

Decoupling phenomena in supercooled liquids: Signatures in the energy landscape

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A significant deviation from the Debye model of rotational diffusion in the dynamics of orientational degrees of freedom in an equimolar mixture of ellipsoids of revolution and spheres is found to begin *precisely* at a temperature at which the average inherent structure energy of the system starts falling with drop in temperature. We argue that this onset temperature corresponds to the emergence of the α -process as a distinct mode of orientational relaxation. Equally important, we find that the coupling between the rotational and translational diffusion breaks down at a still lower temperature where a sharp change occurs in the temperature dependence of the average inherent structure energy.

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The relaxation phenomena in supercooled liquids continue to stimulate intense research interests despite persistent research activity over decades [1, 2]. A major contribution to this activity has come from a variety of experimental techniques, e.g., dielectric relaxation spectroscopy [3], light scattering [4], time resolved optical spectroscopy [5], NMR spectroscopy [6, 7], and optical Kerr effect spectroscopy [8], that probe dynamics of orientational degrees of freedom (ODOF). These experiments reveal an array of dynamical features some of which might owe their origin to the nontrivial interplay between orientational and translational degrees of freedom [9]. On the other hand, a decoupling between rotational and translational diffusion is observed in deeply supercooled molecular liquids in the sense that orientational correlation time continues to track the viscosity as given by the Debye-Stokes-Einstein (DSE) relationship while translational diffusion coefficient does not in contrary to what is predicted by the Debye-Einstein (DE) relation [10, 11]. The $\alpha - \beta$ bifurcation [12, 13, 14], which commonly refers to the bifurcation of two peaks in the dielectric relaxation spectra [12], marks yet another decoupling, this time between two distinct mechanisms for orientational relaxation in liquids composed of non-spherical molecules. The bifurcation temperature T_B was believed to be close to the mode-coupling critical temperature T_c [14], but it has been recently shown in broadband dielectric relaxation measurements that α - and β -relaxations merge together only well above T_c [15].

Here we address the decoupling phenomena from the perspective of potential energy landscape by studying a system with *orientational degrees of freedom* across the supercooled regime. The energy landscape formalism is an approach that explores the features of the underlying potential energy surface of a system for understanding its complex dynamics [16, 17, 18, 19, 20]. In an appealing landscape study of a binary mixture of spheres [20], Sastry *et. al.* found that the onset of non-exponential relaxation in the supercooled regime corresponded to the temperature, below which the dynamics of the system was

influenced by its energy landscape. As in Ref. [20], the focus in most molecular dynamics simulation studies on supercooled liquids, with a few notable exceptions [21], has been on *atomic systems* which involve only translational degrees of freedom (TDOF) [22].

We investigate a binary mixture of 128 Gay-Berne ellipsoids of revolution and 128 Lennard-Jones spheres along an isochore at a series of temperatures down to the deeply supercooled state [23]. The choice of such a system is motivated by the success of binary mixtures of Lennard-Jones spheres [24], that are widely used for computer simulations of supercooled liquids. In our system [23], the interaction between the ellipsoids of revolution is given by the Gay-Berne pair potential [25], which explicitly incorporates anisotropy in both the attractive and the repulsive parts of the interaction with a single-site representation for each ellipsoid of revolution. The interaction potential between a sphere and an ellipsoid of revolution, which is chosen to be a prolate (with aspect ratio $\kappa = 2$), is given by following Cleaver and coworkers [26]. We have determined the set of energy and length parameters such that *neither any phase separation occurs nor any liquid crystalline phase with orientational order appears even at the lowest temperature studied at a high density* [23, 27]. Across the supercooled regime, the diffusion coefficients for both the spheres and the ellipsoids of revolution are found to follow a power law temperature dependence, *i.e.*, $D_t = C_D(T - T_c)^{\gamma_D}$, with $T_c = 0.454$ for the former and $T_c = 0.460$ for the latter. This suggests, within the error limit, the critical temperature T_c to be independent of the type of particle as predicted by the mode-coupling theory (MCT).

In Fig. 1, we show the temperature dependence of the average energy of the inherent structures for our binary system. At high temperatures ($T > 1.0$), the average inherent structure energy remains fairly insensitive to temperature variation. Below $T \simeq 1.0$, this energy decreases progressively up to the lowest temperature studied here.

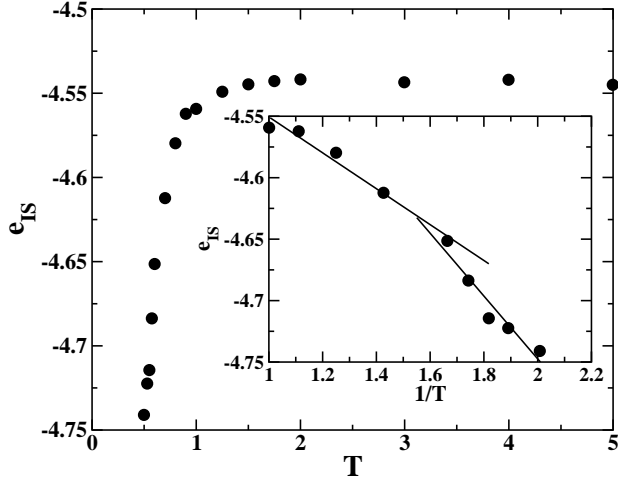


FIG. 1: The average inherent structure energy per particle e_{IS} of our binary system as a function of temperature over the whole temperature range studied. The inset plots e_{IS} versus $1/T$ over the temperature range across which the average inherent structure energy is on a decline. The solid lines are the linear fits to the data over two distinct temperature regimes.

We find that this crossover temperature corresponds to the onset of non-exponential relaxation in the decay of the self intermediate scattering function $F_s(k, t)$ (data not shown). This can be taken as a dynamical signature of the crossover behavior in translational degrees of freedom. Such a crossover in the average depth of the potential energy minima explored by the system has been observed earlier [20], and shown to be consistent with the thermal sampling of a Gaussian distribution of energies for the local minima [19, 28]. The latter, within harmonic approximation, predicts an inverse temperature dependence of the average inherent structure energy [28]. We, however, observe *two distinct temperature regimes*, where the inverse temperature dependence of the average inherent structure energy holds true, *with a sharp change* at a second crossover temperature $T \simeq 0.6$ as illustrated in the inset of Fig. 1. We now investigate whether the temperature dependence of the average inherent structure energy has any correlation with change in the dynamics of orientational degrees of freedom.

Figure 2a shows how the ratio of the first to second rank rotational correlation times, τ_1/τ_2 , evolves as temperature drops. The l -th rank rotational correlation time τ_l is defined as $\tau_l = \int_0^\infty C_l^{(s)}(t) dt$, where $C_l^{(s)}(t)$ is the l -th rank single-particle orientational correlation function:

$$C_l^{(s)}(t) = \frac{\langle \sum_i P_l(\hat{\mathbf{e}}_i(0) \cdot \hat{\mathbf{e}}_i(t)) \rangle}{\langle \sum_i P_l(\hat{\mathbf{e}}_i(0) \cdot \hat{\mathbf{e}}_i(0)) \rangle}, \quad (1)$$

Here $\hat{\mathbf{e}}_i$ is the unit vector along the principal axis of sym-

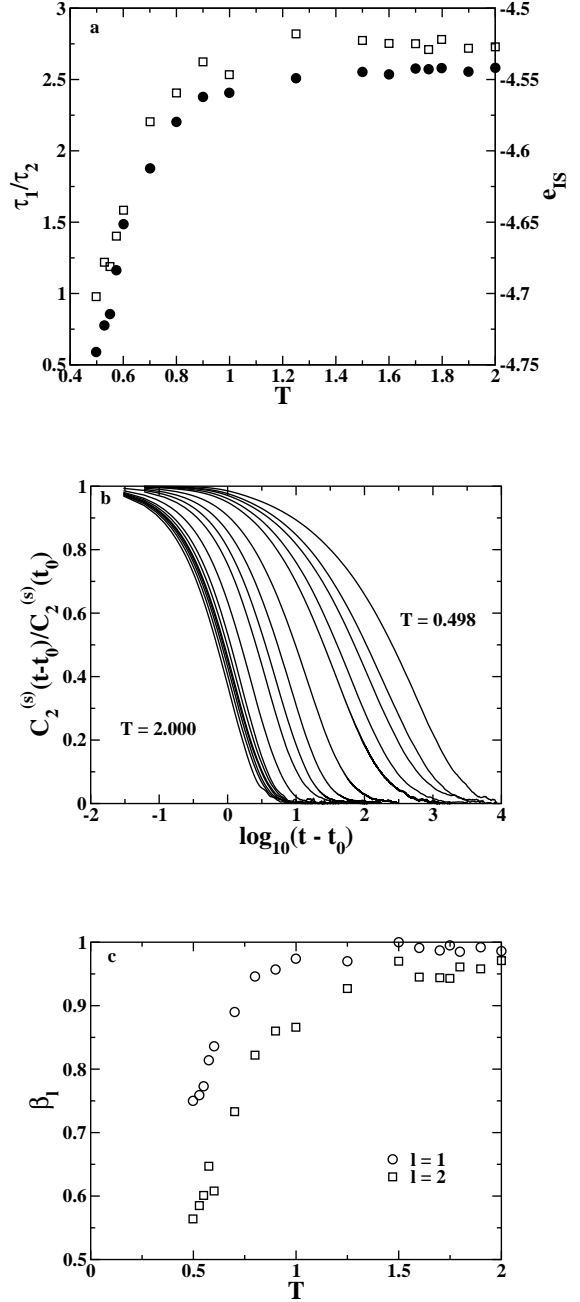


FIG. 2: **a.** The temperature dependence of $\tau_1(T)/\tau_2(T)$, the ratio of the first to second rank rotational correlation times (squares). On a different scale (appearing on the right) shown again is the temperature dependence of the average inherent structure energy per particle e_{IS} for the purpose of comparison (circles). **b.** The time evolution of the single-particle second-rank orientational correlation function at several temperatures with a shift in the time origin to $t_0 = 1.2$ followed by normalization to the corresponding value at t_0 . **c.** The exponents values $\beta_1(T)$ and $\beta_2(T)$, obtained from the fits to the stretched exponential form of the first and second rank single-particle orientational correlation functions, respectively, as a function of temperature.

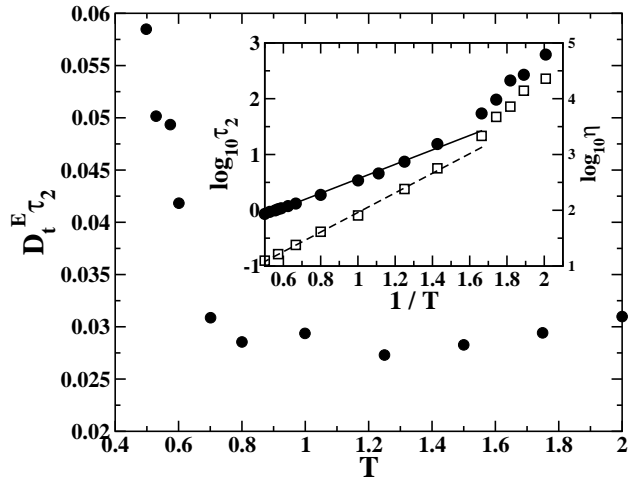


FIG. 3: The product of the translational diffusion coefficient D_t^E and the second-rank rotational correlation time τ_2 for the ellipsoids of revolution as a function of temperature. Inset: The inverse temperature dependence the logarithm of the second-rank rotational correlation time τ_2 (circles). On a different scale (appearing on the right of the inset) shown is the inverse temperature dependence the logarithm of the shear viscosity (squares). The solid and dashed lines are the respective Arrhenius fits to data over a restricted temperature range.

metry of the ellipsoid of revolution i , P_l is the l th rank Legendre polynomial and the angular brackets stand for ensemble averaging. It is evident in Fig. 2a that the ratio has a value close to 3 as predicted by the Debye model of rotational diffusion at high temperatures ($T > 1.0$) and starts declining steadily from $T \simeq 1.0$ until it reaches a value nearly unity at low temperatures. In the diffusive limit, the orientational motion occurs in small steps, while a value for this ratio close to 1 is taken to suggest that the orientational motion takes place via long angular jumps [13].

At high temperatures, the long time decay of $C_2^{(s)}(t)$ is exponential while the Kohlrausch-Williams-Watts stretched exponential form provides a reasonable fit to the long-time behavior at low temperatures. To eliminate the short-time Gaussian time dependence, we show in Fig. 2b the time evolution of the function $C_2^{(s)}(t - t_0)/C_2^{(s)}(t_0)$ for $t > t_0$, and consider the stretched exponential form $\exp[-((t - t_0)/\tau(T))^{\beta_2(T)}]$ that takes into account this transformation to fit the data. The deviation of the exponent $\beta_2(T)$ ($0 < \beta_2(T) < 1$) from unity is a measure of the degree of non-exponential relaxation. Figure 2c shows the temperature dependence $\beta_2(T)$ and also $\beta_1(T)$, the latter corresponding to the long-time decay of $C_1^{(s)}(t)$ (not shown here). While both $\beta_1(T)$ and $\beta_2(T)$ are very close to unity at high temperatures, they

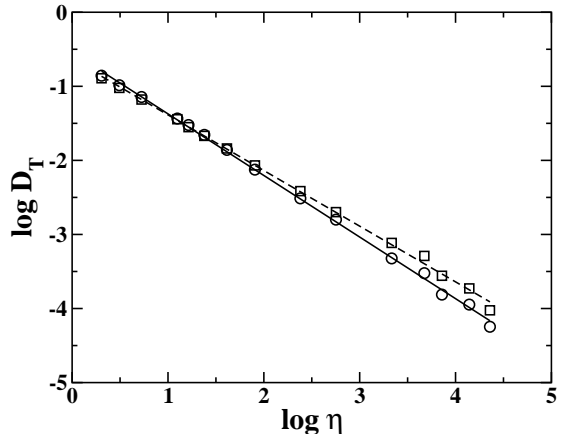


FIG. 4: The translational diffusion coefficient D_t versus the shear viscosity η in a log-log plot for both spheres (circles) and the ellipsoids of revolution (squares). The solid and dashed lines are the respective linear fits.

start dropping as temperature falls. It is evident that *the stretching is more pronounced in the second rank orientational correlation function as compared to the first rank orientational correlation function*. Such an observation has been reported previously while comparing data from dielectric and NMR experiments [7]. We note that the signature of non-exponential relaxation in $C_2^{(s)}(t)$ first becomes appreciable and later gets progressively more pronounced as temperature drops below the onset temperature $T \simeq 1.0$.

It follows from above that the onset of the growth of the depth of the potential energy minima explored by the system correlates with a *change in the mechanism of orientational motion from being simply diffusive*. There is evidence for the β -relaxation to be diffusive in character and the orientational relaxation above T_B is associated with the β -process only [13]. Thus, the onset temperature corresponds to the emergence of the α -process as a distinct mode of orientational relaxation and *appears to be coinciding with the bifurcation temperature T_B* . We, however, find that the latter is somewhat higher than T_c as indeed observed in Ref. [15] in contrary to what often believed. Nevertheless, Fig. 2a illustrates that the decline of the ratio τ_1/τ_2 closely tracks the fall of the average inherent structure energy of the system. Such a correlation, to the best of our knowledge, has not been demonstrated before. Stillinger interpreted the $\alpha - \beta$ bifurcation in terms of the topography of the potential energy landscape [18]. In Stillinger's picture, the β -processes correspond to the elementary relaxations between contiguous basins while the α -processes invoke escape from one metabasin and eventually into other with an involvement

of high free energy of activation. Such a description is consistent with the growth of the depth of the potential energy minima explored by the system below the bifurcation temperature.

We now address the decoupling between rotational and translational diffusion. The combination of the SE and DSE equations predicts the product $D_t\tau_2$ to be independent of temperature even when the macroscopic observable viscosity increases by many orders of magnitude as the glass transition temperature T_g is approached from above [10]. Figure 3 shows that such a relationship breaks down at $T \simeq 0.6$ and below with the product growing fast with decrease in temperature. The inset of Fig. 3 illustrates that the decoupling between the two microscopic observables occurs precisely at the same temperature at which both the orientational correlation time τ_2 and the viscosity start showing steady deviation from the Arrhenius temperature behavior. The inset of Fig. 1 shows that at this temperature the linear variation of the average inherent structure energy with the inverse temperature undergoes a *sharp change with an increase in the rate of fall*.

In Fig. 4, we show the variation of the translational diffusion coefficient D_t with the coefficient of shear viscosity η in a log-log plot over the whole temperature range studied here. The linearity of the curve implies a power law dependence: $D_t \propto \eta^{-\alpha}$, α being the exponent, for both the spheres and the ellipsoids of revolution. We find $\alpha = 0.83$ for the former and $\alpha = 0.75$ for the latter. The *fractional power law dependence* suggests the enhancement of translational diffusion relative to what the SE relationship predicts. The α values obtained here compare well with 0.77, observed by Ediger and coworkers in a direct measurement of self-diffusion of a single-component glass-forming liquid reported recently [29].

We now argue that the deviation from the Debye behavior of rotational diffusion is due to a crossover from a collision dominated to a correlation dominated regime of orientational relaxation. Below $T \simeq 1$, the equilibrium pair correlations are expected to grow as e_{IS} starts its descent. The effects of correlations can be included via the standard Zwanzig-Mori continued fraction representation: $\hat{C}_l(z) = 1/(z + l(l+1)k_B T / (I(z + \hat{\Gamma}_l(z))))$, where the memory kernel $\hat{\Gamma}_l(z)$ can be decomposed in the spirit of MCT as $\hat{\Gamma}_l(z) \simeq \hat{\Gamma}_{coll}(z) + \Delta\hat{\Gamma}_l(z)$, the effect of correlations being contained in $\Delta\hat{\Gamma}_l(z)$, and z stands for the Laplace frequency. The rank dependence of the memory function can be approximately expressed in terms of the torques-torque time correlation function [30]. Because of the up-down symmetry of the ellipsoids of revolution, the contribution of the correlation to $\Delta\hat{\Gamma}_2$ is expected to be larger than that to $\Delta\hat{\Gamma}_1$, particularly at $t = 0$. Thus,

$\hat{\Gamma}_2 > \hat{\Gamma}_1$ and this would lower the value of the ratio τ_1/τ_2 . An opposite trend has been observed for dipolar systems where $\hat{\Gamma}_1 > \hat{\Gamma}_2$ and an upward deviation for the ratio τ_1/τ_2 is observed [30].

In summary, we have established a correlation of the breakdown of the Debye model of orientational relaxation and the $\alpha - \beta$ bifurcation with the manner of exploration of the underlying potential energy landscape in a model system. Equally important, the decoupling between the rotational and translational diffusion is signaled by a sharp rise in the rate of fall of the average inherent structure energy with the inverse temperature.

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