Fragility as a Measure of Dynamic Inhomogeneity of Glass Formers

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The structure and dynamics of glass formers are spatially inhomogeneous with typical scale of nanometers. The influence of this inhomogeneity on the glass transition is considered. Using Lindemann criterion of melting, the locally liquid- and solid-like particles are defined and a percolation problem for liquid and solid clusters is formulated. On the basis of percolation theory it is shown that in strong glass formers the dynamic inhomogeneity is higher than in fragile ones. The standard deviation of the lognormal spatial distribution of the mean square atomic displacements $\langle r^2 \rangle$ is found to be equal to $0.1\div 0.2$ for fragile glass formers, 0.5 for intermediate glycerol and 0.7 for strong B₂O₃. The comparison with the free volume size distribution in a fragile polymer shows a good agreeement with the predictions of the model.

§1. Introduction

One of the important properties for characterizing different glass formers is the degree of fragility. The latter was introduced by Angell¹⁾ and shows the speed with which viscosity of supercooled liquid decreases with T/T_g . The strong liquids exhibit comparatively slow decrease of the viscosity and fragile ones exhibit a fast drop of the viscosity with temperature near T_g . The physical basis of the degree of fragility is still not well understood.²⁾

In the present paper we connect the degree of fragility with the dynamical inhomogeneity of a system. As a parameter which can characterize the dynamical inhomogeneity we choose the mean square thermal atomic displacements $\langle r^2 \rangle$. In a glass, due to the structure fluctuations, $\langle r^2 \rangle$ is different in different points. We will show here that the width of the spatial distribution function of $\langle r^2 \rangle$ is connected with the degree of fragility, being higher in stronger glass formers.

§2. Model

In the model, the Lindemann criterion of melting³⁾ is used which assumes that at the melting temperature $\langle r^2 \rangle$ is equal to a universal fraction of the square interatomic distance. Let us define locally liquid- and solid-like particles as ones with $\langle r^2 \rangle > r_L^2$ and $\langle r^2 \rangle < r_L^2$ respectively, where r_L^2 is some critical value of $\langle r^2 \rangle$. It is assumed that the time window of averaging is not higher than some periods of the atomic vibrations, i.e., it is of the order of a picosecond, to avoid the influence of diffusion on $\langle r^2 \rangle$ in the case of the liquid-like particles. In these terms, a glass former at any temperature contains both liquid- and solid-like regions, their relative concentration being dependent on temperature. Since these regions are distributed randomly, a percolation approach is suitable for the problem. Two percolation thresholds are 388

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characteristic for the system. When temperature is raised, the first one corresponds to a point T_1 where a first infinite liquid-like cluster appears in the system. The second threshold corresponds to a temperature T_2 at which the last infinite solidlike cluster disappears. In the continuum 3D percolation model these two points correspond to a critical concentration $p_c \simeq 15\%$ of liquid- or solid-like particles, respectively.⁴⁾ There is also a third important temperature for the model, namely, the temperature T_L at which averaged over the whole system $\langle r^2 \rangle$, denoted by \bar{r}^2 is equal to the Lindemann value r_L^2 . Obviously, due to the definition, $\bar{r}^2(T_1) \leq r_L^2 \leq \bar{r}^2(T_2)$ holds. We assume that just this temperature, T_L , corresponds to the glass transition, $T_L \simeq T_g$, i.e., $\bar{r}^2(T_g) = r_L^2$. This assumption can be considered as phenomenological observation similar to the Lindemann criterion of melting.^{5),6)}

In addition to T_g there are at least two characteristic temperatures which are used to describe the behavior of the viscosity in the liquid-glass transition. They are the Vogel-Fulcher-Tammann temperature T_0 and the crossover temperature T_c , $T_0 < T_g < T_c$. T_0 is defined by a phenomenological fit of the viscosity at $T > T_g$:⁷⁾ $\eta = \eta_0 \exp(B/(T - T_0))$. The ratio T_g/T_0 is higher in strong glass formers than in fragile one and is one of the possible measures of the degree of fragility.^{2),8)}

The crossover temperature T_c is predicted by the mode coupling theory (MCT) as a temperature of an idealized glass transition. This temperature which for fragile liquids is higher than T_g by 30–50 K ($T_c/T_g = 1.1 \div 1.2$) is found in many experiments (see, e.g., reviews 9) and 10)). T_c may be defined by applying a power law for the temperature dependence of the viscosity, explicitly $\eta \propto (T - T_c)^{-\gamma}$, $T > T_c$. Indications for a crossover temperature are found also in intermediate and strong supercooled liquids, namely, glycerol¹¹⁾ and B₂O₃.^{12),13)} It means that T_c may have physical meaning also in such complex liquids. In glycerol and B₂O₃ the ratio T_c/T_g is sufficiently higher than in fragile liquids and is equal to 1.5–1.6. Below we will show that within the frames of the percolation approach there is a possibility to interpret T_0 , T_c as T_1 and T_2 and the critical exponent γ as a critical index of conductivity.

Close to the percolation threshold, variables related to the percolation can be expressed as a power function of $p - p_c$. In particular, the conductivity σ has the critical exponent t:⁴⁾ $\sigma \propto (p - p_c)^t$, where typically $t \sim 2$ holds. The concentration p(T) of atoms with $\langle r^2(T) \rangle > r_L^2$ close to T_2 can be expanded in power series of $T - T_2$, so results in $\sigma \propto (T - T_2)^t$, $T > T_2$. On the other hand, MCT predicts that within the scenario of an ideal glass transition the self-diffusion coefficient D(T)has to vanish at the crossover point T_c according to a power law as does $1/\eta$:⁹⁾ $D \propto 1/\eta \propto (T - T_c)^{\gamma}$, $T > T_c$, $\gamma = 2 \div 3$.⁹⁾ Comparison of the percolation result for σ with the MCT prediction leads to the hypothesis that T_2 is the crossover temperature T_c .

Computer simulations show that the distribution of $\langle r^2(T) \rangle$ can be described by a lognormal function, ¹⁴⁾ $P(x) = (2\pi\sigma^2)^{-1/2} \exp(-(\ln\langle r^2 \rangle/\bar{r}^2(T))^2/2\sigma^2)$. The width of the distribution, σ , is a measure of the dynamical inhomogeneity. In Ref. 15) it was shown that under the condition that T_1 and T_2 coincide with T_0 and T_c , respectively, one has the following relation: Fragility as a Measure of Dynamic Inhomogeneity of Glass Formers 389

$$\frac{\bar{r}^2(T_c)}{\bar{r}^2(T_q)} = \frac{\bar{r}^2(T_g)}{\bar{r}^2(T_0)} = e^{\sigma}.$$
(2.1)

Since below $T_g \bar{r}^2(T) \propto T$ it means that $\sigma = \ln(T_g/T_0)$. As it was mentioned above, the ratio T_g/T_0 is a measure of the degree of fragility of a glass former. Thus, the spatial fluctuations of $\langle r^2 \rangle$ are higher in strong glass formers than in fragile ones. The width σ of the $\ln \langle r^2 \rangle$ distribution can be chosen as a measure of the inhomogeneity. This parameter, as found from the ratio T_g/T_0 , increases from $0.1 \div 0.2$ for such fragile glass formers like CKN, PS, salol to $0.5 \div 0.7$ for intermediate glycerol and strong B₂O₃ and to $1 \div 1.2$ for the most strong silicates.⁸

The predictions of the model were checked by comparison with the data on $\bar{r}^2(T)$ obtained by inelastic neutron scattering for polybutadiene, polystyrene, selenium, o-terphenil and glycerol.¹⁵⁾ A reasonable agreement was obtained between experimental data and the model. Another possible check comes from the positron annihilation lifetime spectroscopy (PALS) data on the size distribution of the free volume holes. The computer simulations show that distribution of $\ln \langle r^2 \rangle$ coincides with that of $\sim (2/3) \ln V_f / V_0$ where V_0 is some reference volume.¹⁴⁾ This is understandable since the dynamical inhomogeneity is caused by the structural one and the coefficient 2/3 corresponds to what one can expect from dimensional arguments. Hence, according to the model, the size distribution function of the free volume holes should have the larger width σ_f the stronger the glass former. Additionally, the model predicts that $(2/3)\sigma_f \approx \sigma \approx \ln(T_q/T_0)$. There are the PALS data for the distribution of free volumes in poly(vinyl alcohol) (PVA).¹⁶⁾ One can expect that it is a fragile glass former like poly(vinyl acetate). For the latter the fragility is close to that of CKN $^{17)}$ so we take as a rough estimate of σ for PVA the value 0.08^{15} like for CKN. The lognormal fit of the free volume distribution function for PVA from Ref. 16) gives $\sigma_f \approx 0.1$ (Fig. 1) which corresponds to $\sigma \approx 0.07$, in good agreement with the expecting value. Another way to find σ is the examination of deviation from the gaussian law neutron scattering function S(q,t). If $\langle r^2 \rangle$ are inhomogeneously distributed than q-dependence of S(q,t), in general, deviates from the simple $\exp(-Aq^2)$ dependence, typical for dynamically homogeneous harmonic solid.

In the present approach the only parameter which distinguishes strong and fragile liquids is the degree of the dynamical inhomogeneity, i.e., σ . This parameter determines also the relative size of the interval between T_g and T_c . If one supposes that the viscosity in the interval between T_g and T_c depends only on the concentration of the liquid-like regions then in coordinates scaled by the magnitude of this interval one has to obtain a master plot for the viscosity of the strong and fragile liquids. Such coordinate can be chosen, for example, to be $(T_g/T)(T_c - T)/(T_c - T_g)$. In Fig. 2 log $[\eta/\eta(T_g)]$ vs this scaled temperature is shown. Instead of T_c we used some fitting temperature T_x which provides coincidence with a master curve. For the latter, log $[\eta/\eta(T_g)]$ vs the scaled coordinate of OTP with $T_x \equiv T_c$ was chosen. Figure 2 shows the master plot for the viscosity of some liquids, both for fragile (like OTP) and strong (like B₂O₃). Deviations from the master curve occur only at V. Novikov, E. Rössler and V. Malinovsky



Fig. 1. Lognormal fit of the free volume distribution in PVA, PALS data from Ref. 16).

 $T > T_x$. The temperature T_x , which provides the best coincidence with the master plot is close to the T_c values reported in the literature.^{9), 18)} However, for polymers the master curve is different, reflecting the topological difference of the structure between polymeric and non-polymeric materials. In more detail this scaling of the viscosity data is discussed in Ref. 18).



Fig. 2. Logarithm of viscosity in the scaled coordinates, see the text.

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§3. Conclusion

In conclusion, there is a connection between the dynamical inhomogeneity of glass formers and their degree of fragility: strong glass formers are more inhomogeneous than fragile ones. This property is reflected in higher fractional intervals $(T_g - T_0)/T_g$ and $(T_c - T_g)/T_g$ in the strong glasses formers. It is shown that the quantitative measure of the dynamical inhomogeneity, the width σ of the lognormal distribution of $\langle r^2 \rangle$, correlates with the ratio T_g/T_0 , which is one of the definitions of the degree of fragility. In particular, we obtained σ to be equal $0.1 \div 0.2$ for fragile glass formers, 0.5 for intermediate glycerol and 0.7 for strong B₂O₃. This value is also close to 2/3 from the width of the free volume size distribution as it was demonstrated here for a fragile polymer system.

Acknowledgements

This work was supported by INTAS, Grant No. 93-2185-Ext. and RFFI Grant No. 96-02-16202-a. V. N. N. and E. R. acknowledge the support of Sonderforschungbereich 279 Bayreuth.

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