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Macro- and microdefinitions of fragility of hydrogen-bonded glass-forming liquids

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In the present paper, the nature of the fragility of liquids with a developed H-bond network is investigated. It is shown that the effective activation energy of the shear viscosity η and the fragility parameter defined as $m = d\log\eta/d(T_g/T)|_{T=T_g^+}$ are immediately connected with the average number $n_{\mathrm{H}}(T)$ of the H-bond per molecule. The consistency of the macroscopic (m) and the microscopic $[M = d(u_0^2/\langle\vec{u}^2\rangle_{\mathrm{loc}})/d(T_g/T)|_{T=T_g^+}$, where $\langle\vec{u}^2\rangle_{\mathrm{loc}} = \langle\vec{u}^2\rangle_{\mathrm{anharm}} - \langle\vec{u}^2\rangle_{\mathrm{harm}}]$ definitions of the fragility is established.

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I. INTRODUCTION

The temperature dependence of viscosity is usually represented in the form [1]

$$\eta = \eta_0 \exp(E/T) \tag{1}$$

or, in the case of glass-forming systems,

$$\frac{\eta(T)}{\eta_g} = \exp\left[\frac{E}{T_g}\left(\frac{T_g}{T} - 1\right)\right], \tag{2}$$

where E is the activation energy, T_g is the glass transition temperature, and $\eta_g = \eta(T_g)$. Such a character is supported by arguments first given by Frenkel [2].

In general, the activation energy E depends on temperature and varies in a wide interval for different systems. Only for the narrow class of glass-forming systems, conventionally referred to as "strong," such as SiO_2 and GeO_2, do the values E not depend significantly on temperature and are close to each other.

Rigorously speaking, the existence of the temperature dependence of the activation energy contradicts some basic assumptions of the standard activation theory. Following this latter approach in fact, the activation energy can be only depending on density,

$$E = E(n), \tag{3}$$

and therefore it must be constant on isochors. However, the states of glass-forming systems do not only depend on density and temperature. In the following, we will restrict ourselves only to the analysis of the liquids in which the high-viscous states are arising from the formation of the H-bond network. More specifically, we shall take into account glycerol and glycerol-like systems as disaccharides and their water mixtures, which have been extensively investigated by using different and complementary spectroscopic techniques [3–12]. For these systems, two variables of state (n,T) are naturally completed by the additional variable, the average number of H-bonds per molecule n_{H}.

At the thermodynamic equilibrium $n_{\mathrm{H}} = n_{\mathrm{H}}(n,T)$. However, the temperature dependences of density and other thermodynamic variables are mainly determined by the structural characteristics of the H-bond network (see [13]). From this point of view it seems to be natural to suppose that the activation energy for the investigated systems is determined by the temperature dependence of the variable $n_{\mathrm{H}}(T)$. In agreement with such an assumption, even along the isochoric curves, the activation energy will depend on temperature. Along the curves of other types, such as coexistence curves or isobars, the temperature dependence of the shear viscosity is determined by the effective activation energy E_{eff}, the deviation of which from $E(n,T|n_{\mathrm{H}})$ is due to the thermal expansion effects [writing $E(n,T|n_{\mathrm{H}})$, we take into account that n is a function of n_{H}].

In [14], it has been shown that the activation energy E depends on the variable ψ, which has the meaning of the effective number of the degrees of freedom, which turns out to be responsible for the formation of highly viscous states,

$$E(\psi) = E^{(h)}(1-\psi) + E^{(l)}\psi + E^{(i)}\psi(1-\psi) + \cdots. \tag{4}$$

Here $E^{(l)}$ and $E^{(h)}$ denote the asymptotes of the activation energy for low and highly viscous states. With a good accuracy, they can be approximate by linear functions,

$$E^{(l)} = E_0^{(l)} + b^{(l)}(T_S - T), \quad T > T_S, \tag{5}$$

$$E^{(h)} = E_0^{(h)} + b^{(h)}(T_S - T), \quad T < T_S, \tag{6}$$

where E_0 denotes the isochoric value of the activation energy and T_S is the Stickel temperature at which the asymptotes of $\log\eta$ as a function of $1/T$ in low and highly viscous regions intersect.

The fragility parameter m is one of the important characteristics of highly viscous states. By definition [15],

$$m = \left.\frac{d\log\eta}{d(T_g/T)}\right|_{T=T_g^+}. \tag{7}$$

From Eqs. (2) and (7) it follows that the fragility parameter m is connected with the activation energy and the thermal expansion coefficient $b^{(h)}$ by the relation

$$m = \frac{1}{T_g\ln(10)}\left(E_0^{(h)} + b^{(h)}T_g\right). \tag{8}$$

It is not difficult to understand that the sum $(E_0^{(h)} + b^{(h)}T_g)$ is the invariant of the choice of a value η_0. On the contrary, the

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terms $E_0^{(h)}$ and $b^{(h)}$ depend on η_0 (see [14]). Assuming that $\eta_0 = 10^{-2}$ Pa s for glycerol, we obtain

$$E_0^{(h)}/b^{(h)}T_g \approx 1/2, \tag{9}$$

which means that the main contribution to the fragility parameter is given by the term $b^{(h)}T_g$.

The main aim of the present work is to find a relationship between micro- and macrodefinitions of fragility parameters.

II. THE INTERRELATION BETWEEN ACTIVATION ENERGY AND AVERAGE NUMBER OF H-BONDS PER MOLECULE

Let us consider a liquid in which an extended H-bonds network is present. The intensive thermodynamic characteristics, such as the specific volume, entropy, etc., can be represented as a sum of two terms,

$$v_l(T) = v_W(T) + v_H(T), \tag{10}$$

describing the van der Waals and H-bond contributions, respectively. Analogously for the activation energy we have

$$E = E_W + E_H, \tag{11}$$

where typically $E \sim (30\text{–}40)k_BT_g$ and $E_W \leqslant 10k_BT_g$.

Following [13], we apply further to Hilbert's principle [16]. In accordance with it, the behavior of the thermodynamic characteristics caused by the H-bond network is fully determined by the set S_i of so-called "structural functions." The average number of H-bonds per molecule $S_1(T) = n_H(T)$ and the parameter $S_2(T) = \chi_H(T)$, characterizing the bends of H-bonds (e.g., the tetrahedricity parameter for water [17,18]), are the most important among them. Then the H-bond contribution to a thermodynamic parameter $v_H(T)$ is given by the expansion

$$v_H(T) = \lambda_1 n_H(T) + \lambda_2 \chi_H(T) + \cdots. \tag{12}$$

At small bends of H-bonds, one can neglect by the second term [19], therefore

$$v_H(T) = \lambda_1 n_H(T) + \cdots. \tag{13}$$

The main contribution to the activation energy is similarly due to the first structural function,

$$E_H(T) = \gamma_1 n_H(T) + \cdots. \tag{14}$$

Thus, within this approximation, the temperature dependences of $v_H(T)$ and $E_H(T)$ are linear in $n_H(T)$.

The representation of the activation energy in the form (11) can be justified by the following reasons. In pair approximation, the intermolecular potential $U(1,2)$ in water has the structure

$$U(1,2) = U_{hs}(1,2) + U_W(1,2) + U_{el}(1,2) + U_H(1,2) \tag{15}$$

where the first term describes the hard-sphere-type repulsion, whereas $U_W(1,2)$ and $U_{el}(1,2)$ are responsible for the van der Waals and electrical multipole interactions, respectively, and $U_H(1,2)$ is the contribution of short-range anisotropic interaction connected with the formation of H-bonds. In agreement with [20], the contributions $U_W(1,2)$, $U_{el}(1,2)$, and $U_H(1,2)$ can be taken into account with the help of the thermodynamic perturbation theory.

Due to this, $U_H(1,2)$ leads to the additive contribution to the chemical potential of water molecules,

$$\mu(p,T,n_H) = \mu(p,T) + \mu_H(p,T,n_H). \tag{16}$$

With satisfactory accuracy, the interaction between H-bonds can be ignored. Therefore,

$$\mu(p,T,n_H) \approx \lambda_1 n_H + \lambda_2 \chi_H + \cdots. \tag{17}$$

From Eqs. (16) and (17) it follows that in a hydrogen-bonded system (as glycerol) the molecular volume $\partial\phi/\partial p$ takes the structure

$$v(T) = v_W(p,T) + \lambda_1 n_H(P,T) + \lambda_2 \chi_H(P,T) + \cdots. \tag{18}$$

Comparing the formulas (4) and (14) for the activation energy, we obtain

$$1 - \psi(T) \approx \kappa[n_H(T_g) - n_H(T)], \tag{19}$$

where

$$\kappa = \frac{1}{n_H(T_g) - n_H(T_m)}. \tag{20}$$

Thus, in glycerol and glycerol-like liquids, the parameter $[1 - \psi(T)]$ is proportional to the number of H-bonds per molecule.

Taking into account the behavior of $\psi(T)$ [13], we expect that near the glass transition temperature, $n_H(T)$ should be essentially changed. This allows us to interpret T_g as the point of smeared phase transition in the subsystem of H-bonds [21].

This statement does not contradict the current point of view that the glass transition is a kinetic phenomenon. Indeed, the relaxation time, being the most important evolution characteristics of nonequilibrium process, is determined by properties of the system, first by properties of the H-bond network for systems of glycerol-like type. The relaxation time is expected to be longer the higher $n_H(T)$ is. Therefore, the increase of the number of H-bonds per molecule at approaching T_g seems to be natural.

From Eqs. (1), (11), and (14), the equation for the determination of $n_H(T)$ follows:

$$\frac{\partial}{\partial T}\left(\frac{n_H(T)}{T}\right) = -\frac{E_{\exp}(T) - E_W}{\gamma_1 T^2}, \tag{21}$$

where

$$E_{\exp}(T) = \frac{\partial \ln \eta(T)}{\partial(1/T)}. \tag{22}$$

According to Eqs. (11) and (14), $E_{\exp}(T) \approx E_W + \gamma_1 n_H(T)$. To find the value and temperature dependence of $n_H(T)$, we neglect E_W and suppose γ_1 to be equal to $10k_BT_m$, as follows from the estimation for the H-bonding energy in water [22]. As an example, we propose the calculation of the average number of H-bonds per molecule for glycerol and sucrose as

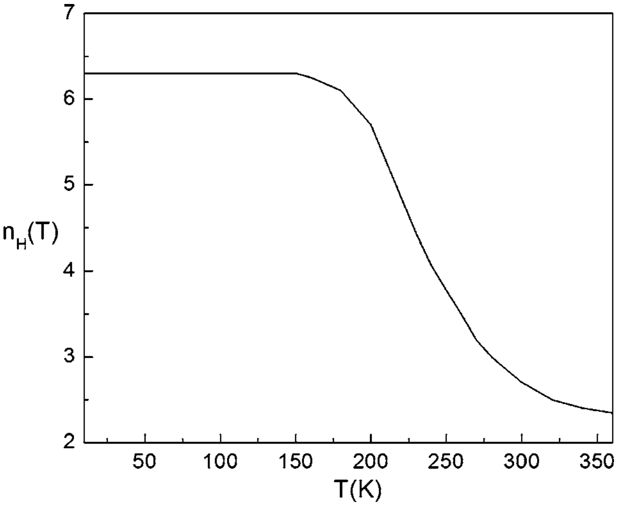

FIG. 1. The average number n_{H} of H-bonds per molecule for glycerol. The solid line reflects the behavior of function $\psi(T)$, normalized on the number of H-bonds per molecule: $n_{\mathrm{H}}(T)=n_{\mathrm{H}}(T_g)-[n_{\mathrm{H}}(T_g)-n_{\mathrm{H}}(T_m)]\psi(T)$.

a function of temperature. Figures 1 and 2 show the result of such a calculation.

As expected, these values of $n_{\mathrm{H}}(T)$ are consistent with Eq. (21). The solid line in Fig. 1 shows the temperature dependence of $n_{\mathrm{H}}(T)=n_{\mathrm{H}}(T_g)-[n_{\mathrm{H}}(T_g)-n_{\mathrm{H}}(T_m)]\psi(T)$, calculated with the help of $\psi(T)$ from [14], where it was found from the analysis of density at approaching the glass transition temperature. Here we used the values $n_{\mathrm{H}}(T_g)=5.9$ and $n_{\mathrm{H}}(T_m)=2.3$. Speaking about the number of H-bonds near the glass transition temperature, we note that a molecule of glycerol can form a maximum of six H-bonds. Hence near T_g the H-bond network becomes ordered (see [21] on the possibility of the phase transition in the subsystem of H-bonds). As seen, the correlation of different estimates for $n_{\mathrm{H}}(T)$ is quite successful.

Similarly to water [23], in low-viscous glycerol, at some temperature T_{H} above the melting point, the developed H-bonds network should destruct. It is interesting that $n_{\mathrm{H}}(T_m)=2.5$ is characteristic for water too [5]. At $T>T_{\mathrm{H}}$, the existence of only linear associates (dimers, trimers, and so on), for which $n_{\mathrm{H}}\leqslant 2$, is expected. The increase of the activation energy for glycerol at lowering the temperature, especially below the melting point, is directly connected with the formation of H-bonds network.

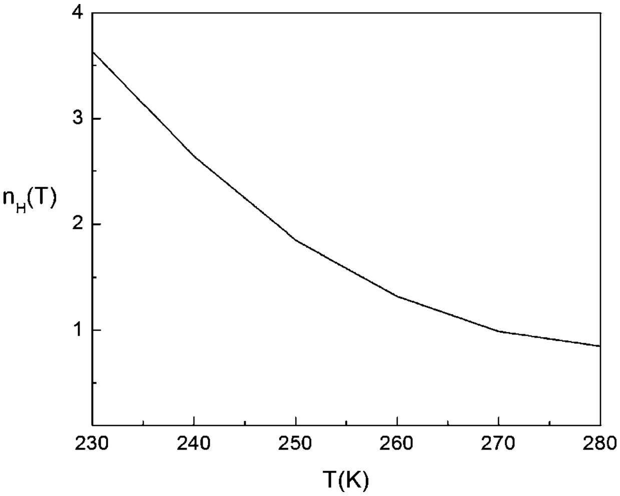

FIG. 2. The average number n_{H} of H-bonds per molecule for sucrose.

Certainly, the energy of an H-bond depends on the type of liquid under consideration. For trehalose, if we take γ_1 approximately twice as small, the value of n_{H} becomes close to that observed for water-trehalose solutions [24]. Note that the number of H-bonds per molecule, determined from the activation energy of the shear viscosity, is essentially smaller than the maximum number $n_{\mathrm{H}}^{(m)}$ of H-bonds that a trehalose molecule can form. So in [3] on the basis of ultrasonic experiments, it was shown that a trehalose molecule in dilute water-trehalose solution can form about 15 H-bonds with water molecules. Due to conformational constraints, a molecule in trehalose melt can form only some part of H-bonds from their maximum number. One can expect that $n_{\mathrm{H}}\leqslant\left(\frac{1}{3}-\frac{1}{2}\right)n_{\mathrm{H}}^{(m)}\sim(5-7)$. Besides, it is necessary to take into account that shear flows do not rupture all H-bonds formed by a molecule. For other disaccharides, the situation is quite similar.

From Fig. 2 it follows that near T_g the approximate equality takes place,

$$|n_{\mathrm{H}}'(T_g)T_g|\approx 0.1n_{\mathrm{H}}(T_g), \tag{23}$$

where $n_{\mathrm{H}}'(T)$ is the temperature derivative of $n_{\mathrm{H}}(T)$.

Taking into account that $E_W\leqslant 10k_BT_m\ll\gamma_1 n_{\mathrm{H}}(T)$, for the fragility parameter of sucrose and other disaccharides we obtain

$$m\approx\frac{1}{T_g\ln(10)}n_{\mathrm{H}}(T_g). \tag{24}$$

Equation (24) is to be considered valid for hydrogen-bonded systems, which, following the Angell classification scheme, turn out to be "intermediate" [15]. Intermediate behaviors can be interpreted in terms of different kinetic (η) and thermodynamic contributions $[\Delta C_p(T_g)]$: thermodynamically strong [small $\Delta C_p(T_g)$] and kinetically fragile systems (non-Arrhenius η behavior) are characterized by a low minima density of the potential energy hypersurface and low energy barriers. Conversely, thermodynamically fragile [large $\Delta C_p(T_g)$] and kinetically strong systems (Arrhenius η behavior) are characterized by a high hypersurface configurational degeneracy and high barrier heights [15]. These behaviors are to be attributed to the presence of two opposite trends. One of these increases the number of minima in the energy hypersurface, hence causes a shift to greater fragility, and the second increases the barrier crossing height, hence shifts the behavior in the opposite direction.

Furthermore some glass-forming polymers, such as for example polyoxide propylene (POP), show a negative correlation between fragilities and C_p^1/C_p^g. Such a negative correlation is opposite to the expectations based on an energy landscape interpretation of fragility and the generally accepted correlations between fragility parameter and C_p^1/C_p^g.

The interpretation is that chain length "postpones" the onset of the glass transition with the result that C_p^l/C_p^g decreases from what it ought to be. From this perspective, polymers would exhibit a greater dynamic fragility than otherwise would be the case for the same measured thermodynamic fragility.

In order to get a better insight into the role of H-bonds, let us compare the behavior of water and glycerol. For water, the van der Waals radius of molecules is smaller than half of the interparticle spacing ($1.5 < 2$ Å, at the crystallization point), whereas the corresponding relation for glycerol satisfies the opposite inequality: $3.3 \geqslant 3$ Å. This means that the rotation of molecules in liquid glycerol is hindered. As a consequence, by decreasing temperature, water molecules, contrary to glycerol ones, are able to change their orientations and to form the H-bond network, characteristic for hexagonal ice. However in glycerol, H-bonds promote the formation of strongly and weakly bound clusters [25,26]. The strongly bound clusters are imperfect nuclei of a solid phase which influence mainly the thermodynamic properties. At the same time, the viscoelastic properties are connected with the time evolution of weakly bound clusters [26,27]. In particular, the relaxation time τ of shear viscosity can be treated as the characteristic evolution time of the weakly bound clusters. If H-bonds weaken the characteristic size of these clusters, the corresponding values of τ and η should diminish.

Finally, note that at high enough pressure, the influence of weakly bound clusters is suppressed and the increase of τ and η will be caused by hard-core effects. At atmospheric pressure, the clusterization in glycerol and glycerol-like liquids, for which $|\langle U_w(1,2)\rangle|$, $|\langle U_{\mathrm{el}}(1,2)\rangle| \ll |\langle U_{\mathrm{H}}(1,2)\rangle|$ as well as their fragility, should be connected with the H-bond network.

III. INTERRELATION BETWEEN MICRO- AND MACRODEFINITIONS OF FRAGILITY

An operative definition for fragility, based on the evaluation by elastic incoherent neutron scattering of the mean square displacement, has been shown in [11,12]. The proposed definition allows us to link a macroscopic transport quantity, i.e., viscosity, with an atomic quantity, namely the nanoscopic mean square displacement.

From a theoretical point of view, the incoherent dynamic structure factor $S_{\mathrm{inc}}(Q,\omega)$ is composed by two contributions: an elastic term $S_{\mathrm{inc}}^{\mathrm{el}}(Q) = S_{\mathrm{inc}}(Q,\omega=0) = I(Q,\infty)\delta(\omega) \cong I(Q,\tau)$ (τ being the experimental resolution time), and a quasielastic term that involves energies $\eta\omega > 0$.

The mean square displacement $\langle \vec{u}^2 \rangle$, which takes into account fluctuations of all particles in the investigated system, is given by [11,12]

$$\langle \vec{u}^2 \rangle = -3 \left. \frac{d\{\ln[S_{\mathrm{inc}}^{\mathrm{el}}(Q)]\}}{dQ^2} \right|_{Q=0} = \sum_{\alpha=1}^{N} x_\alpha \langle r_\alpha^2 \rangle [1 - C_\alpha(\tau)]. \tag{25}$$

Nonetheless, for a given experiment $C_\alpha(\tau)$ is a constant that rescales the observed mean square displacement, and hence $C_\alpha(\tau)=0$ can be assumed [11,12]. For simplicity, in the present analysis the assumption that all particles are dynamically equivalent will be made, therefore in the previous equations x_α has been assumed equal to 1.

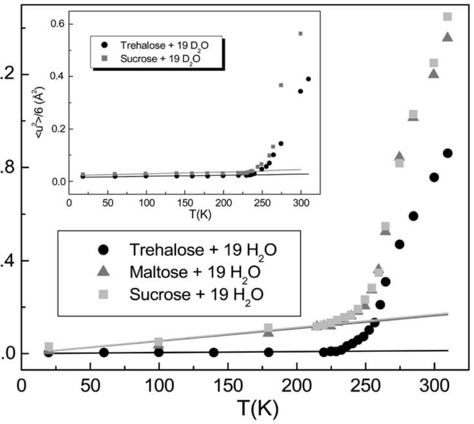

FIG. 3. Temperature dependence of the derived mean square displacements for trehalose, maltose, and sucrose/H_2O and D_2O mixtures [11,12].

Figure 3 shows the temperature dependence of the derived mean square displacements for trehalose, maltose, and sucrose/H_2O and D_2O mixtures. It is evident that a dynamical transition occurs for the investigated systems [11,12]. Below the onset temperature, the elastic intensity has the Gaussian form expected for a harmonic solid. In this Q range, in which the Gaussian model is valid, $\langle \vec{u}^2 \rangle Q^2 < 2$, where $\langle \vec{u}^2 \rangle = \langle \vec{u}^2(T) \rangle - \langle \vec{u}^2(20\text{ K}) \rangle$ is the total mean square displacement of hydrogens, and $S_{\mathrm{inc}}^{\mathrm{el}}(Q) \propto \exp[-\langle \vec{u}^2/6 \rangle Q^2]$, the mean square displacement behavior can be fitted within the framework of the harmonic approximation [11,12]

$$\langle \vec{u}^2(T) \rangle = \frac{h\langle \nu \rangle}{2K} \left(\coth \frac{h\langle \nu \rangle}{2k_B T} - 1 \right), \tag{26}$$

where k_B is the Boltzmann constant, K and $\langle \nu \rangle$ are the average force field constant and the average frequency of a set of oscillators considered as an Einstein solid, respectively, and the term $h\langle \nu \rangle / 2K$ is the zero-point mean square displacement. By fitting according to Eq. (26), we obtain the values of $K = 0.40$, 0.25, and 0.22 N/m for the average force field constant for trehalose, maltose, and sucrose/ H_2O mixtures, respectively, indicating the trehalose/H_2O system as the strongest system.

In order to characterize the anharmonic region, in [11,12] a new calculation for the degree of fragility is shown. Starting from the works on selenium by Migliardo *et al.* [28] and Magazù *et al.* [29], a correlation between viscosity and the atomic mean square displacement was first proposed by Buchenau and Zorn [30]. The proposed interpretative model moves by the following picture for the elementary flow process (the α-relaxation): an atom jumps in the fast processes (β-relaxation motions) with a Gaussian probability distribution characterized by a mean square amplitude $\langle \vec{u}^2 \rangle_{\mathrm{loc}}$ [30], defined as the difference between the mean square displacement of the ordered and disordered phase,

$$\langle \vec{u}^2 \rangle_{\mathrm{loc}} = \langle \vec{u}^2 \rangle_{\mathrm{anharm}} - \langle \vec{u}^2 \rangle_{\mathrm{harm}}. \tag{27}$$

Pratically the same relation can be obtained from the liquid data on the basis of $\langle \vec{u}^2 \rangle_{\mathrm{loc}} = \langle \vec{u}^2 \rangle_{\mathrm{liq}} - \langle \vec{u}^2 \rangle_{\mathrm{hard}}$, where $\langle \vec{u}^2 \rangle_{\mathrm{liq}}$ is the mean square displacement for motion faster than the resolution limit and $\langle \vec{u}^2 \rangle_{\mathrm{hard}}$ takes into account only the typical lattice vibrational frequencies. This linear relation includes both the region below the glass transition temperature and above the melting temperature.

If the amplitude of the fast motion exceeds a critical displacement u_0, a local structural reconfiguration (the α-relaxation) takes place. Assuming the time scale of the fast motion to be independent of temperature, the waiting time for the occurrence of an α-process at a given atom is proportional to the probability to find the atom outside of the sphere with radius u_0. In this picture, one obtains the viscosity [30]

$$\eta = \eta_0 \exp[u_0^2/\langle u^2 \rangle_{\mathrm{loc}}]. \tag{28}$$

Equation (28) allows us to characterize the fragility of the investigated systems since the mean square displacement is measurable even below T_g and above T_m. The linear fitting procedure of log η versus $(\langle \vec{u}^2 \rangle_{\mathrm{loc}})^{-1}$ by Eq. (28) furnishes through its slope the u_0 parameter value.

Roland *et al.* [31,32] recently demonstrated by measurements under high pressure the strong influence of hydrogen bonds on the fragility.

Other authors [33], by using the Voronoi construction, calculated the average free volume along a path of constant density and related it to the Debye-Waller factor, which is measurable by neutron scattering.

Within this picture, the activation energy is linked to the mean square displacement of a molecule by the formula

$$E = T \frac{u_0^2}{\langle \vec{u}^2 \rangle_{\mathrm{loc}}}. \tag{29}$$

Taking into account Eqs. (7) and (27)–(29), the proposed parameter in order to evaluate the "fragility" degree of the investigated systems is written as

$$M = \left. \frac{d(u_0^2/\langle \vec{u}^2 \rangle_{\mathrm{loc}})}{d(T_g/T)} \right|_{T=T_g^+}. \tag{30}$$

It is evident that such a definition implies a fragility parameter depending on the instrumental resolution. On the other hand, we are interested on a comparison of the fragility degree among glass-forming systems and such a comparison is meaningful since the same experimental setup of IN13 with an elastic energy resolution of 8 μeV full width at half maximum was employed [11,12].

In Fig. 4, the fragility parameter values obtained at two different experimental resolutions, specifically at 8 μeV by IN13 and at 150–200 μeV by IN6, are reported. As is evident, the data arrange themselves on a straight line whose slope depends uniquely on the instrumental resolution. The obtained values indicate that the present operative definition for fragility shows a direct proportionality between M and m.

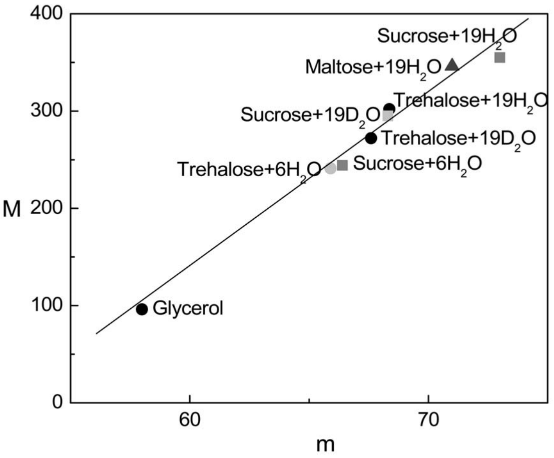

FIG. 4. Linear behavior of the fragility parameter M vs the fragility parameter m. The black lines indicate the best fits [11,12].

Similarly, Ngai *et al.* in [34] found a correlation between the mean square displacement and fragility, while Scopigno *et al.* [35] linked the vibrational properties of the glass below T_g to the fragility degree.

Let us show that the macroscopic and microscopic definitions of fragility are strongly connected.

The mean square displacement of a molecule is an average characteristics of the thermal motion. Therefore, in accordance with the previous discussions on H-bonded systems, $\langle \vec{u}^2 \rangle_v^{-1}$ can be expanded in the series similar to Eqs. (10) and (19),

$$\langle \vec{u}^2 \rangle^{-1} = \langle \vec{u}^2 \rangle_W^{-1} + \gamma_1 n_{\mathrm{H}} + \cdots, \tag{31}$$

where $\langle \vec{u}^2 \rangle_W^{-1}$ is the contribution caused by van der Waals forces. It is also responsible for the thermal expansion effects (see Appendix) and can be removed by the subfraction of $\langle \vec{u}^2 \rangle_{\mathrm{ord}}$. Within the framework of the proposed interpretative model, we obtain

$$M \cong \ln 10 \frac{\gamma_1 T_g}{\lambda_1} m. \tag{32}$$

The previous relation shows and theoretically justifies the proportionality law between the macroscopic and microscopic definitions of fragility.

IV. CONCLUSIONS

In the paper, we consider hydrogen-bonded systems in which highly viscous states are formed mainly owing to the influence of the H-bond network. In this case, with a satisfactory accuracy, the thermodynamic characteristics of the system can be represented by a sum of two contributions, connected to hard core and van der Waals forces as well as to the H-bond network. Following the Hilbert principle approach, the last term is expanded in the series of the structural functions of the H-bond network. Among them, the main role belongs to the number of H-bonds per molecule and the parameter describing the bend of H-bonds. Such a structure should also be inherent to the activation energy of the shear viscosity and to the mean square displacement of a molecule. It is shown that in the region in which the H-bond network is developed, terms caused by the H-bond network dominate. This implies that the activation energy and the inverse mean square displacement of a molecule are proportional to each other.

Finally, the interrelation between the macroscopic definition of fragility and the microscopic definition based on the temperature dependence of the atomic mean square displacement is discussed.

Further, improvements to the presented approach are in progress.

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APPENDIX: THERMAL EXPANSION EFFECTS

If the shear viscosity of ordinary liquids is formed by the activation mechanism, its temperature dependence is described by the formula

$$\eta(T) = \eta_0 \exp\left(\frac{E(n)}{T}\right), \tag{A1}$$

where the activation energy $E(n)$ depends only on density. To determine the numerical values of $E(n)$ is expedient to use isochoric values of the shear viscosity. In this case,

$$E(n) = \left.\frac{\partial \ln \eta}{\partial(1/T)}\right|_{n=\mathrm{const}}. \tag{A2}$$

At displacement along some other line l (the coexistence curve, an isobar, and so on), we can write

$$E^{(l)}_{\mathrm{eff}}(n,T) = \left.\frac{\partial \ln \eta}{\partial(1/T)}\right|_{l}. \tag{A3}$$

The temperature dependence of $E^{(l)}_{\mathrm{eff}}$ arises by the thermal expansion effects, because of the circumstance that the displacements along some line l imply passing from the isochoric curve to another. Therefore, we have

TABLE I. Effective values of the activation energy for argon on isochores and isobars.

Ar			
ρ=const		P=const	
ρ (g/cm^3)	$E^{(\rho)}_{\mathrm{eff}}/k_BT_a$	ρ (atm)	$E^{(P)}_{\mathrm{eff}}/k_BT_a$
1.192	0.812	350	8.021
1.240	0.890	500	8.091
1.340	0.913	750	8.260
1.384	0.967		

$$E^{(l)}_{\mathrm{eff}} = E(n) + \frac{\partial E(n)}{\partial n}\left.\frac{\partial n}{\partial(1/T)}\right|_{l}. \tag{A4}$$

Denoting $\partial E(n)/\partial n = E^{(1)}_n$ and introducing the thermal expansion coefficient $\kappa_l(T) = -(1/n_l(T))(\partial n_l(T)/\partial T)$, we can rewrite the formula (A4) in the form

$$E^{(l)}_{\mathrm{eff}} = E[n(T)] + E_e(n(T),T), \quad E_e(n(T),T) = nE^{(1)}_n[n(T)]\kappa(T). \tag{A5}$$

Let us illustrate the relation between the contributions of the first and second terms in the case of liquid argon, for which there are is detailed literature on shear viscosity at the coexistence curves, isobars, and isochors [36]. In Table I, the viscosity data of liquid argon are shown.

From Table I it follows that the contribution, caused by the thermal expansion effects, exceeds the activation energy in approximately five times. Note that this example has only an illustrative character, because the temperature dependence of the shear viscosity for argon is not described by the activation theory: the values of the activation energy, as obtained from Table I, are smaller than the energy of the thermal noise (k_BT_m) near the melting point.

In [37], there are also detailed data on the shear viscosity of nitrogen. Their processing in [14] shows the importance of thermal expansion effects. Let us note that in the case of glycerol, the heat expansion coefficient near the glass transition temperature changes in approximately 3.5 times, from the value 1.447×10^{-3} at temperature above the glass transition temperature to the value 5.5×10^{-3} in a glassy state.

The analysis of the experimental data [6] for glycerol shows that

$$E[n(T)]:E_{\mathrm{ex}}(n(T),T) \cong 5:1. \tag{A6}$$

Therefore, for glycerol as well as for silicate glasses, the thermal expansion effects are negligibly small.

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