Relationship between Entropic Bottleneck in Free Energy Landscape, Nonexponential Relaxation and Fragility of Glass-Forming Liquids

Dwaipayan Chakrabarti and Biman Bagchi†
Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India
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A mesoscopic model is proposed to explain the anomalous dynamics in a supercooled liquid as its glass transition temperature is approached from above. The model is based on the assumption of β organized α process, with the requirement of coherent excitation of a minimum critical number N_c of β processes in the surroundings of a total N_β. Numerical evaluation of the model shows that the growth in this critical number in the background of a modest N_β can lead to a severe entropic bottleneck and slow down the dynamics to an extent observed near real glass transition. The fragility of the glass-forming liquid is shown to be correlated with the growth of the ratio $\gamma(= N_c/N_\beta)$.

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Relaxation in a viscous liquid above but near its glass transition temperature T_g has been a subject of immense attention in recent time [1, 2, 3, 4, 5, 6, 7]. The dramatic increase in the characteristic relaxation time τ (which varies as much as 15 orders of magnitude for fragile liquids [4, 8]) is most frequently described by the Vogel-Fulcher-Tammann (VFT) equation [9]

$$\tau = A_{VFT}\ exp[B/(T - T_0)], \tag{1}$$

where A_{VFT}, B and T_0 are found to remain constant over a range of $4-5$ orders of magnitude variation of τ. T_0, known as the Vogel temperature, is typically $30-50$ K below T_g. $T_0 = 0$ corresponds to the Arrhenious behavior, characterizing the strong liquid limit. The fragile behavior is further marked by nonexponentiality in the relaxation functions, which can be described by a stretched exponential or Kohlrausch-Williams-Watts function

$$\phi(t) = exp[-(t/\tau)^\beta], \tag{2}$$

where β, $0 < \beta < 1$, is the stretching exponent. For a typical fragile glass-former, β generally decreases from near 1 at high temperatures to below 0.5 close to T_g with a display of nearly monotonic temperature dependence [1]. Experimental and computational studies suggest that the stretched exponential relaxation may owe its origin to the growth of spatially heterogeneous relaxing domains, where each individual exhibits a nearly exponential relaxation with a relaxation time that varies significantly among the individuals [10, 11]. Such heterogeneous domains have been found experimentally to span $2-3$ nm [12, 13]. However, the origin of this modest size of the heterogeneous domains is not clearly understood at present. A consistent description of all the above aspects of dynamics in the supercooled regime has remained a major scientific challenge over many decades.

Several theories suggest the appearance of a growing length scale as the glass transition is approached from above [14]. The celebrated Adam-Gibbs (AG) theory [15] attempts to explain the temperature dependence of relaxation time in terms of a temperature variation of the size z of the cooperatively rearranging region (CRR); the lower limit $z^\star$ is "shown" to follow the relation $z^\star = N_A s_c^\star/S_c$, where $s_c^\star$ is the critical configurational entropy of a CRR corresponding to $z^\star$, S_c is the molar configurational entropy of the macroscopic sample, and N_A is the Avogadro constant. According to AG theory, the sluggishness near T_g is due to the scarcity of the number of configurations available to a CRR, which is reflected in the increasingly smaller value of S_c; the resultant rapid increase in the value of $z^\star$ leads to the divergence of the relaxation time τ. However, experimental [12] and computer simulation [16] studies have failed to find a convincing evidence of a growing length scale near T_g. Nevertheless, AG theory of entropy crisis provides a useful conceptual framework.

Perhaps the most successful quantitative theory of relaxation phenomena in the supercooled liquid state is the mode-coupling theory (MCT) [17, 18]. It is known to become inadequate at low temperatures below T_c, called the MCT critical temperature. This is presumably because of the prevalence of the thermally activated hopping [17, 19] below T_c (unaccounted for in MCT) between the adjacent minima of the energy landscape [6, 20]. Recent computer simulation studies have revealed that hopping is a highly cooperative phenomenon, promoted by many body fluctuations [21]. Computer simulations have further shown that large amplitude hopping of a tagged particle is often preceded by somewhat larger than normal, still small amplitude, but collective motion, of its neighbors. A similar picture of β and α processes was earlier proposed by Stillinger, where the β process corresponds to transitions between inherent structures (IS) within the meta-basin while α process corresponds to transitions between deep meta-basins [6]. Motivated by these findings, we here present a mesoscopic model of relaxation in supercooled liquids ($\sim$ below T_c), where an α process is *promoted by coherent excitations of a minimum number of β processes within a CRR.* The β processes are assumed, as a first approximation, to occur independently. The requirement

†For correspondence: bbagchi@sscu.iisc.ernet.in

of coherence is that a given minimum number N_c among the total number N_β of β processes must be in the excited state during a small interval for an α process (i.e., transition out of a meta-basin) to occur. In our model, a CRR is characterized by an N_β number of identical noninteracting two-level systems (TLSs). Each of these TLSs transits back and forth at equilibrium at temperature T between its two levels, labeled 0 (ground) and 1 (excited). The two levels are separated by an energy ϵ. The waiting time before a transition can occur from the level $i(=0,1)$ is random, but is drawn from a Poissonian probability density function given by

$$\psi_i(t) = \frac{1}{\tau_i} exp(-t/\tau_i), \qquad i = 0, 1, \tag{3}$$

where τ_i is the average time of stay in the level i. If p_i denotes the canonical equilibrium probability of the level i being occupied, detailed balance gives the following relation

$$K = \frac{p_1}{p_0} = \frac{\tau_1}{\tau_0}, \tag{4}$$

where K is the equilibrium constant for the two levels. We define a variable $\zeta_j(t)$, $(j = 1, 2, ..., N_\beta)$, which takes on a value 0 if at the given instant of time t the level 0 of the two-level system j is occupied and 1 if otherwise. $\zeta_j(t)$ is thus an occupation variable. The control variable $Q(t)$ is defined as

$$Q(t) = \sum_{j=1}^{N_\beta} \zeta_j(t). \tag{5}$$

Q(t), which serves as an order parameter, is a stochastic variable in the discrete integer space $[0, N_\beta]$ and carries information of the excitation prevailing in the CRR at time t. The rate of α relaxation depends crucially on Q. For simplicity, we assume here that the relaxation occurs with unit probability at the instant Q reaches N_c, an integer greater than the most probable value of Q, for the first time. This restriction can be removed, but only at the expense of the analytical solution presented below.

We solve the model for the average relaxation time τ, for a a given pair of N_c and N_β, by using the method of mean first passage time [22]. The probability that the stochastic variable Q takes on a value l at time t, $P(l;t)$, satisfies the following master equation

$$\begin{aligned} \frac{dP(l;t)}{dt} &= [(N_\beta - l + 1)/\tau_0]P(l-1;t) \\ &+ [(l+1)/\tau_1]P(l+1;t) \\ &- [(N_\beta - l)/\tau_0]P(l;t) - (l/\tau_1)P(l;t). \end{aligned} \tag{6}$$

The mean first passage time $\tau(l)$, which is the mean time elapsed before the stochastic variable Q (starting from its initial value $l \leq N_c - 1$) reaches N_c for the first time, satisfies the following equation related to the backward master equation:

$$[(N_\beta - l)/\tau_0][\tau(l+1) - \tau(l)] + (l/\tau_1)[\tau(l-1) - \tau(l)] = -1, \tag{7}$$

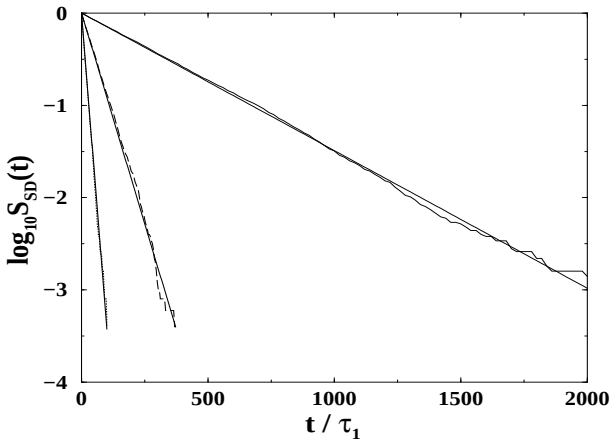

FIG. 1: Semi-log plot of the single domain relaxation function $S_{SD}(t)$ versus t at a given T. The figure is based on the data obtained by simulating the model for single domain relaxation with $\epsilon = k_B T$, k_B being the Boltzmann constant, and $N_\beta = 10$ for $N_c = 6, 7$ and 8 (dotted line, long dashed line, and dot-dashed line, respectively). The solid lines are the straight line fits.

subject to an absorbing boundary condition at $Q = N_c$, $\tau(N_c) = 0$, and a reflecting boundary condition at $Q = 0$, $\tau(-1) = \tau(0)$. We solve Eq. (7) to obtain $\tau(l)$ as a sum over hypergeometric functions $F(a, b; c; z)$

$$\begin{aligned} \tau(l) &= \tau_0(1 + 1/K)^{N_\beta} \\ &\sum_{n=l}^{N_c-1} \frac{F(N_\beta + 1, N_\beta - n; N_\beta - n + 1; -1/K)}{N_\beta - n} \end{aligned} \tag{8}$$

Eq. (8) shows that when the two states are of the same energy, that is, $K = 1$, even then the relaxation slows down significantly. This is purely an entropic effect – a nice example of entropic bottleneck [23]. When there is an energy bias against the excited state (state 1), the bottleneck becomes more severe, as shown below.

The relaxation of the relevant time correlation functions, such as stress and density, is assumed to be caused by the α relaxation. The time dependence of the α relaxation can be quantified by the survival probability correlation function S_{SD}, of the initial meta-basin state. This is obtained by first simulating the model for single domain relaxation. The parameter γ, defined as $\gamma = N_c/N_\beta$, provides a measure of the free energy barrier to relaxation having both the energy and the entropy contributions. Fig. (1) plots the time dependence of the single domain relaxation function $S_{SD}(t)$ in the logarithmic scale at a given temperature for three values of N_c. The straight line fits show a single exponential decay of $S_{SD}(t)$. The time constants obtained are identical to those obtained from our analytical expression, given by Eq. (8). The single domain relaxation is found to slow down considerably, as expected, with increasing γ. Fig. (2) illustrates an exponential dependence of the single domain average relaxation time τ_{SD} on N_β at fixed γ

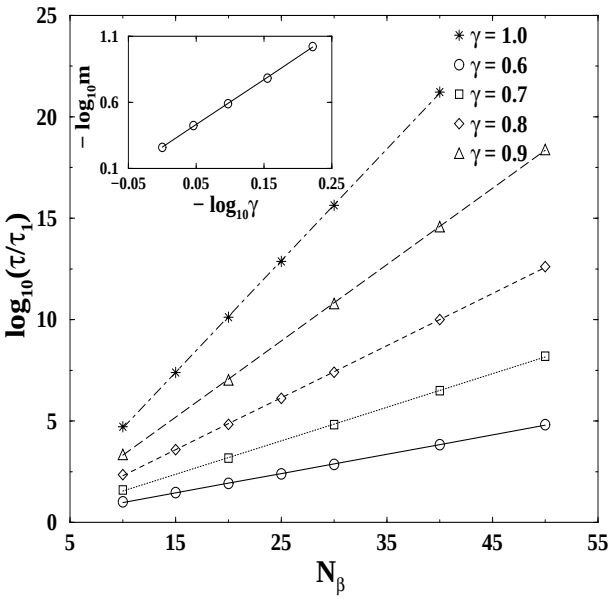

FIG. 2: Dependence of the single domain average relaxation time τ_{SD} on N_β at a given temperature T with $\epsilon/(k_BT) = 1$ for different fixed values of γ. The inset shows the γ dependence of the slope m of the semi-log plot of the scaled τ_{SD} versus N_β.

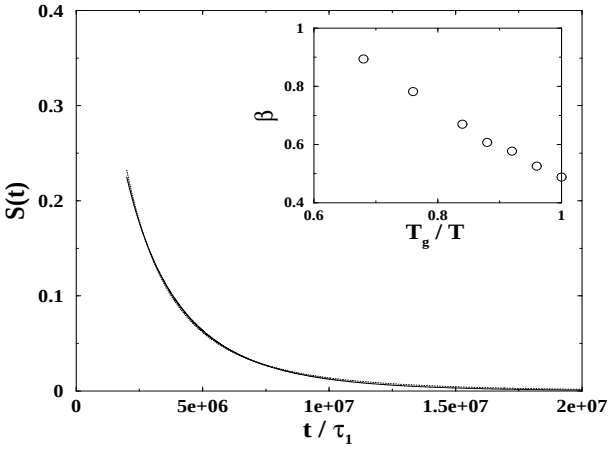

FIG. 3: The long time behavior of the averaged relaxation function $S(t)$. The solid line is a fit to the stretched exponential function with $\tau = 1.100 \times 10^6 \tau_1$ and $\beta = 0.670$. The inset shows the temperature dependence of the stretching exponent β.

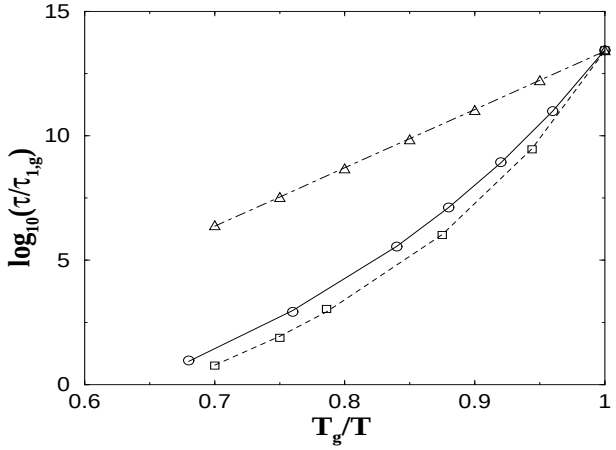

FIG. 4: Arrhenious plot showing the scaled characteristic relaxation time τ as a function of reduced inverse temperature T_g/T. The two sets of data, marked with circles and squares, for τ are obtained from the stretched exponential fit of the long time behavior of the average relaxation function $S(t)$. The circles correspond to the data set obtained from a linear variation of γ from 0.6 to 1.0 as T_g/T is increased from 0.68 to 1.0 with N_β held fixed at 20. The squares denote the data set corresponding to a linear growth of γ with T_g/T, both rising from 0.70 to 1.0, with N_c and N_β varied together, the latter from 10 to 20. The solid and the dotted lines, which are the corresponding fits to the VFT form with $T_0 = 0.689\ T_g$ and $0.789\ T_g$, respectively, illustrate fragile liquid behavior. The data set, marked with triangles, are obtained with γ, N_β, and ϵ all held constant: $\gamma = 1.0$, $N_\beta = 40$, and $\epsilon = k_BT_m$. The data are scaled so as to have the same τ value at T_g as for the other two sets. With no distribution of ϵ, the relaxation is exponential with the time constant τ. The straight line fit corresponding to the Arrhenious behavior is typical of a strong liquid. Here, for the sake of simplicity, numerical evaluation is done by taking $\tau_{SD} = \tau(Q_{mp})$, where Q_{mp} is the most probable value of Q; this involves negligible error.

and T; τ_{SD} is a weighted average of $\tau(l)$ over the initial distribution: $\tau_{SD} = \sum_{l=0}^{N_c-1} P(l;0)\tau(l)$. The dependence, characterized by the slope of the semi-log plot of the scaled τ_{SD} versus N_β, becomes stronger as γ increases. The inset suggests a power law behavior of the slope m, $m \sim \gamma^\nu$ with $\nu \simeq 3.4$. Note that τ_{SD} is also the mean waiting time.

In a heterogeneous environment within a bulk sample, a fluid-like region can be characterized by having, at a given time, on the average, a relatively large number of β processes in the excited state. The reverse is true for solid-like regions. Therefore, a Gaussian distribution of ϵ among CRRs can incorporate the existence of heterogeneous domains into the model (one can also assume an exponential distribution). The present calculation takes the mean $< \epsilon >$ of the distribution to be unity and the standard deviation $\sigma = 0.05$ in the units of k_BT_m, T_m being the melting temperature. T_m is also used to define T_g: $T_g = 2T_m/3$. Furthermore, the model assumes N_c to grow as the reduced inverse temperature T_g/T increases until N_c reaches N_β at T_g. The Gaussian distribution of ϵ results in a continuous distribution of τ_{SD}. The average relaxation function $S(t)$ is calculated from $S(t) = \int_0^\infty d\tau_{SD} g(\tau_{SD}) exp(-t/\tau_{SD})$, where $g(\tau_{SD})$ is the probability density function. The long time behavior of $S(t)$ fits well to the stretched exponential function as shown in Fig. (3). The inset shows a monotonic decrease

of the stretching exponent β with T_g approached from above, as indeed observed experimentally. The study of the temperature dependence of the characteristic relaxation time τ requires time to be scaled by the same unit at all temperatures. τ_1 at T_g, which we denote by $\tau_{1,g}$, is chosen for that. The scaling needs, for a transition state theory (TST) calculation, an input to $\epsilon^{\ddagger}$, the energy barrier to the transition from the level 0 to 1, which is taken to be 4 $k_B T_m$ and held constant. Fig. (4) shows the T_g scaled Arrhenious plot of the characteristic relaxation time. The fit to the VFT equation is good. The growth of γ with T approaching T_g from above determines the fragility, as illustrated in Fig. (4). Strong liquid limit is obtained with γ held fixed at 1. Strong liquids are spatially (and, dynamically) correlated even at high temperatures. This justifies the choice of a higher γ and N_β values in the strong liquid limit.

We have also calculated the waiting time distribution $W(\tau)$ (WTD) [24] for this α process. Even when the distribution of energy gap in the meta basin is Gaussian, WTD is non-Gaussian with a stretching at long τ. The waiting time distribution gets modified if the distribution of energy gap (ϵ) is exponential – the most affected region is obviously the small τ limit.

The present model can be considered as a representative in a simple form of a class of wider, more general models. An immediate generalization will be to include the correlations among the β processes within a CRR. Note that the present model explains the slow down of relaxation in fragile liquids as result of an entropic bottleneck superimposed on the energy constraint and does not require any diverging length scale. The model predicts that the observed 13 orders of magnitude increase in relaxation time originates from the combined effect of energy and entropy, and it is not possible to separate the two effects. The model is based on a requirement of dynamical correlation between the β and α processes. This correlation itself depends on the time scale of separation between the two. In the language of energy landscape [6, 24, 25], the β transitions assumed here occur within the super-structures (meta-basins) of a deep minimum and they promote transitions between two deep minima – that is, among the meta basins. While the model rests on dwindling entropy as the temperature is lowered, it does not invoke any thermodynamic phase transition. Most notably, only a modest growth in the size of CRR, represented here by the size of N_β, is required to capture the experimentally observed slow down.

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