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 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. Further, we find that the coupling between rotational and translational diffusion breaks down at a still lower temperature where a 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 variety of experimental techniques, e.g., dielectric relaxation spectroscopy, light scattering, time resolved optical spectroscopy, NMR spectroscopy, and optical Kerr effect spectroscopy, probe dynamics of orientational degrees of freedom (ODOF) [3]. These experiments reveal an array of dynamical features, which are yet far from being completely understood. 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 contradiction to what is predicted by the Stokes-Einstein (SE) relation [4–8]. The $\alpha - \beta$ bifurcation [9–11], which commonly refers to the bifurcation into two peaks in the dielectric relaxation spectra [9], marks yet another decoupling, this time between two distinct mechanisms for orientational relaxation in liquids composed of nonspherical molecules. The bifurcation temperature T_B was believed to be close to the mode-coupling theory (MCT) critical temperature T_c [11], but it has been recently shown in broadband dielectric relaxation measurements that α and β relaxations merge together only well above T_c [12].

Here we address the decoupling phenomena from the perspective of potential energy landscape by studying a system with orientational degrees of freedom. 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 [13–16]. The onset of nonexponential relaxation in the supercooled regime was found to correspond to the temperature below which the dynamics of the system was influenced by its energy landscape [16]. As in Ref. [16], the focus in most molecular dynamics simulation studies on supercooled liquids, with a few notable exceptions [17], has been on atomic systems, which involve translational degrees of freedom (TDOF) only [18].

We here investigate an equimolar mixture of Gay-Berne ellipsoids of revolution and Lennard-Jones spheres along an isochor at a series of temperatures down to the deeply supercooled state [19]. The choice of such a system is motivated by the success of binary mixtures of Lennard-Jones spheres [20]. In our system [19], 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 co-workers [21]. We have determined the 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 within the simulation time [19,22]. Across the supercooled regime, the translational diffusion coefficients for both the spheres and the ellipsoids of revolution are found to follow a power law temperature dependence: $D_t = C_D(T - T_c)^{\gamma_D}$, with $T_c = 0.454$ for the former and 0.460 for the latter. This, within the error limit, is consistent with the MCT prediction of a critical temperature T_c that is independent of particle types [20].

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. We find that this crossover temperature corresponds to the onset of nonexponential relaxation in the decay of the self intermediate scattering function $F_s(k \simeq k_{\max}, t)$ (data not shown) [16]. The fall of the average inherent structure energy is known to be consistent with the thermal sampling of a Gaussian distribution of energies for the local minima [15,23]. The latter, within the harmonic approximation, predicts an inverse temperature dependence of the average inherent structure energy [23]. We, however, observe two distinct temperature regimes, in each of which the inverse temperature dependence of the average inherent structure energy holds true, with a change in the strength of this dependence at a second crossover temperature $T \simeq 0.6$ as

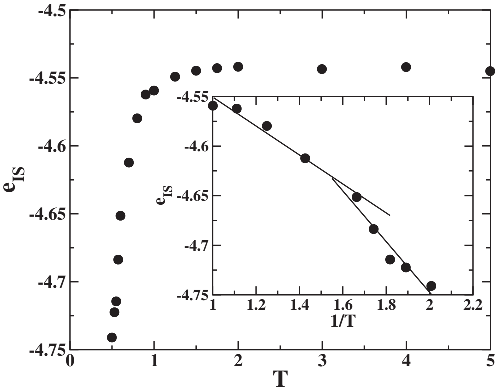

FIG. 1. The average inherent structure energy per particle e_{IS} of our system as a function of temperature over the whole temperature range studied. The inset plots e_{IS} vs $1/T$ over the temperature range across which the average inherent structure energy is on a decline. The solid lines are the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

illustrated in the inset of Fig. 1. We now concentrate on the dynamics of orientational degrees of freedom.

Figure 2(a) shows how the ratio of the first to second-rank rotational correlation time, τ_1/τ_2, evolves as temperature drops. The lth 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 lth rank single-particle orientational time correlation function (OTCF): $C_l^{(s)}(t) = \frac{\langle \sum_i P_l(\hat{\mathbf{e}}_i(0)\cdot\hat{\mathbf{e}}_i(t))\rangle}{\langle \sum_i P_l(\hat{\mathbf{e}}_i(0)\cdot\hat{\mathbf{e}}_i(0))\rangle}$. Here $\hat{\mathbf{e}}_i$ is the unit vector along the long axis of the ellipsoid of revolution i, P_l is the lth rank Legendre polynomial, and the angular brackets stand for ensemble averaging. It is evident in Fig. 2(a) that the ratio has at high temperatures ($T > 1.0$) a value close to 3 and starts declining steadily at $T \simeq 1.0$ until it reaches a value nearly unity at low temperatures. While the Debye model of rotational diffusion which invokes small steps in orientational motion predicts the ratio τ_1/τ_2 to be equal to 3, a value for this ratio close to 1 is taken to suggest the involvement of long angular jumps [10]. The ratio was observed to deviate from the Debye limit at lower temperatures in earlier molecular dynamics simulations [24], which showed the Debye model to hold good at high temperatures. The temperature dependence of the ratio was subsequently interpreted by the coupling model [25].

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. 2(b) 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 $\beta_2(T)$ $[0 < \beta_2(T) \leq 1]$ from unity is a measure of the degree of nonexponential relaxation. The inset of Fig. 2(a) 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 start falling as temperature drops. It is evident that the stretching is more pronounced in the second-rank OTCF than it is in the first-rank OTCF as observed experimentally [26,27]. We note that the signature of nonexponential 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 [10]. Thus, the onset temperature can be

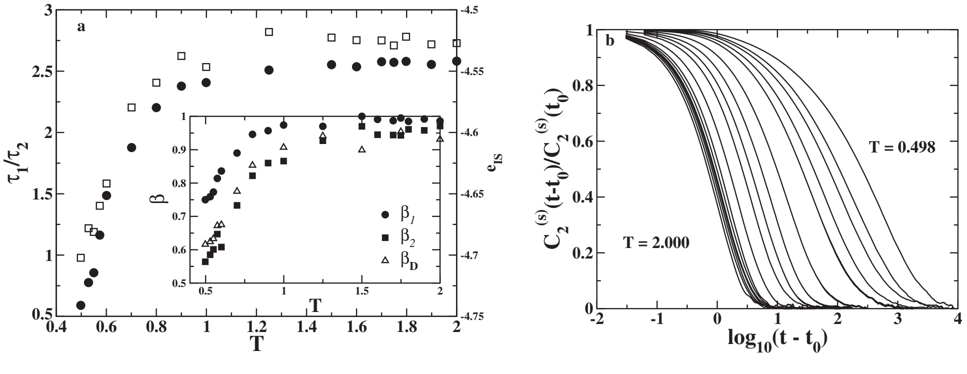

FIG. 2. (a) The temperature dependence of $\tau_1(T)/\tau_2(T)$, the ratio of the first to second-rank rotational correlation time (squares). On a different scale (appearing on the right) shown again is the temperature dependence of the average inherent structure energy per particle e_{IS} for the purpose of comparison (circles). Inset: the values for the exponents $\beta_1(T)$, $\beta_2(T)$, and $\beta_D(T)$ obtained from the fits to the stretched exponential form of the first- and second-rank single-particle OTCFs and $F_s(k \simeq k_{\max}, T)$ data, respectively, for the ellipsoids of revolution as a function of temperature. (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.

taken to correspond 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. [12], on the contrary to what is often believed. Stillinger interpreted the $\alpha - \beta$ bifurcation in terms of the topography of the potential energy landscape [14]. 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 on approaching the glass transition temperature T_g from above [5]. 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 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 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. 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 0.74 and 0.77, observed by Ngai *et al.* and Ediger and co-workers, respectively [28,29].

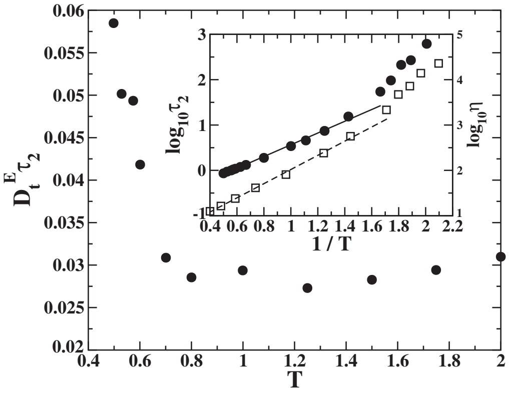

FIG. 3. The product of the translational diffusion coefficient D_t^E and the second-rank rotational correlation time τ_2 for the ellipsoids of revolution as a function of temperature. Inset: the inverse temperature dependence of the logarithm of τ_2 (circles). On a different scale (appearing on the right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

It is interesting to compare the temperature dependence of $D_t\tau_1$ with that of $D_t\tau_2$ [30]. $D_t\tau_1$ shows much weaker temperature dependence, if at all (data not shown). This follows from a weaker dependence of τ_1 on viscosity as compared to τ_2. The observed behavior of $D_t\tau_1$ with temperature appears to pose difficulty to some explanation for the decoupling between rotational and translational diffusion in terms of dynamical heterogeneity [29,30]. On the other hand, such an observation is not inconsistent with the coupling model [31], which invokes different coupling parameters for translational and rotational diffusion as well as for the first-rank and second-rank OTCFs [7,26]. For the sake of comparison, we show in the inset of Fig. 2(a) the temperature dependence of the stretch exponent β_D obtained by fitting the $F_s(k, t)$ data for the ellipsoids of revolution to the stretched exponential function.

Thus, it would be worthwhile to discuss the landscape manifestation of dynamical heterogeneity in the view that the latter is believed to play a central role in the decoupling between rotational and translational diffusion [3,32]. The diversity of the depth of the metabasins and of their connecting pathways in configuration space are expected to result in a broad spectrum of relaxation times underlying dynamical heterogeneity. A recent study has indeed found the dynamics within and transitions between the metabasins to be spatially heterogeneous [33]. When dynamical heterogeneity in the present system was probed by the time evolution of translational non-Gaussian parameter $\alpha_2^{(T)}(t)$ [19], the appearance of a shoulder in between the initial

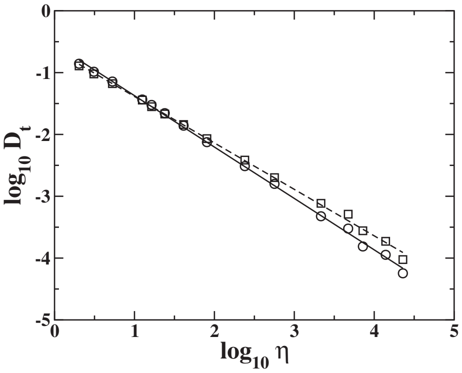

FIG. 4. The translational diffusion coefficient D_t vs the shear viscosity η in a log-log plot for both the spheres (circles) and the ellipsoids of revolution (squares). The solid and dashed lines are the respective linear fits.

rise and the subsequent growth of $\alpha_2^{(T)}(t)$ to its maximum value was observed. We find that the first appearance of the shoulder upon decreasing temperature coincides with the onset temperature.

In summary, we have established a correlation between the breakdown of the Debye model of rotational diffusion and the manner of exploration of the underlying potential energy landscape in a model system. Further, the decoupling between rotational and translational diffusion is signaled by a rise in the rate of fall of the average inherent structure energy with the inverse temperature. Such correlations between the decoupling phenomena and the features of the energy landscape, to the best of our knowledge, have not been demonstrated before.

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