Role of orientation disorder in the formation of fragility of glassy water and glycerol-like liquids

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The role of H bonds in the formation of the fragility and dielectric properties of highly viscous liquids is investigated. The heuristic supposition about the proportionality between the logarithm of the shear viscosity and oscillatory contributions to the mean-square displacement of a molecule is presented. Concrete calculations are carried out for the H-bond subsystem of the two-dimensional model lattice water. The conjecture on the interrelation between the phase transition in the subsystem of H bonds and the glassification point is formulated. It is shown that (i) the glassification temperature is proportional to the H-bonding energy and (ii) the fragilities of glycerol-like liquids differ from each other as a consequence of distinct interaction energies between H bonds. The existence of a close connection between the fragility parameter and dielectric permittivity is established.

I. INTRODUCTION

Presently, peculiarities of highly viscous states of liquids and their transition to glasslike states are treated within the phenomenological representations [1–3]. In such a picture the glassification is the kinetic phenomenon, and some nontrivial properties of highly viscous states, in the first place, the specificity of nonequilibrium behavior, find satisfactory qualitative explanation. However, in order to understand the nature of the static shear viscosity and the fragility of systems, the microscopic features of the thermal motion of molecules should be taken into account [4]. It seems that the interconnection between microscopic and macroscopic properties of systems near the glassification point is revealed to the greatest extent for spin systems, the interaction constants of which are the random quantities [5,6].

The main attention in the present paper is focused on microscopic prerequisites of the glass transition in glycerol-like liquids in which H bonds are the most characteristic peculiarities of the intermolecular interaction. More exactly, we suppose that the change of the H-bonds ordering is a necessary condition for the glass transition in such liquids. In connection with this, we study in detail the influence of the H-bond network on the fragility and dielectric permittivity. For this purpose we use the two-dimensional lattice water model proposed in Ref. [7]. We suppose the most general properties of the H-bond subsystem in water to remain qualitatively the same for glycerol and glycerol-like liquids. More exactly, we will analyze the specificity of the orientation disorder in liquids with developed H-bond network.

Let us consider the definition of the fragility parameter and its connection with the properties of the H-bond subsystem. It follows from the macroscopic definition of the fragility [8–11],

$$f_M = \left. \frac{\partial \log_{10} \eta}{\partial (T_g/T)} \right|_{T=T_g}, \qquad (1)$$

that this problem is related to the origin of the shear viscosity η. Furthermore in Ref. [4,12], the microscopic fragility parameter

$$f_m = \left. \frac{d(u_0^2/\langle u^2 \rangle_l)}{d(T_g/T)} \right|_{T=T_g}, \qquad (2)$$

proportional to f_M, is introduced. Here

$$\langle u^2 \rangle_l = \langle u^2 \rangle_{dis} - \langle u^2 \rangle_{ord} \qquad (3)$$

and $\langle u^2 \rangle_{dis}$ and $\langle u^2 \rangle_{ord}$ are the mean-square displacements of a proton caused by vibrational degrees of freedom in disordered (as determined from elastic neutron scattering data [12]) and crystal-like state, respectively, u_0^2 is the characteristic increment of $\langle u^2 \rangle_{dis}$ about a point $T=T_g$. Note that the quantity $\langle u^2 \rangle_{dis}$ also enters in the incoherent cross section for cold neutrons as the Debye-Waller factor

$$f_{dw} = \exp\left(-\tfrac{1}{6}\langle u^2 \rangle_{dis} \vec{k}^2\right), \qquad (4)$$

where $\vec{k}$ is the transfer wave vector for scattered neutrons.

It was shown in Refs. [4,12] that the proportionality between f_M and f_m takes place for many glycerol-like glass-forming liquids. This fact allows one to suggest that f_m can serve as a microscopic measure of fragility.

This microscopic definition (2) is very useful for the investigation of the role of H bonds in the formation of fragility. In general, molecules drift and rotate. As a result, the displacements of protons, which give the main contribution to the neutron scattering, can be represented in the form

$$\langle u^2 \rangle_{dis} = \langle u^2 \rangle_{tr} + \langle u^2 \rangle_{rot}, \qquad (5)$$

where the subscripts "tr" and "rot" denote the terms caused by the translational and rotational motions. Using the results for the hexagonal ice [13], one can show that the contributions $\langle u^2 \rangle_{tr}$ and $\langle u^2 \rangle_{rot}$ are practically the same: $\langle u^2 \rangle_{tr} \approx \langle u^2 \rangle_{rot}$. It seems natural that the similar relation between $\langle u^2 \rangle_{tr}$ and $\langle u^2 \rangle_{rot}$ exists also for highly viscous states in which the average number of H bonds per molecule is close to that for the corresponding crystal. Therefore, the careful study of orientation disorder and rotational oscillations is very important to understand the nature of the fragility.
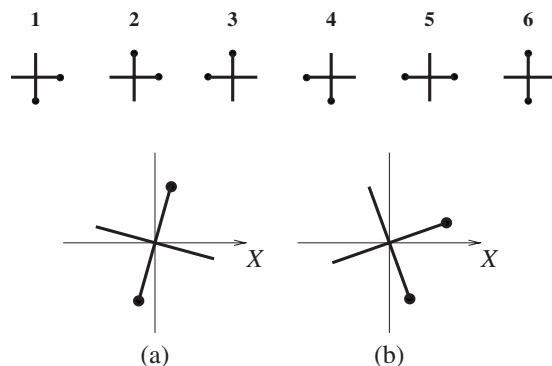
FIG. 1. Schematic representation of the model with the six ways ($\alpha = 1 \ldots 6$) of arranging the protons (solid circles) of a "flat" water molecule at fixed orientation of active ends (top), and specification of the state of a molecule at the site: (a) $\alpha = 6$, $\varphi = -15°$; $\alpha = 2$, $\varphi = 20°$. The state of the ith molecule is unambiguously described by the set of two variables $\{\alpha, \varphi\}_i$.

H bonds play a very important role also in water. Equation (2) can therefore be used for determination of the fragility of the H-bond network in water. Here the main problem is related to the correct account of the strong correlations between H bonds. For three-dimensional water this problem still remains unsolved. However, the effective methods were developed for the description of the strong H-bond correlations in two-dimensional lattice water [7]. It was shown that at a certain temperature the H-bond network undergoes a sharp first-order phase transition at which the number of H bonds per molecule considerably changes. As it follows from the qualitative arguments formulated above, we expect $\langle u^2 \rangle_{dis}$ to change essentially as well. In real water the translational motion of molecules will smear the sharp phase transition. However, the tendency in the behavior of $\langle u^2 \rangle_{dis}$ should remain.

In accordance with our intentions formulated above, we consider (i) the most important details of the phase transition in the subsystem of the H-bond network in two-dimensional water; (ii) the temperature dependence of the oscillatory contributions to $\langle u^2 \rangle_{dis}$ and similar characteristics as well as some correlation functions for the angular variables that describe thermal motion in lattice system; (iii) H-bond contributions to the fragility and dielectric permittivity.

II. MODEL HAMILTONIAN

The lattice model of the two-dimensional water [7] is the generalization of two-dimensional model of Pauling ice [14]. In this model four active ends of a molecule—two donor and two acceptor—are located at the ends of the perpendicular line segments. Contrarily to the Pauling ice model, molecules can rotate about the axis perpendicular to the crystal plane. The state of the ith molecule is unambiguously described by the set of two variables $\{\alpha, \varphi\}_i$ (see Fig. 1). The discrete variable α_i can take 6 values, just as in the case of Pauling ice. This variable enumerates the discrete states, corresponding to all possible dispositions of two "negative charges" on four ends of the crosslike molecule. In any of

these states ith molecule can rotate on the angle φ_i. For unambiguous description of rotations it is necessary to restrict changes of the angular variable by limits: $-\pi/4 \leqslant \varphi_i \leqslant \pi/4$. Note that in the Pauling ice model there are only six discrete states for a molecule. It is assumed that the states of two nearest neighbors, turned to each other by the same ends (charges), are forbidden. This assumption takes place in our model only if the rotation angles φ_i, φ_j of the nearest molecules do not exceed some limiting value:

$$|\varphi_i|, |\varphi_i| < \Phi. \tag{6}$$

The value of Φ is implied to be close to the amplitude of the angular oscillations of water molecules in ice, therefore $\Phi < (\ll) \pi/4$. We choose the parameter Φ in such a way that

$$d = \frac{\pi}{4 - \Phi} \Big/ \Phi = 8. \tag{7}$$

An H bond between the nearest neighbors forms if (1) the rotation angles satisfy the inequality (6), and (2) the discrete variables α_i, α_j set the compatible states, in which molecules are turned to each other by ends with opposite charge. The H-bonding energy is set to $-\mu_0$, and remains the same for all φ_i, φ_j that satisfy condition (6). If any of these angles exceeds Φ, the H bond does not form and the energy of such a state is zero.

Thus, the energy of intermolecular interaction is equal to

$$
\varepsilon_H(\alpha_i, \varphi_i; \alpha_j, \varphi_j)
= \begin{cases}
+\infty, & \text{if } \alpha_i, \alpha_j \text{ are noncompatible}, & |\varphi_i|, |\varphi_j| < \Phi, \\
-\mu_0, & \text{if } \alpha_i, \alpha_j \text{ are compatible}, & |\varphi_i|, |\varphi_j| < \Phi, \\
0, & \text{if } |\varphi_i| > \Phi \text{ and (or)} & |\varphi_j| > \Phi.
\end{cases}
\tag{8}
$$

In real water the interaction of H bonds is also essential. To model this interaction, we use the following reasons. The most symmetric and energetically profitable configuration in the distribution of protons and the electron density corresponds to the configuration, in which a molecule forms four H bonds with its nearest neighbors. Due to this, we choose the interaction energy as

$$
\varepsilon_{HH}(i, \{j\}_i) = \begin{cases}
-\gamma\mu_0, & \gamma \ll 1, & \text{if } (n_H)_i = 4, \\
0, & \text{in the opposite case,}
\end{cases}
\tag{9}
$$

where $\{j\}_i$ denotes four neighbors of the ith molecule. Since the interaction energy depends on the states of five molecules (including a central molecule and four of its nearest neighbors), the irreducible five-particle interaction should be taken into account in concrete calculations. As a result, the Hamiltonian of the system can be represented in the form

$$H = \sum_{\langle i,j \rangle} \varepsilon_H(i,j) + \sum_{i,\{j\}_i} \varepsilon_{HH}(i, \{j\}_i) \tag{10}$$

where symbol $\langle i,j \rangle$ denotes the nearest neighbors. For real three-dimensional (3D) water other mechanisms of the H-bonds interaction are also important [15,16].

We will henceforth put $\mu_0 = 1$, which is equivalent to measuring temperature in units of μ_0.
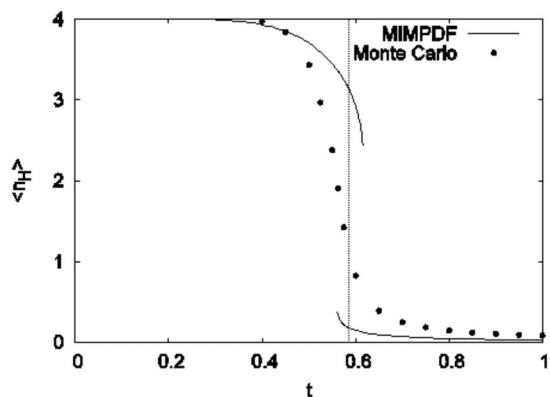
FIG. 2. Temperature dependence of the average number of H bonds per molecule as obtained with MMPIDF in nine-particle approximation (solid line) and Monte Carlo simulation (circles). $t = T/\mu_0$ is the dimensionless temperature.

III. PHASE TRANSITION IN THE SUBSYSTEM OF H BONDS

To investigate the phase diagram of the lattice water model, the Monte Carlo (MC) simulation of the system described by the Hamiltonian equation (10) was undertaken. At each simulation, a random initial configuration of the system was chosen on a 256×256 square lattice. A classical Metropolis MC algorithm [17,18] was used. After $10^8 – 10^9$ equilibration steps, the averages were accumulated for 10^8 MC steps.

The temperature dependence of the average number of H bonds per molecule, $\langle n_H \rangle(t)$, where $t = T/\mu_0$ is dimensionless temperature, is presented in Fig. 2 for $\gamma = 0$. It manifests a smooth transition from the two-dimensional ice state ($\langle n_H \rangle \approx 4$) to the liquid state ($\langle n_H \rangle \ll 4$). Figure 3 demonstrates the dependence of the transition temperature, defined as the temperature at which $\langle n_H \rangle = 2$, upon the value of the parameter γ [see Eq. (9)]. Note that, rigorously speaking, the temperature t_0 of the phase transition should be determined from the con-
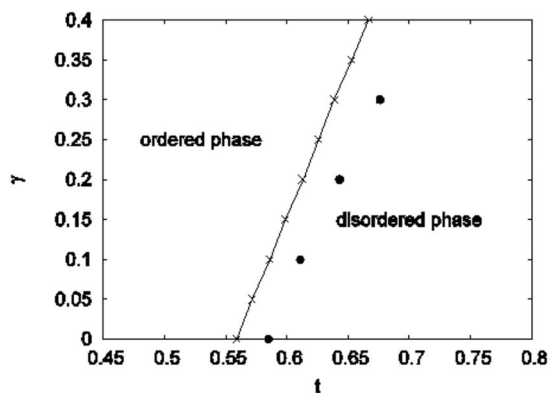

FIG. 3. Phase diagram of lattice water model. The temperature of the phase transition, defined as the temperature at which $\langle n_H \rangle = 2$, at different values of the parameter γ was obtained with MMPIDF (circles) and Monte Carlo simulation (crosses). Solid line is a guide to eye.

dition $F_{ord}(t_0) = F_{dis}(t_0)$, where F_{ord} and F_{dis} are the free energies of the system in ordered and disordered states. Applying to Ref. [7], one can show that the value determined in such a way is very close to $\tilde{t}_0$ calculated from the equation $n_H(\tilde{t}_0) = 2$.

As it can be expected for the system with finite number of microscopic states, the water model does not manifest sharp transition on a finite lattice. This problem can be overcome in MC simulations by using finite size scaling [18]. This has indeed been done in several other lattice models with success [19–21]. However, in the present paper we will use the method of many-particle irreducible distribution functions (MMPIDF) for further investigation.

MMPIDF is a method developed by the authors [22] and is the generalization of the Kikuchi cluster variational method [23] and of the Bethe-Peierls quasichemical approach [24]. The distinctive feature of this method is the perturbation theory, in which the order of approximation is determined by the size of the compact cluster taken into account in the calculations. MMPIDF essentially improves the results obtained within the mean-field approximation if the correlation radius noticeably exceeds the interparticle spacing. This method fills the gap between the mean-field approximation, in which the correlation radius is zero, and the renormalization-group approach, in which the correlation radius tends to infinity.

The method has been applied to the lattice water model [7], starting from the consideration that the most symmetric and energetically favorable configuration of the electron and proton density distribution occurs when a molecule forms four H bonds with its nearest neighbors. Hence for the interaction energy of the bonds the form (9) has been chosen.

The MMPIDF allows us to conclude that in the subsystem of H bonds the first-order phase transition takes place at $t = t_0$. However, it is necessary to note the following peculiarities of different approximations. The character of the phase diagram is especially sensible to the values of two key parameters of the Hamiltonian: γ and d. For $d = 8$, noted above, the states of the system change continuously for $\gamma < 0.22$ in two-particle approximation and for $\gamma < 0.17$ in four-particle approximation. In the narrow temperature interval the average number of H bond per molecule decreases from $n_H \approx 4$ up to $n_H \approx 0$. In the nine-particle approximation the transition between these states is sharp for all $\gamma \geq 0$. In this approximation the ordered ($n_H \approx 4$) and disordered ($n_H \approx 0$) metastable phases can also exist. The former is observed at $t_0 < t < t_1(\gamma)$ and the latter at $t_2(\gamma) < t < t_0$. Thus $t_1(\gamma)$ or $t_2(\gamma)$ can be interpreted as the spinodal points. At approaching $t_1(\gamma)$ or $t_2(\gamma)$ from the side of the metastable states, heat capacity of the system diverges. Note that the intervals $t_1(\gamma) - t_0$ and $t_0 - t_2(\gamma)$ depend also on the order of approximation: they are the narrowest in the nine-particle approximation.

The dependence of t_0 on γ obtained in the nine-particle approximation is shown in Fig. 3. It is evident from the inspection of the average $\langle (\delta \delta_H)^2 \rangle$ calculated by the MMPIDF method and presented in Fig. 4 that the spinodals of the system are situated above and below t_0, which explains the essential increase in $\langle (\delta n_H)^2 \rangle$ near t_0.

Here the impression can appear that the first-order phase transition is an artifact, arising in higher orders of the pertur-
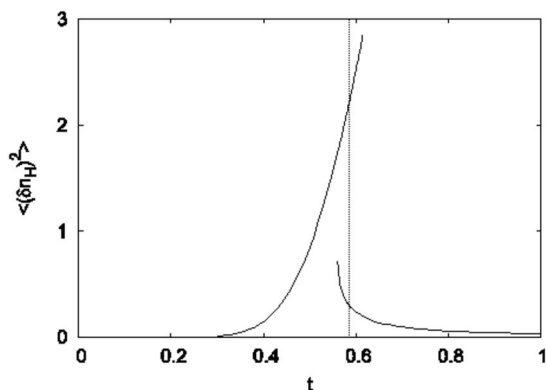
FIG. 4. Dispersion $\langle(\delta n_H)^2\rangle$ of the number of H bonds per molecule, calculated by the MMPIDF method, versus temperature. The spinodals of the system are situated above and below t_0, which explains the essential increase in $\langle(\delta n_H)^2\rangle$ near t_0.

bation theory. To clarify this question, let us consider the character of the phase transition at other values of the parameter d. One can show that the phase transition for $\gamma=0.3$ is continuous in all orders of the perturbation theory if $d<d_0$, where $d_0\approx5$. In the opposite case $(d>d_0)$ the phase transition becomes sharp, and this conclusion does not depend on the order of the perturbation theory. Thus, the consideration of fine correlation effects is essential to identify the character of the phase transition only for the boundary value $d=d_0$. It is necessary to emphasize that the regular description of correlations in the MIMPDF method is not equivalent to the mean-field approximation. Even the minimal two-particle approximation in our approach is finer than standard versions of the mean-field description. In connection with this we note that the correspondence can be established between our model, in which φ changes continuously, and the discrete models investigated in [25,26]. In [26] a version of the mean-field approximation was developed. Within this approximation it was shown that for large enough values of parameter q, related to Φ in our model, the subsystem of H bonds undergoes to the first-order phase transition. Note, that the dimensionless temperature t_0 for the phase transition is a function of the both key parameters: $t_0=t_0(\gamma,d)$. The calculations show that t_0 diminishes when d increases. In particular, in the approximation of two variational parameters $t_0(0.31,8)=0.63$ and $t_0(0.31,32)=0.41$. The similar dependence of t_0 upon the parameter describing the sharpness of H bonds is also expected for the three-dimensional systems. Therefore, an estimate $t_0\sim0.1$ seems to be quite reasonable in this case, i.e., the phase transition in the subsystem of H bonds takes place at the room temperatures or lower ones.

The passage from lattice to disordered disposition of water molecules is accompanied by the effective change of Φ or q (see [26]), and therefore it can lead to the smearing of the phase transition in the subsystem of H bonds. In this case the situation is in many respects similar to that for spin systems with random distribution of the interaction constants [5,6].

In the following section we will use MMPIDF to calculate the equilibrium correlation functions.

IV. EQUILIBRIUM FLUCTUATIONS AND CORRELATION FUNCTIONS

The macroscopic thermodynamic functions, which are the most important in our consideration, are immediately related to the equilibrium averages $\langle\varphi^2\rangle$, $\langle\varphi^4\rangle$ and the correlation function $\langle\varphi_1^2\varphi_2^2\rangle$, where 1 and 2 denote pairs of the nearest neighbors (due to spatial homogeneity, the averages $\langle\varphi_i^2\rangle$, $\langle\varphi_j^2\rangle$ and $\langle\varphi_i^2\varphi_j^2\rangle$, where i and j denote pairs of nearest neighbors, do not depend on the choice of i and j). To calculate the value of $\langle\varphi^{2n}\rangle$, the one-particle distribution function $g_1(\alpha,\varphi)$ is needed,

$$\langle\varphi^{2n}\rangle = \sum_{\alpha=1}^{6}\int_{-\pi/4}^{\pi/4}\varphi^{2n}g_1(\alpha,\varphi)d\varphi, \quad n=1,2,\ldots . \quad (11)$$

In our model, the function $g_1(\alpha,\varphi)$ is independent of the parameter α and is a "piecewise" continuous function of the rotational angle φ. For $|\varphi|<\Phi$ and $\Phi<|\varphi|<\pi/4$ the function $g_1(\alpha,\varphi)$ takes different constant values

$$g_1(\alpha,\varphi) = \begin{cases} \dfrac{G_1(1)(d+1)}{3\pi}, & |\varphi|<\Phi, \quad \alpha=1-6, \\ \dfrac{G_1(0)(d+1)}{3\pi d}, & \Phi<|\varphi|<\dfrac{\pi}{4}, \quad \alpha=1-6, \end{cases}$$
$$(12)$$

where $G_1(1)$ is the total probability for a molecule to be found in the angular interval $(-\Phi,\Phi)$ and $G_1(0)$ is the probability to be turned on an angle greater then Φ. The normalizing rule demands $G_1(1)+G_1(0)=1$.

Substituting Eq. (12) into Eq. (11) and integrating, we obtain

$$\langle\varphi^{2n}\rangle = \frac{1}{(2n+1)(d+1)^n}\left(\frac{\pi}{4}\right)^{2n}$$
$$\times\left[G_1(1)+\left(\sum_{p=0}^{2n}(d+1)^p\right)G_1(0)\right]. \quad (13)$$

The value of $\langle\varphi^{2n}\rangle$ together with the probabilities $G_1(0),G_1(1)$ depend on order k of approximation, therefore we will write $G_1^{(k)}(0),G_1^{(k)}(1)$ and $\langle\varphi^{2n}\rangle^{(k)}$. The temperature dependence of $\langle\varphi^2\rangle^{(9)}$ is given in Fig. 5.

In our model the correlation function $\langle\varphi_1\varphi_2\rangle$ for the nearest and arbitrary neighbors equals zero, $\langle\varphi_1\varphi_2\rangle=0$, because the formation (or breaking) of an H bond depends only on the absolute values of the corresponding angles. For the nearest neighbors, the nonzero correlation function $\langle\varphi_1^2\varphi_2^2\rangle$ is expressed through probability functions $G_2(2)$, $G_2(1)$, and $G_2(0)$, where the subscript "2" indicates the order of the correlation function. Here $G_2(2)$ is the total probability for both molecules to be turned on angles not exceeding Φ, the function $G_2(1)$ is the total probability to find a state in which one of two angles exceeds Φ, while another is less than Φ, and the probability for both molecules to be turned on angles $\Phi<|\varphi_1|,|\varphi_2|<\pi/4$ is designated by $G_2(0)$. The character of
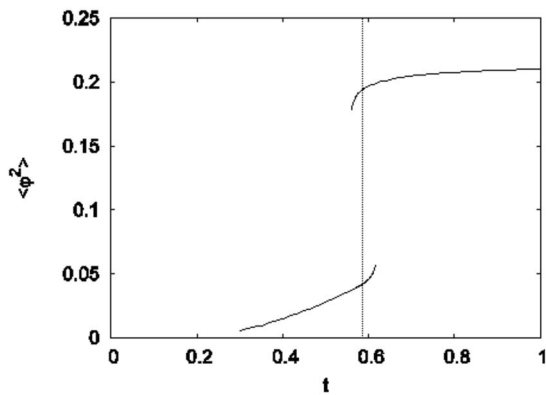
FIG. 5. Temperature dependence of the mean-square value $\langle \varphi^2 \rangle$. The value of $\langle \varphi^{2n} \rangle$ together with the probabilities $G_1(0)$, $G_1(1)$ depend on order k of approximation. Here $\langle \varphi^2 \rangle^{(9)}$ is considered.

temperature dependence of the correlation function $\langle \varphi_1^2 \varphi_2^2 \rangle$ for two nearest neighbors is shown in Fig. 6.

The average $\langle \cos(\varphi_1 - \varphi_2) \rangle = R(2) + R(1) + R(0)$ can be calculated exactly. Here $R(2)$, $R(1)$, $R(0)$ are the contributions from the regions of angles φ_1 and φ_2 at which (i) the H bond forms $(R(2))$; (ii) one of the molecules of a pair can form the H bond while another one cannot $[R(1)]$; (iii) both molecules of a pair are turned on large angles and cannot form H bonds $[R(0)]$ (see Fig. 7). Each contribution can be expressed in terms of the complete probability to find a pair of molecules. The additional information about $G_1(0), G_1(1)$ and $G_2(2)$, $G_2(1)$, $G_2(0)$ is given in the Appendix.

The average number of H bonds per molecule and the average of the square of the number of bonds are given by formula
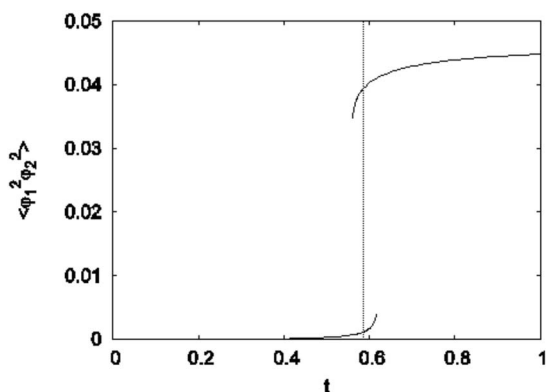

FIG. 6. Temperature dependence of the correlation function $\langle \varphi_1^2 \varphi_2^2 \rangle$ expressed through probability functions $G_2(2)$, $G_2(1)$, and $G_2(0)$, where the subscript "2" indicates the order of the correlation function. Here $G_2(2)$ is the total probability for both molecules to be turned on angles not exceeding Φ, the function $G_2(1)$ is the total probability to find a state in which one of two angles exceeds Φ, while another is less than Φ, and the probability for both molecules to be turned on angles $\Phi < |\varphi_1|, |\varphi_2| < \pi/4$ is designated by $G_2(0)$.
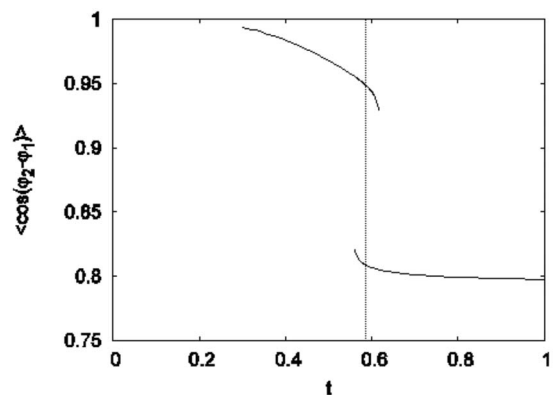

FIG. 7. The behavior of $\langle \cos(\varphi_1 - \varphi_2) \rangle = R(2) + R(1) + R(0)$ versus temperature. Here $R(2)$, $R(1)$, $R(0)$ are the contributions from the regions of angles φ_1 and φ_2 at which (i) the H bond forms $[R(2)]$; (ii) one of the molecules of a pair can form H bond while another one cannot $[R(1)]$; (iii) both molecules of a pair are turned on large angles and cannot form H bonds $[R(0)]$.

$$\langle n_H^m \rangle = \sum_{p=1}^{4} p^m W(p), \quad m = 1, 2, \tag{14}$$

where $W(p)$ is the probability for a molecule to form p H bonds. The values $W^{(k)}(p)$ can be expressed via five-particle probabilities $G_5(\ldots)$, which are cumbersome even at $k = 2$ [see Ref. [7], Eqs. (58)–(60)]. The dispersion $\langle (\delta n_H)^2 \rangle = \langle (n_H)^2 \rangle - \langle n_H \rangle^2$, calculated in the nine-particle approximation, is presented in Fig. 4.

V. MICROSCOPIC DEFINITION OF FRAGILITY

By definition [8], the macroscopic fragility parameter f_M is related to the shear viscosity η by Eq. (1). Since η is the macroscopic characteristic of liquid, it is appropriate to refer to the quantity, defined by Eq. (1), as the macroscopic fragility parameter. The logarithm of the shear viscosity was observed to be inverse proportional to the part of the vibrational contribution to the mean-square displacement of a molecule caused by the disorder effects in liquid [27]:

$$\log_{10} \eta \sim \langle \mathbf{u}^2 \rangle_l^{-1}. \tag{15}$$

The proportionality described by Eq. (15) is illustrated in Fig. 8 for glycerol. Note that it takes place below the glassification point as well as above the melting temperature. Taking into account the proportionality of $\log_{10} \eta$ and $\langle \mathbf{u}^2 \rangle_l^{-1}$, the heuristic microscopic definition of the fragility, Eq. (2), has been proposed [12].

In the temperature interval $(235-320)$ K the behavior of the shear viscosity of water in supercooled and normal states is mainly determined by the H-bond interactions [28]. In this temperature region the average number of H bonds per molecule is greater than 2, so one can speak about the developed H-bond network. Due to this, the molecular vibrations in water are mainly determined by the H-bond interactions.

The quantity $\langle u^2 \rangle_l$ can be written in the framework of the 2D lattice model of water as
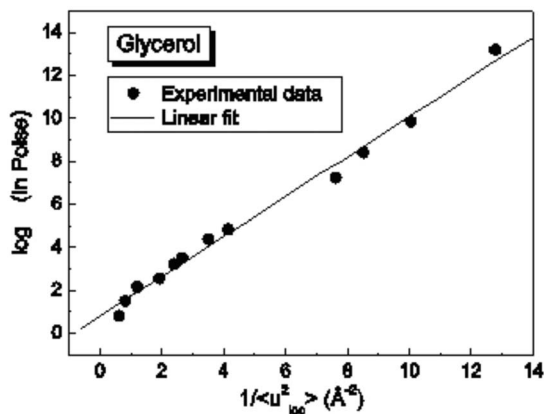
FIG. 8. Linear behavior of $\log_{10} \eta$ versus $\langle \mathbf{u}^2 \rangle_l^{-1}$ for glycerol. It takes place below the glassification point as well as above the melting temperature.

$$\langle \mathbf{u}^2 \rangle_l = r_p^2 (\langle \varphi^2 \rangle_{dis} - \langle \varphi^2 \rangle_{ord}), \qquad (16)$$

where r_p is the average H-bond length. We take the value $|\mathbf{u}_0|$ equal to

$$u_0^2 = \langle \mathbf{u}^2 \rangle_{dis} \big|_{T_0^+} - \langle \mathbf{u}^2 \rangle_{dis} \big|_{T_0^-}, \qquad (17)$$

where T_0 is the temperature of the phase transition in the subsystem of the H-bond network.

To determine the fragility parameter f_m according to Eqs. (2) and (3), it is necessary to evaluate the mean-square displacement $\langle \mathbf{u}^2 \rangle_{ord}$ of a molecule for the ordered state. In the framework of a 2D lattice model of water, $\langle \mathbf{u}^2 \rangle_{ord}$ is identified with the mean-square displacement of protons situated at two ends of a crosslike molecule. The fully ordered state in the considered model is realized only at $T=0$, although the average number of H bonds per molecule remains close to 4 in the larger part of the temperature interval $(0, t_0)$ (see Fig. 2). In fact, nonzero values of $\langle \varphi^2 \rangle$ only arise due to the break of H bonds, i.e., in consequence of violation of the ordering (small oscillations of molecules in the considered model of water are absent). Therefore, $\langle \mathbf{u}^2 \rangle_{ord}$ should be set to zero.

As a result, the contribution of H bonds to the fragility parameter at the point t_0^+, considered by us as the prototype of glassification point, can be estimated by formula

$$f_m \approx - \frac{t^2}{t_0} \frac{d(u_0^2 / \langle \mathbf{u}^2 \rangle_{dis})}{dt} \bigg|_{t=t_0^+}. \qquad (18)$$

Here, as in the Introduction, we suppose that the change of the H-bonds ordering is a necessary condition for the glass transition in glycerol-like liquids. Note that the distinct analog of the point t_0 in real water or its models is absent, since in our model all sites of the square lattice are occupied by molecules and the lattice type remains invariable.

As it follows from Fig. 9, the contribution of H bonds to the fragility decreases with the growth of the parameter γ which describes their interaction. The decrease of $\langle \varphi^2 \rangle$ at $\gamma \neq 0$, in comparison with the case $\gamma = 0$, is physically natural. Note that the temperature t_0 of the phase transition in the
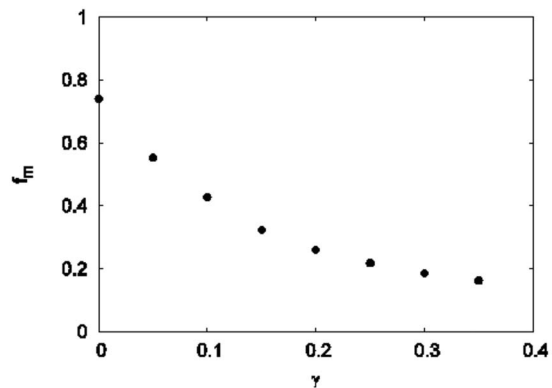

FIG. 9. Dependence of the microscopic fragility parameter f_m on the parameter γ. The contribution of H bonds to the fragility decreases with growth of the parameter γ which describes their interaction.

subsystem of H bonds increases with γ. The situation in real ice is slightly different because $\langle \mathbf{u}^2 \rangle_{ord}$ is mainly determined by elastic vibrations. Although they can also be introduced into the 2D water model, the breaking of H bonds is the most important reason for changes in fragility. The dependence of the fragility parameter upon γ is expected to be observable for liquids-homologues similar to disaccharides: trehalose, maltose, and sucrose [4].

VI. DIELECTRIC PERMITTIVITY

It can be shown that the dielectric permittivity of the 2D square lattice water, in which we neglect the electron polarizabilities and take into account only the dipole correlations of the nearest neighbors, takes the form

$$\frac{\varepsilon - 1}{\varepsilon + 1} = \frac{1}{2} \pi \beta n (\mathbf{d}_1^2 + 4 \langle \mathbf{d}_1 \cdot \mathbf{d}_2 \rangle), \qquad (19)$$

$\mathbf{d}_i$ being the dipole moment of the ith molecule, n being the density of the sites, and $\beta = 1/k_B T$. Let $k_B T_d = \mathbf{d}_1^2 / a^2$, where a is the lattice constant, be the characteristic dipole temperature. Since $na^2 = 1$, the formula (19) can be rewritten as

$$\frac{\varepsilon - 1}{\varepsilon + 1} = \frac{\pi}{2\tau} [1 + 4 \langle \cos(\varphi_2 - \varphi_1) \rangle], \quad \tau = \frac{T}{T_d}. \qquad (20)$$

It follows from Figs. 5 and 6 that $\langle \varphi^2 \rangle \lesssim 0.15$ and $\langle \varphi_1^2 \varphi_2^2 \rangle \lesssim \langle \varphi^2 \rangle^2$. Therefore, the value of $\cos(\varphi_2 - \varphi_1)$ can be approximated by several first terms,

$$\frac{\varepsilon - 1}{\varepsilon + 1} = \frac{\pi \zeta}{2t} \left[5 - 4 \langle \varphi^2 \rangle + \frac{1}{3} (\langle \varphi^4 \rangle + 3 \langle \varphi_1^2 \varphi_2^2 \rangle) \right], \qquad (21)$$

where $\zeta = T_d / \mu_0$. The correlation function $\langle \varphi_1^2 \varphi_2^2 \rangle$ is presented in Fig. 6.

Let ε_0 be the dielectric permittivity of two-dimensional ice at the melting temperature T_m. Taking into account that the values of all angular contributions are small, we can write
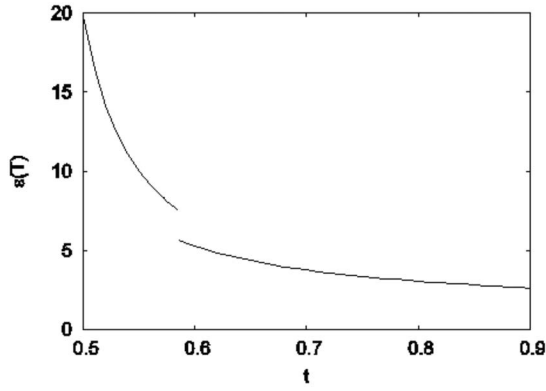
FIG. 10. Temperature dependence of the dielectric permittivity calculated according to $\varepsilon(t) = \varepsilon_0 - \frac{5\pi\zeta}{6}(\varepsilon_0+2)^2 \left[\frac{1}{t_0} - \frac{1}{t} - \frac{4}{5}\left(\frac{\kappa(t_0)}{t_0} - \frac{\kappa(t)}{t} \right) \right.$ $\left. + \cdots \right]$ with $\zeta = 0.1$. ε_0 is the dielectric permittivity of two-dimensional ice at the melting temperature T_0 and $\kappa(t) = \langle \varphi_1^2 \rangle(t)$. The values of all angular contributions are small.

$$\varepsilon(t) = \varepsilon_0 - \frac{5\pi\zeta}{6}(\varepsilon_0+2)^2 \left[\frac{1}{t_0} - \frac{1}{t} - \frac{4}{5}\left(\frac{\kappa(t_0)}{t_0} - \frac{\kappa(t)}{t} \right) + \cdots \right],$$

$$(22)$$

where $\kappa(t) = \langle \varphi_1^2 \rangle(t)$. As it should be, dielectric permittivity of the subsystem decreases when temperature grows (see Fig. 10). At the order-disorder phase transition dielectric permittivity changes stepwise by the value

$$\varepsilon_I(t_0) - \varepsilon_l(t_0) = \frac{2\pi\zeta}{3}\frac{(\varepsilon_0+2)^2}{t_0}[\kappa(t_0^+) - \kappa(t_0^-)]. \qquad (23)$$

VII. DISCUSSION

In the present paper the main attention is focused to the microscopic basis for the glassification of highly viscous glycerol-like liquids, their fragility and dielectric permittivity. The existence of H bonds is the characteristic feature of these liquids. H bonds play the leading role in the intermolecular interactions. Therefore it is natural to expect that H-bond networks of such liquids are responsible for their most important macroscopic properties.

To carry out concrete calculations, we apply to the subsystem of 2D model lattice water. Properties of this system are investigated with the help of the MMPIDF method and MC simulations. It was shown that the subsystem of H bonds near $t_0 \approx 0.6$ ($t = T/\mu_0$) undergoes the first-order phase transition. The ordered phase in which $\langle n_H \rangle \approx 4$ passes to the disordered one with $\langle n_H \rangle < (\ll) 1$. Such a transition is accompanied by strong change in the thermal motion-molecular rotations.

We suppose that (i) such a character of behavior is also inherent to H-bond networks of glycerol and glycerol-like liquids and (ii) the glassification of these liquids is inherently connected with the smeared phase transition in their H-bond subsystems. Let us consider some arguments supporting this point of view. It is generally accepted [1,2] that the glassifi-

cation point T_g has kinetic nature. At approaching T_g the shear viscosity and the relaxation time τ_α for the anisotropy mode [29] (α mode, according to [1]) considerably grow or tend to infinity.

Among different formulas for the shear viscosity and the α-relaxation time we use the exponential representation of the activation theory, since the activation energy can be naturally interpreted. In accordance with this we put

$$\eta \sim \tau_\alpha \sim \exp(E_a/k_B T). \qquad (24)$$

The local state of glycerol-like liquids is characterized by temperature and density n, as well as the number of H bonds per molecule n_H, therefore

$$E_a = E_a(n, n_H).$$

If temperature changes at fixed pressure or a system is on the vapor-liquid coexistence curve then $E_a = E_a(n(T), n_H(T))$. Thus, the activation energy becomes effectively temperature dependent. Applying the Hilbert's principle [30,31], it was shown in Ref. [4] that

$$E_a = E_a(n(T), n_H(T)) \approx E_W(n(T)) + \varepsilon_H n_H(T), \qquad (25)$$

where $E_W \sim k_B T_m$ is the contribution caused by dispersive forces (T_m is the melting temperature) and $\varepsilon_H \sim 10 k_B T_m$ is the H-bonding energy. Since the main contribution to the activation energy is given by H bonds, the expression (25) can be used for the determination of the temperature dependence of $n_H(T)$. In such a way it was found in Ref. [4] that the values of $n_H(T)$ for glycerol change by a factor of 2 and more in the temperature interval $\sim 50\,°C$ near the glassification point. The similar variation of $n_H(T)$ can be naturally interpreted as the smeared phase transition in the subsystem of H bonds.

As noted in Sec. V, the glassification temperature T_g is expected to be connected with the H-bonding energy μ_0 and dependent on the parameters of type γ and d. The direction of the shift of T_g produced by the H-bonds interaction is presented in Fig. 3. We have studied in detail the fluctuational averages $\langle \varphi^2 \rangle$, $\langle \varphi^4 \rangle$, $\langle \cos(\varphi_1 - \varphi_2) \rangle$ that determine the fragility and dielectric properties of highly viscous liquids near their glassification points. Here the existence of strong correlation between $\log_{10} \eta$ and the mean-square displacement of a molecule is taken into account. We have demonstrated that different values of the fragility of liquids homologues can be explained by the difference in the interaction energies between H bonds in them. This circumstance should also manifest in Raman spectra: the shift of H-bond band is expected to be proportional to γ.

Other interesting two-dimensional lattice water models have been proposed in Refs. [32–35]. The main attention is paid to the construction of the phase diagram, in particular, to the existence of two phases of "high and low density water." In [32–34] the authors consider the number of H bonds related to a molecule and here the number of H bonds formed by a molecule is taken into account, therefore a normalization factor is present. In [32–34] $n_H(T)$ decreases smoothly when temperature grows. The most probable fac-

tors leading to such a behavior of $n_H(T)$ are the low value of the parameter q in [34] ($q=6$) and the disorder in the disposition of molecules.

Within our approach one can conclude that the value of the fragility parameter is connected with the dielectric permittivity of the system near T_g since they both are mainly determined by the average $\langle\varphi^2\rangle$. We plan to study this question in detail in a separate work. Note that the averages $\langle n_H\rangle$, $\langle\delta n_H^2\rangle$, $\langle\varphi^2\rangle$ and so on allow us to construct the structural functions of the H-bond network [36] that play a very important role in the description of thermodynamic properties of the systems. In fact, our calculations justify the existence of strong correlation between the values of $1/\langle\varphi^2\rangle$ and n_H near the temperature t_0 of the phase transition in the subsystem of H bonds, that was supposed in Ref. [4] on the basis of the Hilbert's principle. Indeed, in Ref. [4] it was motivated that near the glassification point of glycerol-like liquids the quantity $\langle u^2\rangle_{dis}$ is connected with the average number of H bonds per molecule by the relation

$$\langle u^2\rangle_{dis} \approx [\langle u^2\rangle_w^{-1} + \lambda n_H(T)]^{-1},$$

where $\langle u^2\rangle_w$ is the contribution caused by the van der Waals (dispersive) forces and λ is the proportionality coefficient. For the lattice water $\langle u^2\rangle_w^{-1}=0$. Assuming T_g to be identical to $T_0 \approx 0.6\mu_0$, we expect that

$$\frac{\langle u^2\rangle_{dis}(T_g^+)}{\langle u^2\rangle_{dis}(T_g^-)} \approx \frac{n_H(T_g^-)}{n_H(T_g^+)}.$$

As it follows from Fig. 2 and Fig. 5, this relation is satisfied. However, away from t_0 ($t>t_0$) the agreement becomes only qualitative. In this temperature region the rotation of molecules tends to be quasifree, so the reasoning of Ref. [4] becomes inapplicable. In addition, the values of $\langle \mathbf{u}^2\rangle_l$ can also be used to estimate the Debye-Waller factor for water and other liquids with H bonds, since the accuracy of its experimental determination can in some cases be unsatisfactory depending on instrumental characteristics. More detailed consideration of these questions is at present the subject of study and will be carried out in a separate work.

APPENDIX

In this appendix the explicit expressions are presented for the functions $G_2^{(k)}(2)$, $k=2,4$, which have the simplest form. They are calculated in Ref. [7] with the help of the MMPIDF (method of many-particles irreducible distribution functions), completed by the direct variational method and the method of quasiactivities. In this paper all calculation are carried out within the method of quasiactivities, which includes smaller number of variational variables and is fully equivalent to the direct variational method for $k=2,4$. In accordance with [7],

$$G_2^{(2)}(2) = \frac{18}{\Omega^{(2)}(z,t)} \exp\left(\frac{1}{t}\right), \tag{A1}$$

$$\Omega^{(2)}(z,t) = 18 \exp\left(\frac{1}{t}\right) + 72zd + 36(zd)^2, \tag{A2}$$

where z is the quasiactivity of states $\{\alpha,\varphi\}$ for which $|\varphi| > \Phi$. The function $G_2^{(4)}(2)$ has the structure

$$G_2^{(4)}(2) = \frac{1}{\Omega^{(4)}(z_1,z_2,t)} \times \left[82 \exp\left(\frac{4}{t}\right) + \frac{6^4}{2}z_2^2 d \exp\left(\frac{2}{t}\right) \right.$$
$$\left. + \frac{6^4}{2}z_2^2 z_1 d^2 \exp\left(\frac{1}{t}\right) \right], \tag{A3}$$

$$\Omega^{(4)} = 82 \exp\left(\frac{4}{t}\right) + 6^4 z_2^2 z_1 d \exp\left(\frac{2}{t}\right) + 6^4 z_2^2 z_1 d^2 \exp\left(\frac{1}{t}\right) + 4$$
$$\times 6^4 z_2^2 z_1^2 d^3 + 6^4 z_1^4 d^4, \tag{A4}$$

where z_1 is the quasiactivity of states of two neighbor molecules for which $|\varphi_1|,|\varphi_2|>\Phi$, z_2 is the quasiactivity of states corresponding to either $|\varphi_1|<\Phi$ and $|\varphi_2|>\Phi$ or $|\varphi_1| >\Phi$ and $|\varphi_2|<\Phi$. The expression for $G_2^{(9)}(2)$ is cumbersome (the normalizing factor has 102 terms) and is therefore not presented. The functions $G_2^{(k)}(0)$ and $G_2^{(k)}(1)$ have the analogous structure.

In the framework of the MMPIDF the functions $G_1^{(k)}(0)$ and $G_1^{(k)}(1)$ have more complicated form. Their explicit expressions are written in Ref. [7].

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