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Abstract
The aim of the present paper is to investigate the behaviour of the kinematic viscosity, mean-square displacement and free volume of glycerol in order to theoretically and experimentally evaluate the fragility degree. Starting from the dependence of viscosity on temperature, the behaviour of the mean-square displacement and free volume of glycerol is analysed in order to point out the linear relationships between the logarithm of viscosity and the excess mean-square displacement and the excess free volume. As a conclusion, two fragility definitions, based on the observed links, are discussed.

1. Introduction

Among glass-forming liquids, hydrogen-bonded systems tend to be unusual as regards their supercooling propensity and highly complex behaviour in the supercooled state (Martinez and Angell 2001, Angell *et al* 1994, Debenedetti and Stillinger 2001, Huang and McKenna 2001). The fact that they tend to vitrify more readily than the general rule $\frac{T_b}{T_m} > 2.0$, T_b being the boiling temperature and T_m being the melting temperature (e.g. for glycerol $\frac{T_b}{T_m} = 1.9$), would indicate that in the supercooled liquid state they have large activation energies and relatively small departures from Arrhenius behaviour. In recent times the departures from the Arrhenius behaviour and other related properties (e.g. non-exponential behaviour and non-linearity of relaxation) have been discussed in terms of the strong–fragile liquids classification (Martinez and Angell 2001, Debenedetti and Stillinger 2001). In such a classification scheme, an extreme is represented by conformity to the Arrhenius equation

$$\eta = \eta_0 \exp\left(\frac{E_a}{k_B T}\right), \tag{1}$$

where E_a is the activation energy and k_B is the Boltzmann

constant, while the other extreme is represented by a marked departure from Arrhenius behaviour, which at the limit becomes a first-order transition from fluid to glass, unless a first-order fragile-liquid-to-strong-liquid transition occurs (Angell *et al* 1994, Martinez and Angell 2001, Debenedetti and Stillinger 2001).

In terms of the Adam–Gibbs theory of relaxation for viscous liquids and in terms of the density of minima of the potential energy hypersurface characteristic of the molecular systems, the small number of minima on the surface is characteristic of a strong liquid, whereas the much more degenerate surface is descriptive of fragile liquids (Martinez and Angell 2001, Angell *et al* 1994). Glycerol is considered as anomalous due to the large change in heat capacity which it experiences at the glass transition, and it occupies an intermediate position in the Angell classification.

The leading idea of this work is to emphasize the correlation between the mean-square displacement and free volume and the kinematic viscosity of glycerol, and to compare the fragility definitions as obtained by elastic neutron scattering and positron annihilation lifetime spectroscopy findings.

2. Theoretical background

The incoherent dynamic structure factor $S_{incoh}(Q, \omega)$ is composed of two contributions: an elastic contribution

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$S_{\text{incoh}}^{\text{el}}(Q) = I(Q, \infty)\delta(\omega) \cong I(Q, \tau)$ (τ being the experimental resolution time), and a quasielastic contribution that involves energies $h\omega > 0$. $S_{\text{incoh}}^{\text{el}}(Q)$ is related to the normalized elastic intensity by $S_{\text{incoh}}^{\text{el}}(Q) \cong I(Q, t) = \sum_{\alpha=1}^{N} x_\alpha \exp[-\frac{Q^2}{3}\langle r_\alpha^2 \rangle[1 - C_\alpha(t)]]$, where $\langle r_\alpha^2 \rangle$ is the equilibrium mean-square displacement and $C_\alpha(t)$ is the stationary position relaxation function (determination of which requires knowledge of the self-pair correlation function describing the time propagation of the particle in the potential). $S_{\text{incoh}}^{\text{el}}(Q)$ relaxes to $I(Q, \infty)$ when the resolution time is long enough such that $C_\alpha(t) \to 0$ (Bicout and Zaccai 2001, Zaccai 2000). The mean-square displacement is given by

$$\langle u^2 \rangle = -3 \frac{\mathrm{d}\{\ln[S_{\text{incoh}}^{\text{el}}(Q)]\}}{\mathrm{d}Q^2}\bigg|_{Q=0} = \sum_{\alpha=1}^{N} x_\alpha \langle r_\alpha^2 \rangle[1 - C_\alpha(t)]. \tag{2}$$

For a given experiment $C_\alpha(t)$ is a constant that rescales the observed mean-square displacement, and therefore $C_\alpha(t) = 0$ can be assumed. Furthermore, for simplicity in the present analysis the assumption that all particles are dynamically equivalent can be made; therefore $x_\alpha = 1$ can be assumed (Bicout and Zaccai 2001, Zaccai 2000). The mean-square displacements originating from harmonic vibrational motions can be expressed by

$$\langle \Delta u^2(T) \rangle = \left[\frac{h\langle v \rangle}{2K_{\text{force}}} \right] \coth\left(\frac{h\langle v \rangle}{2K_{\text{B}}T} - 1 \right), \tag{3}$$

where K_{force} is the average force field constant of a set of oscillators considered as an Einstein solid. Because a force constant is not defined for anharmonic motions, an operational approach in which the 'resilience' of an anharmonic environment is quantified by a pseudo-force constant $\langle k \rangle$ calculated from the derivative of the scan at $T\langle k' \rangle = 2k_{\text{B}}/(\mathrm{d}\langle u^2 \rangle/\mathrm{d}T)$, giving rise to the relation $\langle k \rangle = 0.001\,38/(\mathrm{d}\langle u^2 \rangle/\mathrm{d}T)$, has been suggested (Bicout and Zaccai 2001, Zaccai 2000).

It is important to notice that the experimentally determined mean-square displacement depends on the resolution of the spectrometer (Becker *et al* 2004). The energy resolution can be incorporated into the analysis as follows. At low Q the elastic scattering, by taking the slope of the natural logarithm of the elastic scattering as a function of Q^2, can be expressed as follows:

$$\langle \Delta u^2 \rangle_{\text{exp}} = \langle \Delta u^2 \rangle_{\text{conv}} - \langle \Delta u^2 \rangle_{\text{res}}, \tag{4}$$

where $\langle \Delta u^2 \rangle_{\text{conv}}$ is the long-time converged mean-square displacement (which is finite for a spatially confined system) while $\langle \Delta u^2 \rangle_{\text{res}}$ arises from quasielastic scattering not resolved by the instrument, and is therefore due to motions too slow to be detected:

$$\langle \Delta u^2 \rangle_{\text{res}} = \sum_{l>0} a_l \frac{2}{\pi} \arctan \frac{\Delta \omega}{k_l}. \tag{5}$$

Here the k_l define characteristic timescales of relaxation processes ($\tau_l \sim 1/k_l$), $\Delta\omega$ is the width of the resolution function (half-width at full maximum), and a_l is the maximal
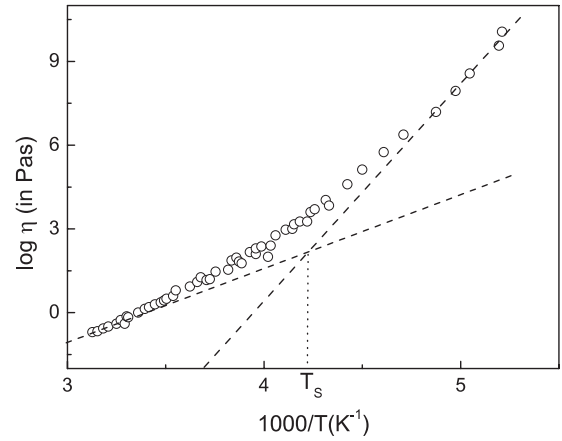

Figure 1. Viscosity of glycerol as a function of temperature. The dashed lines are the asymptotes for low and high viscous regions. The Stickel temperature T_{S} is indicated.

contribution of relaxation process l to the mean-square displacement (Becker *et al* 2004). Therefore the $\langle u^2 \rangle$ values include all contributions to motions in the accessible space and time windows, from vibrational fluctuations (usually expressed as a Debye–Waller factor) as well as from diffusional motions.

Now let us consider the temperature dependence of the free volume. The basic idea here is that molecules need 'free' volume in order to be able to rearrange. As the liquid contracts upon cooling, less free volume becomes available. Cohen and collaborators (Cohen and Turnbull 1959) defined the free volume V_{f} as that part of the excess volume ΔV which can be redistributed without energy change. Assuming a Lennard-Jones potential function for a molecule within its cage in the condensed phase, it can be shown that at small ΔV considerable energy is required to redistribute the excess volume; however, at ΔV greater than some value ΔV_{g}, most of the volume added can be redistributed freely. As a result, the transition from glass to liquid may be associated with the introduction of appreciable free volume into the system.

3. Results and discussion

Figure 1 shows the viscosity of glycerol as a function of temperature. Experimental data have been taken from Martinez and Angell (2001). In the model we are proposing, an important parameter is the Stickel temperature T_{S}, which marks both a change in the susceptibility spectra of glass formers (Blochowicz *et al* 2006) and the departure of the relaxation times from the Vogel–Tammann–Fulcher (VTF) function (Paluch *et al* 2003).

In the present model, the Stickel temperature is evaluated considering the low viscosity region, chosen in the 192–205 K range, and the high viscosity region, chosen in the 307–320 K range. The next step is to linearly fit the two different regions by two asymptotes, whose equations are

$$\log^{\text{low}} \eta = \log^{\text{low}} \eta_0 + b^{(\text{l})} \cdot (1/T) \tag{6a}$$
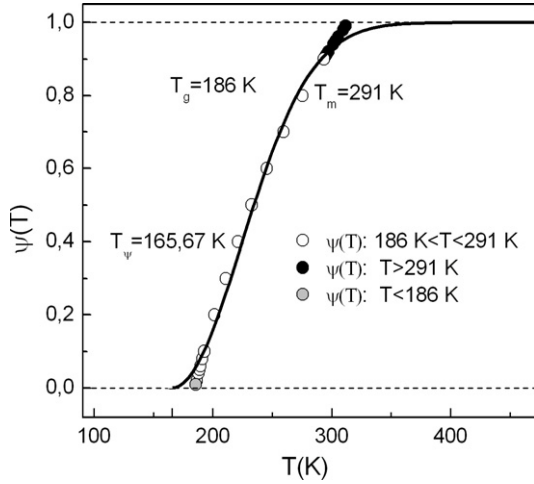$$\log^{\text{high}} \eta = \log^{\text{high}} \eta_0 + b^{(\text{h})} \cdot (1/T) \tag{6b}$$

Figure 2. Temperature dependence of the ψ function.

Figure 3. Mean-square displacements as a function of temperature. The arrow indicates the distance between the experimental data and the Stickel temperature, which is a measure of fragility.

for low and high viscous regions, respectively, which in the case of glycerol have the form

$$\log^{low} \eta = -8.68 + 2547.68 \cdot (1/T) \qquad (7a)$$

$$\log^{high} \eta = -32.28 + 8091.40 \cdot (1/T). \qquad (7b)$$

The Stickel temperature is evaluated by identifying the temperature value where the two asymptotes intersect. In the case of glycerol viscosity, the value obtained for the Stickel temperature is $T_S = 234.74$ K.

From the asymptotes (7a) and (7b), the following set of straight lines has been created:

$$\log \eta [\log^{high} \eta_0 + b^{(h)} \cdot (1/T)](1 - \psi)$$
$$+ [\log^{low} \eta_0 + b^{(l)} \cdot (1/T)]\psi, \qquad (8)$$

namely

$$\log \eta = [-32.28 + 8091.40 \cdot (1/T)] \cdot (1 - \psi)$$
$$+ [-8.68 + 2547.68 \cdot (1/T)] \cdot \psi, \qquad (9)$$

where ψ fulfils the requirements

$$\psi(T) = \begin{cases} 1 & \text{in low viscous states } T > T_L \\ 0 & \text{in high viscous states } T > T_S, \end{cases} \qquad (10)$$

where T_L is 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.

The ψ parameter is proportional to the number of degrees of freedom which are responsible for the formation of highly viscous states and manifested in α relaxation.

By using the following model function for the fitting (Blazhnov *et al* 2006),

$$\psi(T) = \begin{cases} 1 - \exp\left[-\left(\dfrac{T - T_\psi}{\Delta_\psi}\right)^n\right] & T > T_\psi \\ 0 & T < T_\psi, \end{cases} \qquad (11)$$

we obtain the result shown in figure 2, and for the fitting parameters the values of $T_\psi = 165.67$ K and $\Delta_\psi = 82.67$ K.
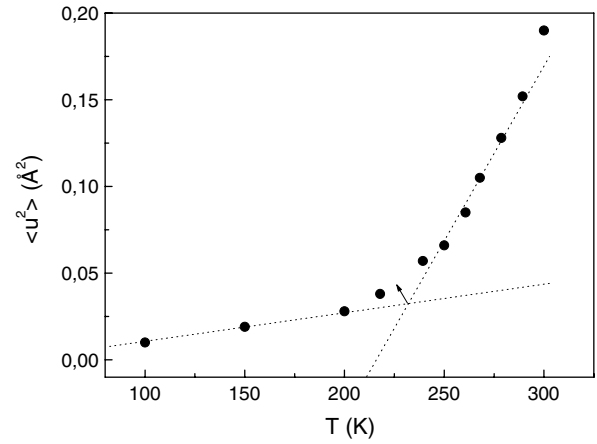
Once the ψ function has been determined, it will be possible to express the activation energy, its derivative and other quantities such as the mean-square displacement as a function of ψ, $\langle u^2 \rangle = \langle (u^l)^2 \rangle (1 - \psi) + \langle (u^h)^2 \rangle \psi + \cdots$, as well to connect the fragility of the system to the distance between the Stickel point and the experimental data. In fact, if we consider the distance between the curve and the straight-line asymptotic interpolation,

$$D = \tfrac{1}{2} b^{(l)} T_S, \qquad (12)$$

we observe that it takes large values for the substances that are 'fragile' according to Angell's classification.

The fragility parameter m is connected with the activation energy and the thermal expansion coefficient $b^{(h)}$ by the relation (Blazhnov *et al* 2006)

$$m = \frac{1}{T_g \ln(10)} (E_0^{(h)} + b^{(h)} T_g). \qquad (13)$$

The quantity $(E_0^{(h)} + b^{(h)} T_g)$ is invariant about the choice of value for η, while the terms $E_0^{(h)}$ and $b^{(h)}$ depend on η. Assuming $\eta_0 = 10^{-2}$ Pa s for glycerol, we obtain

$$E_0^{(h)}/b^{(h)} T_g \approx 1/2, \qquad (14)$$

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

Figure 3 shows the mean-square displacements as a function of temperature for glycerol (Cornicchi *et al* 2004) as determined by elastic neutron scattering measurements performed by using the backscattering spectrometer IN13 at the Institute Laue Langevin (Grenoble, France), which is characterized by a relatively high energy of the incident neutrons (16 meV), which makes it possible to span a wide range of momentum transfer $Q (\leqslant 5.5 \text{ Å}^{-1})$ with a very good energy resolution ($\sim 8 \mu$eV). It can be observed that a dynamical transition, marking a change from a harmonic to an anharmonic region in which new degrees of freedom are activated, occurs. The interpretative model proposed to
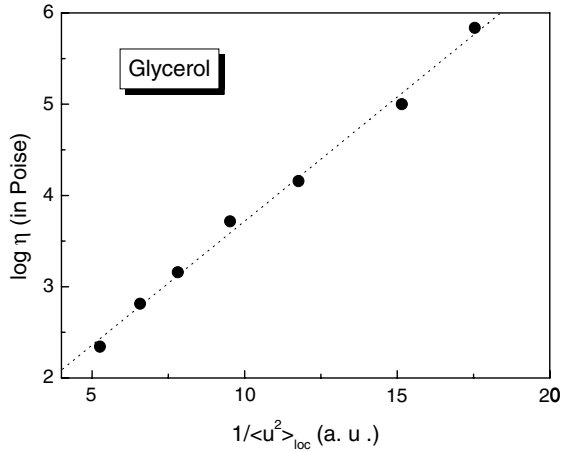
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Figure 4. Linear dependence of viscosity on the local mean-square displacement.

Figure 5. Free-volume behaviour as a function of temperature.

describe the observed behaviour is furnished 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 $\langle u^2 \rangle_{\text{loc}}$, defined as the difference between the mean-square displacement of the ordered and disordered phase (Magazù *et al* 2004):

$$\langle u^2 \rangle_{\text{loc}} = \langle u^2 \rangle_{\text{anharm}} - \langle u^2 \rangle_{\text{harm}}. \tag{15}$$

If the amplitude of the fast motion exceeds a critical displacement u_0, a local structural reconfiguration (the α-relaxation) takes place. Assuming the timescale 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 the sphere with radius u_0. In this picture, one obtains for the viscosity (Magazù *et al* 2004)

$$\eta = \eta_0 \exp[u_0^2 / \langle u^2 \rangle_{\text{loc}}]. \tag{16}$$

This relation has been tested for the first time on the experimental data obtained by using extended x-ray absorption fine-structure (EXAFS) investigations by Migliardo and Magazù on selenium (Galli *et al* 1986, Burattini *et al* 1988). In figure 4, the linear dependence of viscosity on the local mean-square displacement for glycerol is shown.

In figure 5, the free-volume behaviour as a function of temperature for glycerol (Bartos *et al* 2001) is reported.

The free volume (Cohen and Turnbull 1959) can be expressed by

$$V_{\text{f}} = V - V_{\text{occ}} \tag{17}$$

and denoted as the hole free volume. This volume appears due to dynamic disorder in the liquid which gives rise to an exess in respect to the occupied volume V_{occ}.

In the free-volume theory, viscosity is related to free volume through the relation

$$\eta = \eta_0 \exp(\delta V_0 / V_{\text{f}}), \tag{18}$$

where V_0 is the critical value for free volume and δ is a numerical factor introduced by taking into account the
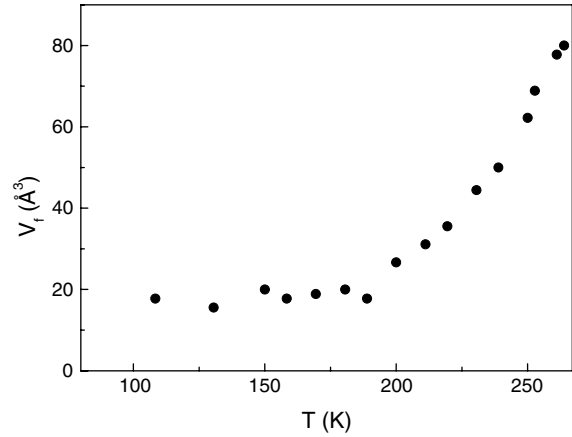
overlap of free volume, which can be neglected, obtaining the expression

$$\eta = \eta_0 \exp(V_0 / V_{\text{f}}). \tag{19}$$

Therefore the linear dependence of $\log \eta$ versus $\langle u^2 \rangle_{\text{loc}}^{-1}$ finds a correspondence with the linear dependence of $\log \eta$ versus the total free volume as evaluated from positron annihilation lifetime spectroscopy measurements. Figure 6 shows the linear dependence of the logarithm of viscosity on the free volume for glycerol.

Evaluating the 'fragility' degree by elastic neutron scattering measurements (Magazù *et al* 2004) as follows:

$$M_u = \left. \frac{\text{d}(u_0^2 / \langle u^2 \rangle_{\text{loc}})}{\text{d}(T_{\text{g}} / T)} \right|_{T = T_{\text{g}}^+}, \tag{20}$$

it has been demonstrated that a linear relationship between M_u and m exists.

On the basis of the analogy found between the relationships linking on the one hand the viscosity and mean-square displacement and on the other hand the viscosity and free volume, we propose the following definition of local

Figure 6. Linear dependence of the logarithm of viscosity on the free volume.

fragility:

$$M_V = \left.\frac{\mathrm{d}(V_0/V_f)}{\mathrm{d}(T_g/T)}\right|_{T=T_g^+}. \qquad (21)$$

This definition implies that the excess free-volume evaluation allows us to estimate the fragility degree directly. The values obtained by using the above-described procedure are $M_u = 96$ and $M_V = 98$.

In order to link the macroscopic definition of fragility, as obtained by viscosity data, and the microscopic definition of fragility, as obtained by the evaluation of the mean-square displacement by elastic neutron scattering measurements, we observe that the mean-square displacement of a molecule is an average characteristic of the thermal motion. Therefore the mean-square displacement can be expanded in the series

$$\langle u^2 \rangle^{-1} = \langle u^2 \rangle_W^{-1} + \gamma_1 n_H + \cdots, \qquad (22)$$

where $\langle u^2 \rangle_W^{-1}$ is the contribution due to the van der Waals forces and n_H is the number of H-bonds per molecule. Within the framework of the proposed interpretative model, we obtain (Blazhnov *et al* 2006)

$$M_u \cong \ln 10 \frac{\gamma_1 T_g}{\lambda_1} m. \qquad (23)$$

Equation (23) theoretically justifies the observed proportionality between the macroscopic m, evaluated by measuring a macroscopic quantity, i.e. viscosity, and microscopic M_u, evaluated by measuring a microscopic quantity, i.e. mean-square displacement, definitions of fragility.

4. Conclusions

In this work the link between viscosity and mean-square displacement and between viscosity and free volume is discussed. The approach is applied on the experimental data collected on glycerol. Through the established proportionality law between the M_u and M_V fragility parameters and the m fragility parameter, it is therefore possible to obtain information on the fragility degree of glass-forming systems using spectroscopic techniques such as elastic neutron scattering, EXAFS and positron annihilation spectroscopy.

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