

## Slow relaxation near structural and orientational transitions in glass-forming liquids and solids

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We argue that the fragility observed near the glass-transition temperature complies with the growing correlation length conception for the entire family of glass-forming materials. The analysis is given through the percolation-theoretical treatment of the relaxation dynamics considered in an effective medium of dimension  $\bar{d}$ . For long-lived clusters of characteristic radius  $R_0$  dynamical correlations are introduced through the relaxation time  $\tau_0 \propto R_0^z$ . The relaxation function is given in an explicit Kohlrausch-Williams-Watts form with the stretch exponent  $\beta = \bar{d}/(z + \bar{d})$  that results in the fragility  $m = m_0/(1/\beta - 1)$ . It is shown that within the low-frequency domain the cluster-growing correlations are consistent with the Dixon-Nagel master curve and fit the idea of universality of glass-transformation features in solids and liquids. [S1063-651X(98)08601-2]

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The presence of non-Debye relaxation near the temperature of structural glass transformation  $T_g$  is a common feature of all glass-forming materials. The late-time relaxation dynamics is well described by only two temperature-dependent parameters  $\beta$  and  $\tau_\beta$  through the phenomenological stretched-exponential form given for the relaxation function and known as the Kohlrausch-Williams-Watts (KWW) form, namely,  $\phi(t) \propto \exp(-(t/\tau_\beta)^\beta)$ , with  $0 < \beta < 1$ . The question arises whether these or others dynamical parameters related to them can definitively represent the underlying, microscopically different mechanisms of structural and orientational relaxations in diverse materials. Combining results of a number of theoretical models, emphasized in KWW-type relaxation, with experimental findings investigators arrived at different standpoints. The fundamental significance of the stretched exponent  $\beta(T_g)$  in molecular and electronic glasses has been formulated [1] very recently: “the reduction of  $\beta$  with temperature reflects the contraction of configurational space and its eventual stabilization due to structural arrest at  $T = T_g$ ” as opposed to the statement [2] that “no special significance can be attributed to the numerical value of  $\beta$ .”

Recently, a bulk of response data from glass-forming liquids (simple and complex molecular liquids, molten salts, hydrogen-bond alcohols, and polyalcohols), amorphous polymers, and glassy crystals studied using dielectric, viscoelastic, calorimetric, and optical techniques has been quantitatively and qualitatively analyzed [3]. All of these have been analyzed in terms of the observable stretched exponent  $\beta_g$  [ $= \beta(T_g)$ ] and so-called fragility,  $m = d \log_{10}(\tau^{-1})/d \log_{10} T$  at  $T = T_g$ , which, respectively, characterize the degree of deviation of the relaxation dynamics from the standard Debye and Arrhenius behavior. For the entire family of glass-forming materials, except orientational glasses, a certain correlation between  $\beta_g$  and  $m$  has been numerically established (see Fig. 2 in Ref. [3]). One of the goals of the current Brief Report is to introduce qualitative relationships

between fundamental dynamic parameters in order to gain a deeper physical insight into the universal features of the glass-transition phenomena.

The sophisticated analysis [4] of data on primary dielectric response in some overcooled molecular and alcoholic liquids carried out in a wide range of temperatures and frequencies resulted in the model-independent scaling scheme, known as the Dixon-Nagel master curve. This provides a good testing probe and challenges modern theories of structural glass transition. The mode-coupling theory, which predicts a sequence of relaxation mechanisms in structural relaxation and explains the high-frequency departure from the KWW form within the Dixon-Nagel master curve, though, does not lead to the stretched-exponential-type solutions in an analytical form in the low-frequency region, where the KWW form fits well [5]. Qualitatively the same can be referred to as Hunt's percolation analysis [6] of the primary dielectric relaxation given through the universal scaling form [4]. The departure from the apparent KWW form in dipole liquids as well as in electronic and ionic glasses was interpreted [6] as a crossover from *independent* hopping transitions at high frequencies to *correlated* transitions near the relaxation peak frequency. No theoretical predictions have been made [6] for the strong-correlated low-frequency region. The entire frequency region was studied *phenomenologically*. It has been quantitatively justified within the framework of mesoscopic domains through the so-called “dynamical correlation coefficient” by Chamberlin [7] using concepts of the percolation cluster theory. In the current Brief Report we emphasize spatial correlations characteristic of late-time dynamics employing concepts of the kinetic theory of phase transitions [8]. This scheme avoids phenomenological parameters and provides an analysis of the geometrically originated structure relaxation through the principal dynamical parameters accessible in real experiments.

The structure-disorder freezing is followed by strengthening of dynamical correlations and evolves smoothly from Debye behavior as the temperature approaches the transition from above [4,6,7]. Hence, the relaxation function can be defined in terms of the Debye-type pretransition clusters, namely,

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$$\phi(t) = \langle \varphi_R \rangle, \quad \varphi_R = \exp - \frac{t}{\tau_R},$$

$$\langle \dots \rangle = \int_0^\infty \dots P_R dR, \quad T > T_g. \quad (1)$$

The configurational average is performed by the radius-size-cluster distribution function treated in a generalized Poisson-like form, namely,  $P_x = Cx^u \bar{d}^{-1} \exp - x^{\bar{d}}$  with  $x = R/R_0$ . Here  $R_0$  stands for the characteristic cluster radius and  $C$  is a normalization constant. Formally,  $P_x$  describes the probability to find a cluster  $R > R_0$  in a medium, with effective dimension  $\bar{d}$ , where the relaxation takes place. Its parameters can be established through the size distribution function given in the Stauffer scaling form for percolating clusters [see Eq. (2.22) in Ref. [9]] if one takes into consideration the volume-size relation  $V_R \propto s \propto R^{d_c}$  ( $d_c$  stands for the finite-size cluster dimension and  $s$  is the number of percolation sites or bonds). In the spirit of the phase-ordering kinetic theory [8] let us employ the algebraic form for the cluster relaxation time  $\tau_R = \tau_0 (R/R_0)^z$ , where  $\tau_0$  is the characteristic cluster relaxation time and  $z$  is the cluster-growth dynamical critical exponent. Physically, this implies that the growing scaling length  $R_0(t) \propto t^{1/z}$  is expected for long-lived “survival” clusters [8]. Mathematically, the proposed algebraic scaling provides a way to put the cluster evolution mechanism through relevant dynamical parameters in an explicit form. Evaluation of the integral (1) performed by the standard saddle-point method ( $t \gg \tau_\beta$ ) yields

$$\phi(t) \propto \exp - \left( \frac{t}{\tau_\beta} \right)^\beta, \quad \text{with}$$

$$\beta = \frac{\bar{d}}{z + \bar{d}}, \quad \tau_\beta = \tau_0 \beta (1 - \beta)^{1/\beta - 1}, \quad (2)$$

where the ignorable (within the late-time dynamics) preexponential factor  $(t/\tau_\beta)^{-\alpha}$ , related to small clusters, is omitted. Remarkably, the stretched exponent formula  $\beta$  (2) generalizes the result  $\beta = d/(2+d)$  known from the  $d$ -dimensional trapping model employing the Brownian diffusion of particles [see, e.g., Eq. (3.7) in Ref. [1]].

Let us discuss the range of validity of the proposed description through the Dixon-Nagel master curve. The KWW form is restricted within the high-frequency wing  $\omega > \omega_p$  ( $\approx \tau_0^{-1}$ ,  $\omega_p$  is the peak frequency) by the abscissa variable value equal to 3 that corresponds to  $\omega_0$  within the context of the percolation treatment given in Ref. [6]. This is supported by Fig. 3(c) in Ref. [4] for the case of supercooled liquids as well as by Fig. 4(a) in Ref. [10] for orientational glasses. In the frequency regime  $\omega_0 < \omega < \omega_c$  ( $\omega_c \approx \omega_p$  is the critical percolation frequency, with [6]) association of molecules into clusters with enhancement of correlations takes place [6]. The susceptibility of the model under discussion is given in Fig. 1. As seen, the correlated cluster approach (1) is compatible with the scaling form [4] below the abscissa equal to 1 or, approximately, within the region given by  $\omega < \omega_p(1 + w/2)$ . The latter includes the low-frequency wing of the susceptibility presented in  $\chi - \omega$  coordinates. There-

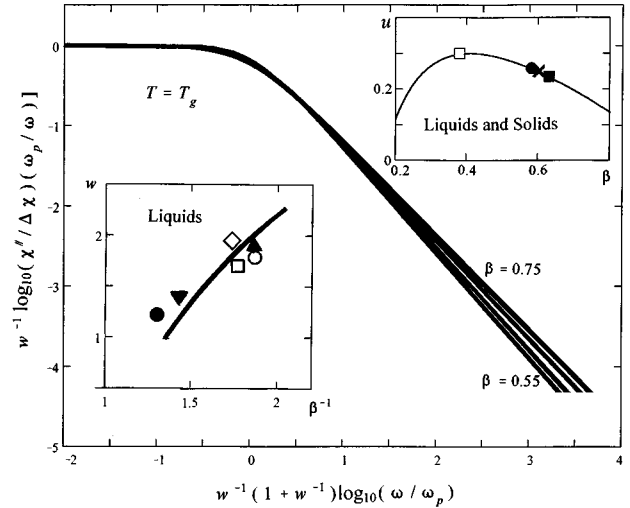


FIG. 1. Dixon-Nagel master curve for glass-forming liquids at transition temperature vs the stretched exponent  $\beta$ . Solid lines correspond to numerical evaluation of the susceptibility  $\chi(\omega) = \langle (1 - i\omega\tau_R)^{-1} \rangle$  through Eq. (1) for  $\beta = 0.55, 0.6, 0.7$ , and  $0.75$  with  $u = 0.23$ . Left inset: Solid line—normalized half maximum width  $w(\beta) = 6(1 - \beta)/[1 + \beta(7u - 1)]$  established through the high- $\omega$  asymptotic relation  $\chi''(\omega) \propto \omega^{-A}$  with  $A = u\beta/(1 - \beta)$  and interpolated to the intermediate frequencies with  $A = 6(1 - w^{-1})/7 - 1$  justified with Fig. 3(b) in Ref. [4]. Points correspond to experimental data [4] extrapolated to  $T = T_g$  for liquids from propylene glycol (●) to salol (▲) (for other notations see Fig. 2 in Ref. [4]). Right inset: Solid line—solution of the equation  $w(\beta) = \beta^{-1}$  for the distribution function parameter  $u$  (1). Points and their notations correspond to overall experimental data [3] for liquids (■), polymers (□), network (●), and orientational glasses (×).

fore this range is due to the long-lived ( $t > \tau_0$ ) and big ( $R > R_0$ ) clusters which obey the algebraic scaling  $\tau_R \propto R^z$  with  $z = \bar{d}(\beta^{-1} - 1)$ .

Until now no assumptions have been made on the temperature dependence of the characteristic cluster radius. We are going to demonstrate that experimental data [3] strongly corroborate the cluster-size growing conception. Indeed, if one admits  $dR_0/dT < 0$  at  $T = T_g$  the relation

$$m = m_0 \left( \frac{1}{\beta_g} - 1 \right) \quad \text{with } m_0 > 0 \quad (3)$$

immediately follows from the fragility definition given above and Eq. (2). In Fig. 2 the cluster-growth conception is verified for the entire glass-former family. This result [11] can be compared with those established numerically [3] ( $m = a - b\beta_g$ ) and phenomenologically [12] ( $m = a\beta_g^{-2} + b$ ; see also Ref. [13]). Figure 2 also demonstrates the universality of the structure-glass-transformation mechanisms in different materials.

To be more specific, we involve the Vogel-Fulcher fitting form in the cluster characteristic relaxation time through  $\tau_0(T) \propto \exp D/\varepsilon(T)$  with  $\varepsilon(T) = (T - T_0)/T_0$ . This results in  $m = D(1 + \varepsilon_g)/\varepsilon_g^2 \ln 10$  with  $\varepsilon_g = \varepsilon(T_g)$ . The material-dependent parameter  $D$  has been systematically measured and, as established numerically,  $D = m_2/(m - m_1)$  with  $m_1 = 16$  and  $m_2 = 590$  (see Fig. 1 in Ref. [3]). To search distinguished characteristics for a given class of glasses let us complete these two equations by Eq. (3). Consequently, we come to a new equation  $\beta(\varepsilon_g)$ , the solution of which is

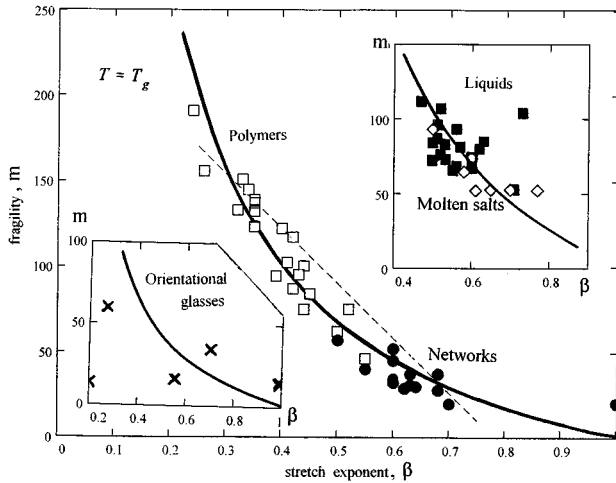


FIG. 2. Fragility vs stretched exponent for the structural glass family. Solid lines correspond to Eq. (3) for liquid and molten salt ( $m_0=100$ ), polymer and network ( $m_0=70$ ), and orientational ( $m_0=40$ ) glass-forming materials. Dashed line corresponds to the equation  $m=250-320\beta_g$  established in Ref. [3]. Points and their notations for liquids (■), molten salts (◇), polymers (□), network (●), and orientational glasses (×) correspond to experimental data in Ref. [3].

displayed in Fig. 3 for structurally and orientationally disordered materials. Besides the qualitative agreement with experimental findings, this solution is consistent with Monte Carlo simulations [14,15] which exhibit the KWW-type relaxation of the orientational order parameter above the transition temperature. This study has been carried out on the basis of the Potts-glass model known [16,17] as the generic model for the class of orientational glasses. As established recently on the microscopic basis, orientationally disordered (but site ordered) materials near the glass transition are driven by spatially correlated [17] random-bond interactions which dominate over the intrinsic [18] and/or extrinsic [19] random-field effects. In addition to Fig. 2, Fig. 3 illustrates that materials that are different on the microscopic level manifest universal features of glass transformation.

Among various glass formers special attention should be paid to structurally disordered  $\text{GeO}_2$  and orientationally disordered  $\text{RbCN}$  and neoxeganol (see Table I in Ref. [3]) as well as to structural and orientational glass models introduced in the molecular dynamic simulation studies [20]. All these systems preserve quasi-Debye dynamics and/or quasi-Arrhenius behavior down to the transition temperature. Following classification introduced by Angell and co-workers [3] and discussed by Souletie [21] this case can be referred to as the “strong system” limit ( $T_0 \ll T_g$ ). Additionally, the solution given in Fig. 3 requires  $\beta_g \rightarrow m_0/(m_1+m_0)$  with  $m \rightarrow m_1$  and  $T_0 \rightarrow 0$ . On the contrary, the extremely “fragile systems” ( $T_0 \approx T_g$ ) are characterized by  $\beta_g = m_0 \varepsilon_g / \sqrt{m_2}$  and  $m = \sqrt{m_2} / \varepsilon_g$ .

The power scaling form for the characteristic cluster time  $\tau_0 \propto (T - T_c)^{-z\nu}$  has also been employed to describe the primary relaxation in liquids, polymers, and molten salts by fitting experimental data on viscosity [2,21]. As established, in the “strong system” region ( $T_c > T_g$ ) the low-viscosity data result in  $z\nu \approx 6$  and in the “fragile system” region ( $T_c \approx T_g$ )  $z\nu \approx 15-25$  (see, respectively, Table I and Fig.

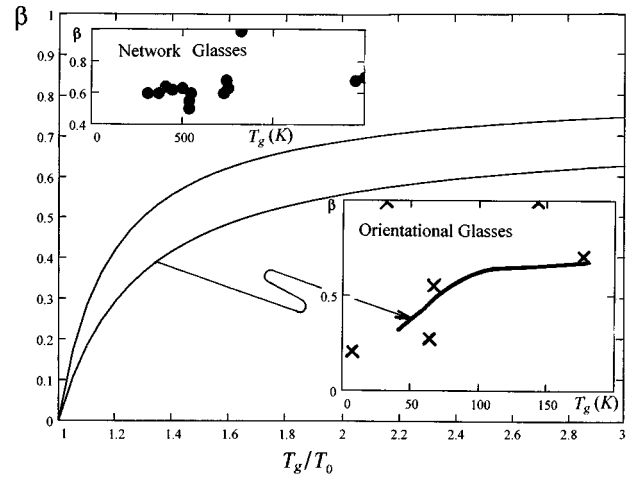


FIG. 3. KWW-form stretched exponent against the reduced transition temperature. Lines: solutions of the three-equation system composed for fragility derived within the Vogel-Fulcher fitting form. Upper and lower lines are given for  $m_0=70$  and  $40$ , respectively, established in Fig. 2. Left inset: experimental data for  $\beta_g$  derived for network glasses [3]. Right inset: crosses—experimental data for orientational glasses [3]. Solid line—Monte Carlo simulation results for the Potts-glass model [14] (see also Fig. 4.12 in Ref. [15]).

8(b) in Ref. [21] and Figs. 13–15 in Ref. [2]). Unlike the analysis given in Ref. [21] these results can now be understood on the basis of equation  $z\nu = \nu \bar{d} (\beta^{-1} - 1)$  and the stretched exponent data accumulated in Ref. [3]. Discussion of the cluster-growing kinetic mechanisms [8] relevant to the structure glass problem will be given elsewhere. Immediate estimations show that for the entire family of glass materials  $\nu \bar{d}$  is far above the fragile limit  $\nu \bar{d} = 1$  forbidden thermodynamically [21].

To summarize, the relaxation effects are discussed in view of recent findings on structural and orientational disorder freezing in glass-forming materials. The percolation-theory-cluster analysis is given in terms of the dynamically correlated clusters relaxing in an effective medium of dimension  $\bar{d}$ . The dynamic correlations are introduced through Debye-type relaxation time which increases algebraically with the cluster size. Eventually, the principal characteristics of non-Debye and non-Arrhenius dynamics, namely, the stretched exponent  $\beta = \bar{d}/(z + \bar{d})$  and the fragility (3)  $m(\beta)$  emerge naturally as explicit functions of fundamental parameters of the system. As shown, the late-time spatial correlations introduced into the relaxing model system through the algebraic scaling are compatible with the low-frequency part of the Dixon-Nagel master curve interpolated to the glass-transition temperature  $T_g$ . Finally, we have demonstrated that, regardless of the requirement of divergence of the correlation length, the evolution of the system upon cooling down to  $T_g$  is accompanied by the cluster growing. This is consistent with the structural and orientational rearrangements observed near the glass transition both in solids and liquids [3].

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- [1] J.C. Phillips, Rep. Prog. Phys. **59**, 1133 (1996).
- [2] W. Götze and L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992).
- [3] R. Böhmer, K.L. Ngai, C.A. Angell, and D.J. Plazek, J. Chem. Phys. **99**, 4201 (1993).
- [4] P.K. Dixon, L. Wu, S.R. Nagel, B.D. Williams, and J.P. Carini, Phys. Rev. Lett. **65**, 1108 (1990).
- [5] B. Kim and G. Mazenko, Phys. Rev. A **45**, 2993 (1992).
- [6] A. Hunt, J. Phys.: Condens. Matter **6**, 8087 (1994).
- [7] R.V. Chamberlin, Europhys. Lett. **33**, 545 (1996); Phys. Rev. B **48**, 15 638 (1993); Phys. Rev. Lett. **66**, 959 (1991).
- [8] The phase-ordering kinetics deals with the dynamical evolution of the system from the initially disordered state ( $T > T_c$ ) to the final state ( $T < T_c$ ), which can be thermodynamically nonachievable due to divergence of the longest relaxation time, see review by A.J. Bray, Adv. Phys. **43**, 357 (1994).
- [9] M.B. Isichenko, Rev. Mod. Phys. **64**, 961 (1992).
- [10] D.L. Leslie-Pelecky and N.O. Birge, Phys. Rev. Lett. **72**, 1232 (1994).
- [11] Our estimations based on the realistic domain of parameters show that the additional term  $\propto \ln(1 - \beta_g)$ , caused by  $\beta(T)$ , is ignorable.
- [12] T.A. Vilgis, Phys. Rev. B **47**, 2882 (1993).
- [13] J. Hodge, J. Non-Cryst. Solids **202**, 164 (1996).
- [14] H.O. Camersing and K. Binder, J. Phys. A **21**, 4053 (1988).
- [15] U.T. Hochli, K. Knorr, and A. Loid, Adv. Phys. **39**, 405 (1990).
- [16] K. Binder and J.D. Roger, Adv. Phys. **43**, 357 (1994).
- [17] V.B. Kokshenev, J. Low Temp. Phys. **104**, 1 (1996); Solid State Commun. **92**, 587 (1994).
- [18] V.B. Kokshenev, Phys. Rev. B **53**, 2191 (1996).
- [19] R. Blinc, T. Apih, J. Dolinšek, M. Šprogar, and B. Zalar, Phys. Rev. B **52**, 15 217 (1995).
- [20] R.M. Ernst, S.R. Nagel, and G.S. Grest, Phys. Rev. B **43**, 8070 (1991); C. Dasgupta, A.V. Indrani, S. Ramaswamy, and M.K. Phani, Europhys. Lett. **15**, 307 (1991).
- [21] J. Souletie, J. Phys. (France) **51**, 883 (1990).