion effects. In other words, the effective values of the isobaric activation energy are the functions of temperature: $E_{\eta}^{(\text{eff})} = E_{\eta}^{(\text{eff})}(T)$. We emphasize that the inequality $E_{\eta}^{(\text{eff})}/k_B T_a > 1$ cannot be considered as the evidence of the activation nature of the viscosity formation process.

The temperature dependence of the activation energy of viscosity on the liquid-gas coexistence line appears to be even more complicated. Apparently, this conclusion remains valid for the liquids with more complex molecular structure, particularly for glass-forming liquids.

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