Emergence of cooperatively reorganizing cluster and super-Arrhenius dynamics of fragile supercooled liquids

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In this paper we develop a theory to calculate the structural relaxation time τα of fragile supercooled liquids. Using the information of the configurational entropy and structure we calculate the number of dynamically free, metastable, and stable neighbors around a central particle. In supercooled liquids the cooperatively reorganizing clusters (CRCs) in which the stable neighbors form “stable” nonchemical bonds with the central particle emerge. For an event of relaxation to take place these bonds have to reorganize irreversibly; the energy involved in the processes is the effective activation energy of relaxation. The theory brings forth a temperature Tα and a temperature dependent parameter ψ(T) which characterize slowing down of dynamics on cooling. It is shown that the value of ψ(T) is equal to 1 for T>Tα indicating that the underlying microscopic mechanism of relaxation is dominated by the entropy driven processes while for T<Tα, ψ(T) decreases on cooling indicating the emergence of the energy driven processes. This crossover of ψ(T) from high to low temperatures explains the crossover seen in τα. The dynamics of systems that may have similar static structure but very different dynamics can be understood in terms of ψ(T). We present results for the Kob-Anderson model for three densities and show that the calculated values of τα are in excellent agreement with simulation values for all densities. We also show that when ψ(T), τα and other quantities are plotted as a function of T/Tα (or Tα/T) the data collapse on master curves.

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I. INTRODUCTION

When a liquid is supercooled bypassing its crystallization, it continues to remain structurally disordered, but its dynamics slows down so quickly that below a temperature, called the glass temperature Tg, the structural relaxation takes such a long time that it becomes almost impossible to observe [1]. The structural relaxation time, τα, represents the time required for the liquid to return to equilibrium after a small perturbation. The super-Arrhenius temperature dependence of τα (or the viscosity) is the defining characteristic of a ‘fragile’ liquid [2, 3]. The super-Arrhenius behavior suggests that the effective activation energy for the relaxation in a fragile liquid increases with decreasing temperature. The underlying reason for such a behavior is understood in terms of increasing the cooperativity of relaxation on cooling. The cooperativity can be defined in terms of number of particles which move in some sort of concert in order for an elementary relaxation event to occur. These particles may be distributed in a region without forming a compact structure and share the space with other particles [4, 5]. In such a situation it would not be possible to characterize cooperativity in terms of a spatial length. Alternatively, one can think of a compact cooperative region defined by a length ξ; the number of particles in the region varies as ξd, where d is spatial dimension [6, 7]. To have a precise picture of cooperativity (or the cooperative region), its determination as a function of temperature and calculation of the effective activation energy from microscopic interactions between particles have been the major focus of the theoretical description of supercooled liquids and the glass transition [6–23].

Is there any local structural order in a liquid that grows rapidly on cooling and can be associated with the cooperativity? This question has been the subject of much activity of last several years [12–23] as its resolution would lead to a better understanding of glassy phenomena and would provide insights into the underlying microscopic mechanism of the relaxation. However, liquid structure determined from scattering experiments that give information at the level of two-point correlation functions, such as the structure factor and the pair correlation function shows no such local order. This led to the conclusion that if at all there is any local order linked to the cooperativity, it would have to be very subtle and hidden to the pair correlation function. This spurred several proposals of local preferred structure such as the “point-to-set length” [17–20] and the “patch correlation length” [21–23] with varying success. The main difficulty is that one does not know how to distinguish an amorphous ordered structure from the one that exists in a normal liquid [8].

In the Adam and Gibbs theory [6] as well as in the random first order transition (also known as the mosaic) theory [7, 24, 25] the cooperative region is expressed in terms of the configurational entropy. Adam and Gibbs visualized a supercooled liquid as progressively organizing in larger and larger cooperative regions that have to collectively reorganize and proposed that the number of particles in a “cooperatively rearranging region (CRR)” is inversely proportional to the configurational entropy $S_c$. Since the configurational entropy $S_c(T)$ decreases on lowering the temperature, the number of particles in the cooperative region increases. The relaxation time τα is
the time needed to rearrange the region and is given by

$$\tau_\alpha = \tau_0 \exp \left[ \frac{A}{T S_c(T)} \right],$$  \hspace{1cm} (1.1)

where $A$ is a temperature independent phenomenological parameter, and $\tau_0$ is the microscopic timescale.

On the other hand, the mosaic theory assumes nucleation of so-called “entropic droplets” between different metastable configurations that makes the supercooled liquid as a patchwork of local metastable configurations. A static length $\xi$ in terms of which the size of the droplet is expressed is shown to be $\xi = (Y(T)/T S_c(T))^{\frac{1}{d}}$ where $d$ is the spatial dimension, $\theta$ is an exponent related to the interface energy and $Y(T)$ is the surface tension [24, 25]. The relaxation time is related to the configurational entropy by relation,

$$\tau_\alpha = \tau_0 \exp \left[ \frac{1}{T} \left( \frac{Y(T)}{T S_c(T)} \right)^\phi \right],$$  \hspace{1cm} (1.2)

where $\phi = \frac{d - \xi}{d}$. In order to find values of $\xi(T)$ and $\tau_\alpha(T)$ one has to know values of $Y(T)$ and $\theta$.

It has recently been shown [26] that in a supercooled (supercompressed) liquid some particles get localized in potential wells and form long-lived (stable) nonchemical bonds between them. A cluster of these bonded particles collectively rearranges and creates an effective potential energy barrier due to the interaction between the particles. A supercooled liquid can therefore be considered as a network of particles connected with each other by (nonchemical) bonds with life-time varying from microscopic to macroscopic time. We now describe how to calculate the number of these particles from the data of radial distribution function.

### A. Separation of $g(r)$ into parts representing particles of different dynamical states

The radial distribution function which for a simple liquid is defined as [28]

$$g(|r_1^2 - r_2^2|) \equiv g(r) = \frac{1}{N^p} \sum_{j \neq k} N \sum_{j} \delta(|\vec{r} - \vec{r}_j + \vec{r}_k|),$$  \hspace{1cm} (2.1)

where $N$ is number of particles, $\rho$, the number density and the angular bracket denotes the ensemble average, tells us what is probability of finding a particle at a distance $r$ from a reference (central) particle. The average number of particles lying within the range $r$ and $r + dr$ from the central particle in 3-dimensions is $4\pi \rho g(r)r^2dr$. Since $g(r)$ defined by Eq. (2.1) has no information about particle momenta, one can not say how many of these particles located in the region at a given time will remain there forever unless disturbed and how many of them will subsequently move away. To get such information we define $g(r)$ of a binary mixture in the center-of-mass coordinates as [26],

$$g_{ab}(r) = \left( \frac{\beta}{2\pi\mu} \right)^\frac{3}{2} \int dp \ e^{-\beta(\frac{p^2}{2\mu} + w_{ab}(r))},$$  \hspace{1cm} (2.2)

where $\beta = (k_B T)^{-1}$ is the inverse temperature measured in units of the Boltzmann constant $k_B$, $p$ is the relative momentum of a particle of mass $\mu = m/2$. The
The depth of the effective potential (potential of mean-force) where \( \beta \) is the reduced effective potential between a pair of particles of species \( \alpha \) and \( \gamma \) separated by distance \( r \) (expressed in unit of \( \sigma_{\alpha\alpha} \)) in a system of Lennard-Jones at a density \( \rho = 1.20 \) and temperature \( T = 0.45 \). \( \beta w_{\alpha\alpha}^{(i)}(r), r_{ih} \) are, respectively, value and location of \( i \)-th maximum and \( r_{ih} \) is the location on the left hand side of the shell where \( \beta w_{\alpha\alpha}^{(i)}(r) = \beta w_{\alpha\alpha}^{(i)}(r_{ih}) \) (shown by dashed line). The location \( r_{ii} \) and \( r_{sh} \) are values of \( r \) on the left and the right hand side of the shell where \( \beta w_{\alpha\alpha}^{(i)}(r) = [\beta w_{\alpha\alpha}^{(i)}(r) - \psi] \) (shown by full line). \( \beta w_{\alpha\alpha}^{(i)}(r) \) is the depth of the \( i \)-th shell.

The averaged number of particles that form bonds with the central particle can be found from a part of \( g_{\alpha\gamma}(r) \) defined as

\[
g^{(b)}_{\alpha\gamma}(r) = 4\pi \left( \frac{\beta}{2\mu_\alpha^2} \right) \frac{3}{2} e^{-\beta w_{\alpha\gamma}^{(i)}(r)} \int_0^{\infty} \sqrt{2\mu} [w_{\alpha\gamma}^{(i)}(r) - w^{(i)}_{\alpha\gamma}(r)] \times e^{-\beta r^2/2\mu} r^2 \, dp, \tag{2.3}
\]

where summations are over all shells and over all species and \( \rho_\gamma \) is number density of \( \gamma \) species. This number \( n^{(b)}_{\alpha\gamma} \) increases rapidly on lowering the temperature and increasing the density due to an increase in the number of shells surrounding the central particle and increase in values of maximum and minimum of each shell.

Since these bonded particles in each shell have a wide range of energies lying between maximum and minimum of the shell, they oscillate with a wide range of frequencies. However, all those particles whose energies are close to the maximum (barrier height) may not remain bonded for long due to fluctuations embedded in the system (bath) which drive them to escape the barrier. This is an entropy driven process. In case of an athermal system where only packing constraints matter, there are no energy parameters whatsoever, the bath drives all those particles of \( i \)-th shell whose energies lie between \( \beta w_{\alpha\gamma}^{(i)} - 1 \) and \( \beta w_{\alpha\gamma}^{(i)} \) out of the shell \([26]\). But in a thermal system, the entropy driven process is opposed by the energy driven process; the system gains entropy but loses internal energy when particles escape the shell and reverse happens when particles remain in the shell. This competition results in a diminishing bath role in driving particles out of shells. This led us to introduce a temperature dependent parameter \( \psi(T) \) \((\leq 1)\) such that only those particles of \( i \)-th shell whose energy lie between \( \beta w_{\alpha\gamma}^{(i)} - \psi \) and \( \beta w_{\alpha\gamma}^{(i)} \) are able to escape the shell. However, as is well known, the value of \( \psi \) in a normal (high temperature) liquid is one. The departure from 1 is excepted to take place at lower temperatures where the role of energy parameters become important. In Sec. II B we describe a method to determine its value.

The bonded particles can be divided into two groups, one that consists of particles who are able to escape from the shell and the ones which survive fluctuations and remain bonded unless disturbed. The first group of particles is all those particles whose energies lie between \( \beta w_{\alpha\gamma}^{(i)} - \psi \) and \( \beta w_{\alpha\gamma}^{(i)} \) and momenta between
The averaged number of s-particle bonded with a central particle in a binary mixture is

\[ n^{(s)} = n_a^{(s)} + n_b^{(s)} \]  

We have to know value of \( \psi \) as a function of \( T \) and \( \rho \) to calculate value of \( n^{(s)}(T) \) and \( n^{(m)}(T) \) in a given system.

### B. Determination of temperature dependence of \( \psi \) and the number of particles in a cooperatively reorganizing cluster

We call the cluster formed by \( n^{(s)} \), s-particles bonded with the central particle as a cooperatively reorganizing cluster (CRC). For an event of structural relaxation to take place, the cluster has to reorganize irreversibly; the energy involved in this rearrangement is the energy with which the central particle is bonded with s-particles. These particles are distributed in shells around the central particle that share the region with other (mobile) particles. As the structure of the cluster is not compact it cannot be measured in terms of spatial length. The CRC, therefore, differs from the Adam and Gibbs [6] “cooperatively rearranging region (CRR)” which is taken to be a compact structure [6, 17]. The cooperativity here is defined in terms of number of bonds, \( n^{(s)} \), formed by a particle with its neighbors. As the temperature is lowered, the number \( n^{(s)} \) as well as the energy of each bond in the cluster would increase. As a consequence, the relaxation time growth with decreasing temperature is a super-Arrhenius i.e., faster than an exponential in inverse temperature.

Following Adam and Gibbs [6] we assume that the relation between the number of particles in a CRC and the configurational entropy can be written as,

\[ n^{(s)}(T) + 1 = \frac{K}{S_c(T)} \]  

where \( K \) is a temperature independent constant and \( S_c \) is the configurational entropy per particle of the system. Values of \( S_c \) as function of temperature are found from relation \( S_c(T) = S_{\text{total}}(T) - S_{\text{vib}}(T) \) where \( S_{\text{total}} \) is sum of the ideal gas entropy plus excess entropy arising due to interactions between particles and \( S_{\text{vib}} \) is the vibrational entropy arising due to short-time vibrational motions in a local potential energy minimum. Ingenious simulation techniques developed recently [29, 30] have made it possible to find accurate values of \( S_c \) in supercooled region. In present calculations we use values of \( S_c \) reported in Ref. [31].
In order to determine value of \( K \) we first take \( \psi = 1 \) in Eqs. (2.8-2.10) and calculate \( n^{(s)}(T) \) at different temperatures. Values of \( n^{(s)}(T) \) are then used in Eq. (2.11) to calculate \( K \). In Fig. 2 we plot \( K \) vs \( T \) at densities \( \rho = 1, 2, 1.4 \) and 1.6. In all the cases we find that \( K \) is constant above a temperature denoted as \( T_a \); both \( K \) and \( T_a \) depend on \( \rho \). However, for \( T < T_a \), \( K \) deviates from its constant value; this we attribute to the fact that taking \( \psi = 1 \) for \( T < T_a \) is not valid. As argued above, the value of \( \psi \) is expected to decrease from its high-temperature value on cooling below \( T_a \) due to the increasing role of energy driven processes which counter the escape of particles from shells. We have more to say about the constant \( K \) in Sec. V, where we calculate its value from the data of \( \tau_\alpha \) and show that it is indeed temperature independent and equal to the high temperature value shown in Fig. 2.

Assuming that \( K \) remains constant at all temperatures and has value determined from high temperature result plotted in Fig. 2 and listed in Table I, we determine \( n^{(s)}(T) \) from Eq. (2.11). The known values of \( n^{(s)}(T) \) allow us to find temperature dependence of \( \psi \) from Eqs. (2.8-2.10). We plot \( \psi(T) \) vs \( T \) in Fig. 3. We note that in all cases \( \psi = 1 \) for \( T > T_a \) but decreases rather sharply for \( T < T_a \). Values of \( T_a \) for the three densities are given in Table I. In this table we also list, for comparison sake, values of “onset temperature” \( T_{onset} \) and mode-coupling temperatures \( T_{mc} \). The \( T_{onset} \) is defined as the crossing temperature of pair and excess entropies \([32]\) and \( T_{mc} \) is found by fitting data of \( \tau_\alpha \) in a power law form, \( \tau_\alpha \propto (T - T_{mc})^{-\gamma} \) predicted by mode-coupling theory (MCT) \([33]\). According to MCT, \( T_{mc} \) is a temperature at which \( \tau_\alpha \), diverges; a prediction which is not

![Fig. 2. Values of \( K \) as a function of temperature \( T \) found when \( \psi = 1 \) was taken in calculating values of number of \( s \)-particles. The deviation of value of \( K \) from its constant value at low temperature is due to the fact that taking \( \psi = 1 \) at \( T < T_a \) is not valid. Symbols represent calculated values and curves are least-square fit.](image2)

![Fig. 3. Values of \( \psi(T) \) as a function of temperature \( T \) at different densities. Symbols represent calculated values and curves are least-square fit.](image3)

| \( \rho \) | \( K \) | \( T_a \) | \( T_{onset} \) | \( T_{mc} \) |
|---|---|---|---|---|
| 1.2 | 3.10 | 0.68 | 0.77 | 0.43 |
| 1.4 | 2.80 | 1.43 | 1.50 | 0.93 |
| 1.6 | 2.75 | 2.68 | 2.86 | 1.76 |
observed. The temperature $T_a$ falls into the high-temperature regime where slowing down of dynamics is slower from a low temperature region where slowing down of dynamics is faster.

We now use value of $\psi$ found at a given $T$ and $\rho$ in equations derived above to calculate different parts of $g_{\alpha\gamma}(r)$ and number of $m$- and $s$-particles. In Fig. 4 we plot $g_{\alpha\gamma}(r)$, $g_{\alpha\gamma}^{(b)}(r)$ and $g_{\alpha\gamma}^{(s)}(r)$ as a function of distance $r$ for two temperatures $T = 0.45$ and 1.0 and the density $\rho = 1.2$ to show their temperature dependence. In Fig. 5 we explicitly show the spatial range of $g_{\alpha\gamma}(r)$, $g_{\alpha\gamma}^{(b)}(r)$ and $g_{\alpha\gamma}^{(s)}(r)$.

In Fig. 6 we plot number of total ($n_1^{(f)}(T)$) (dotted line), bonded ($n_1^{(b)}(T)$) (dot-dashed line), metastable ($n_1^{(m)}(T)$) (dashed line) and stable ($n_1^{(s)}(T)$) (full line) particles occupying the first coordination shell as a function of $1/T$.

$$g_{\alpha\gamma}^{(f)}(r) = g_{\alpha\gamma}(r) - g_{\alpha\gamma}^{(b)}(r), g_{\alpha\gamma}^{(m)}(r) = g_{\alpha\gamma}^{(b)}(r) - g_{\alpha\gamma}^{(s)}(r)$$

and $g_{\alpha\gamma}^{(s)}(r)$ for species $a$ at $\rho = 1.2$ and $T = 0.45$. From the figure one notes that while $g_{\alpha\gamma}^{(s)}(r)$ is confined in the first shell with length scale of the order of one particle diameter, $g_{\alpha\gamma}^{(m)}(r)$ extends to several shells with length scale of the order of several particle diameter. In this context it is important to realize the role of $\psi$; as $\psi$ decreases on lowering the liquid, contributions to $g^{(s)}(r)$ starts coming from other shells extending the associated length scale.

At a temperature where $\psi$ becomes zero all bonded particles become $s$-particles and length scale of $g^{(s)}(r)$ will be same as that of $g(r) - 1$.

In Fig. 6 we plot number of total particles ($n_1^{(f)}(T)$), bonded particles ($n_1^{(b)}(T)$), $m$-particles ($n_1^{(m)}(T)$) and $s$-particles ($n_1^{(s)}(T)$) occupying the first shell as a function of inverse of the temperature ($1/T$). We note that at high temperatures most particles are free, while few are $m$-particles and very few are $s$-particles. As the system is cooled, $n_1^{(m)}$ remains almost constant but $n_1^{(s)}$ increases though slowly up to $T = T_a$. But for $T < T_a$, $n_1^{(m)}(T)$ decreases while $n_1^{(s)}(T)$ increases with increasing rate at the cost of both free and $m$-particles. As stated above this rate will rapidly increase on further lowering of temperature resulting in a rapid increase in the number of $s$-particles. To have a precise nature of this increase we need to have data of $g_{\alpha\gamma}(r)$ at lower temperatures.

### III. Calculation of the Potential Energy Barrier and the Relaxation Time

The potential energy barrier (activation energy) to relaxation, as stated above, is equal to the energy with which a particle is bonded with $s$-particles. Thus

$$\beta E^{(s)}(T, \rho) = 4\pi \sum_{\gamma} x_{\gamma} \rho_{\gamma} \int_{r_{\gamma}^{(i)}}^{r_{\gamma}^{(f)}} \left[ \beta u_{\alpha\gamma}^{(m)} - \psi(T) - \beta w_{\alpha\gamma}^{(s)}(r) \right] g_{\alpha\gamma}^{(s)}(r)r^2 dr,$$

where energy is measured from the effective barrier $\beta w_{\alpha\gamma}^{(m)} - \psi(T)$. In Fig. 7 we plot values of $\beta E^{(s)}$ vs
1/T for different densities. In all the cases we see sharp rise in $\beta E^{(s)}$ below $T_a$.

The energy $\beta E^{(s)}$ can be considered as the activation energy in the Arrhenius law,

$$\tau_\alpha(T, \rho) = \tau_0 \exp[\beta E^{(s)}(T, \rho)].$$  \hspace{1cm} (3.2)

In Fig. 7 we compare calculated results with values found from computer simulations [31, 34] for $\rho = 1.2, 1.4$ and 1.6. In all the cases we find very good agreement between calculated and simulation values.

### IV. THE TEMPERATURE $T_a$ AND THE DENSITY SCALING

The density dependence of $T_a$ is shown in Fig. 8. In the figure full circles denote calculated values and the curve represents a fit with a power law form: $T_a = a_0 \rho^{\gamma}$ with $a_0 = 0.287$ and $\gamma = 4.757$. If we renormalize the temperature $T$ by $T_a$ and plot values of $\psi(T)$ as a function of $T/T_a$ we find a very good collapse data of $\psi$ at different densities as shown in Fig. 9(a). Similarly when we plot $\rho^{(s)}(\rho, T)$, $\beta E^{(s)}(\rho, T)$ and $\tau_\alpha(\rho, T)/\tau_0$ as a function of $T_a/T$ we find a very good collapse on master-curves as shown in Fig. 9(b), (c) and (d), respectively.

Scaling of thermodynamics and dynamic properties in terms of $\rho^{\gamma}/T$ was argued to be a property of “strongly correlating liquids” [35]. These liquids have strong correlations between their constant-volume equilibrium fluctuations of potential energy $U(t)$ and virial $W(t) = -1/3 \sum_i \vec{r}_i \cdot \Delta \vec{r}_i U(\vec{r}_i, \cdot \cdot \cdot, \vec{r}_N)$ where $U(t)$ is the total potential energy at time $t$ and $\vec{r}_i$ is the position of particle $i$ at time $t$. The correlation is characterized by a single parameter $\Gamma$, defined by a linear fit through a scatter plot of time fluctuations of $U$ and $W$. For the strongly correlating liquids $\Gamma \simeq \gamma$. The parameter $\gamma$ found from the slope of correlation plot as shown in Ref. [34] has some arbitrariness; it varies between 4.5 and 5.1 for the model of Eq. (1.3). If we ignore this variation, the value can be considered to be in good agreement with the one found from the density dependence of $T_a$. This suggests that $T_a$ is related to the “hidden scale invariance” [35, 36] and is a result of strong $WU$ correlations.
where we marked the two regions and determined from the radial distribution function, a compact structure characterized by a static length \( (\text{cooperatively rearranging region}) \) which is taken to be CRC is, however, not the same as the Adam-Gibbs, CRR including momentum distribution in its definition. The relaxation as a function of \( T \) is shown to be the cooperative rearrangement of the pair correlation function" is suggested earlier the CRC structure can be porous; the number of particles in it can increase without increasing its size.

\[ \psi \]

\[ \beta E \]

\[ \frac{\beta E}{\psi} \]

The cooperativity of relaxation is defined in terms of the number of particles (or bonds) \( n \) which are connected with the central particle in a CRC. For an event of relaxation to take place these bonds have to rearrange irreversibly; the energy involved in this process is the effective activation energy \( \beta E \) of relaxation. As the system is cooled, both the number \( n \) and the energy of each bond increase; the combined effect makes the \( \beta E \) to increase rapidly as temperature is lowered. A fit of (collapsed) data of \( \beta E \) with a power law form \( \beta E = b_0 \{n\}^\delta \) with \( b_0 = 0.415 \) and \( \delta = 1.73 \) is shown in Fig. 10.

The parameter \( \psi(T) \) which is introduced to measure the effect that the bath creates to stabilize the size of CRC gives insight into the processes underlying the slowing down of dynamics. The value of \( \psi(T) \) takes a turn from its high temperature value of 1 at \( T = T_a \) and starts decreasing as \( T \) is lowered. There is a crossover region (see Figs. 3 and 9) which separates the high temperature behavior from the low temperature behavior. Exactly same behavior is seen (see Figs. 7 and 9) in \( \tau_a \); a crossover from the high temperature \( (T > T_a) \) behavior to the low temperature \( (T < T_a) \) behavior takes place in the same way as it happens in the case of \( \psi \). This is more clearly seen in Fig. 11 where we marked the two regions with straight lines to separate the crossover region. This brings forth the underlying cause for the temperature dependence of \( \tau_a \). The crossover region marks the change from the dominance of the entropy driven process to the dominance of the energy driven processes in the system on cooling.

Both \( \psi \) and \( T_a \) depend on details of the inter-particle interactions. Value of temperature \( T_a \) is sensitive to the attraction in the potential; its value would increase on increasing the attraction. Since the rate of slowing down of dynamics increases for \( T < T_a \) the two systems with the same repulsion but a different attraction in the pair...
potential would show very different dynamics while $g(r)$ of the two systems may appear similar. This will be investigated in detail in our next publication.

We wish to emphasize that though Eq. (2.11) lacks theoretical rigour [17, 37] it, as has been shown in Sec. II B, correctly describes the relationship between number of particles in a CRC and the configurational entropy. Here, we adopt a method different from the one described in Sec. II B and show that the number of particles in a CRC are inversely proportional to the configurational entropy and calculate the constant $K$. In particular, we now use data of $\tau_\alpha/\tau_0$ determined from simulations in Eq. (3.2) to calculate $\beta E^{(s)}$ at different temperatures and then use these values in Eqs. (2.8-2.10) to calculate values of $\psi(T)$ and $n^{(s)}(T)$ [38]. The plot of $n^{(s)}(T)$ vs $1/S_c(T)$ in Fig. 12 for the three densities show that $n^{(s)}(T) + 1$ is indeed inversely proportional to $S_c$ and the proportionality constant $K$ is temperature independent. Values of $K$ found from the slope of curves of different densities are same as the one given in Table I.

In summary, by including momentum distribution in the definition of the radial distribution function $g(r)$ and using the information of the configurational entropy $S_c$, we calculated the number of free, metastable, and stable particles distributed in coordination shells surrounding a central particle at different temperatures and densities.

It is shown that in supercooled liquids slowing down of dynamics is due to the emergence of cooperatively reorganizing clusters (CRCs) in which the central particle forms (nonchemical) “stable bonds” with neighboring stable particles. The number of bonds with which the central particle is bonded with neighbors defines the cooperativity of relaxation. For an event of relaxation to take place these bonds have to reorganize irreversibly. The energy involved in this process is the effective activation energy $\beta E^{(s)}$ of relaxation. The number of bonds and the energy of each bond of the CRC increase in lowering the temperature and increasing the density. When $\beta E^{(s)}$ is substituted in the Arrhenius law, a super-Arrhenius feature emerges. Results found for $\tau_\alpha$ for the Kob-Anderson model system are in very good agreement with simulation results. The temperature dependence of $\tau_\alpha$ is explained, in terms of the parameter $\psi(T)$ which measures the effect of fluctuations embedded in the bath on stabilizing the size of CRC.

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