Decoupling of self-diffusion and structural relaxation during a fragile-to-strong crossover in a kinetically constrained lattice gas

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We present an interpolated kinetically constrained lattice gas model which exhibits a transition from fragile to strong supercooled liquid behavior. We find non-monotonic decoupling that is due to this crossover and is seen in experiment.

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The viscosity of glassformers increases by several orders of magnitude upon cooling near the glass transition temperature. For strong glassformers, this increase is Arrhenius, that is, the viscosity increases exponentially with inverse temperature, whereas, for fragile glassformers, this increase is super-Arrhenius [1, 2, 3]. Recent experimental and theoretical evidence indicate that fragile glasses can undergo a crossover to strong behavior at low enough temperatures [4, 5, 6]. Here, we show that a fragile-to-strong crossover can be modeled by a union of two kinetically constrained lattice gas models [7, 8, 9], and that, for this model, the variation of the product of the self-diffusion constant and the structural relaxation time is non-monotonic with temperature as a result of the crossover. The viscosity of salol seems to exhibit a fragile-to-strong crossover with lowering temperature [6, 10], and non-monotonic decoupling behavior similar to what we find in our model has been observed for the product of the shear viscosity and dielectric relaxation time in salol [11].

Our interpolated model is based upon the kinetically constrained triangular lattice gas (TLG) models introduced by Jäckle and Krönig [8]. These two-dimensional models are variants of lattice models proposed by Kob and Andersen [9]. Each site of the triangular lattice has six nearest neighbor sites and can hold at most one particle. A particle at site $\mathbf{i}$ is allowed to move to a nearest neighbor site, $\mathbf{i}'$, if (i) $\mathbf{i}'$ is not occupied and (ii) the two mutual nearest neighbor sites of $\mathbf{i}$ and $\mathbf{i}'$ are also empty. These rules coincide with a physical interpretation of steric constraints on the movement of hard core particles in a dense fluid [8]. We call the model with these rules the (2)-TLG because both mutual nearest neighbors need to be empty in order to facilitate movement. The model where the constraints are more relaxed we call the (1)-TLG: movement is allowed as long as either of the mutual nearest neighbors is empty. As with other kinetically constrained lattice gas models, the TLG has no static interactions between particles other than those that prohibit multiple occupancy of a single lattice site. These models exhibit all the salient features of glassformers (see, for example, [7, 8, 12, 15] such as dynamical slowdown, heterogeneity and lengthscale growth. Moreover, the (2)-TLG is a fragile glassformer and the (1)-TLG is a strong glassformer [12].

To study crossover behavior, we introduce a model

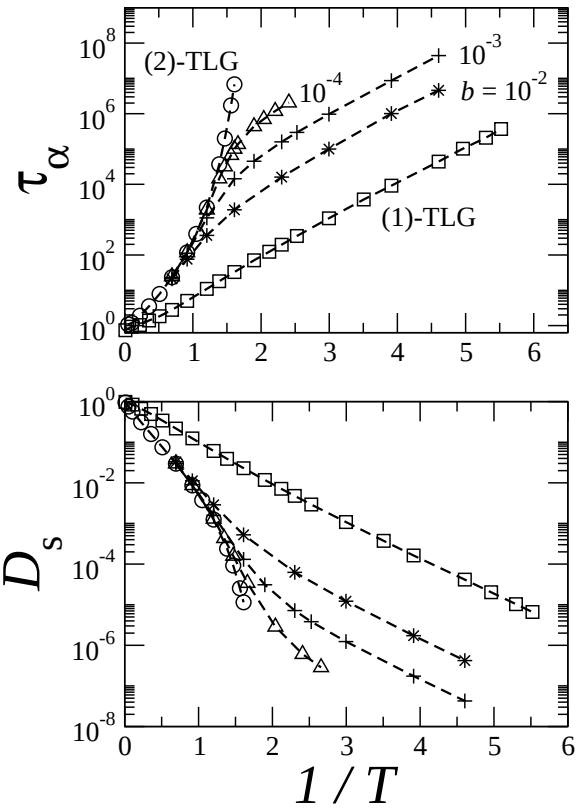

FIG. 1: Simulated structural relaxation time, τ_α (top), and self-diffusion constant, $D_{\rm S}$ (bottom), as a function of inverse temperature at various values of the asymmetry parameter, b: $b = 0$ (circles), $b = 10^{-2}$ (stars), $b = 10^{-3}$ (pluses), $b = 10^{-2}$ (triangles) and $b = 1$ (squares). The same labelling convention is used for all figures. Dashed lines are guides to the eye and, unless otherwise indicated, statistical uncertainties are the size of the symbols used.

which interpolates between the (2)-TLG and the (1)-TLG. A similar model which interpolates between the symmetrically and asymmetrically constrained Ising chains (i.e., the Fredrickson-Andersen [13] and East [14] models) predicts crossover behavior of relaxation times [5]. For our studies, we introduce a parameter b, ranging from zero to one, which controls the dynamics in the following way. When $b = 0$, the only allowed move set is that of the (2)-TLG. When $b > 0$, a move from the

(1)-TLG move set is allowed with probability b. Finally, when $b = 1$, the model is the (1)-TLG. Results for the extreme cases of $b = 0$ and $b = 1$ have been presented elsewhere [12]. In the present study, we perform additional simulations at three intermediate values of b and over several densities, ρ. At each (ρ, b) state point, 32 to 64 independent trajectories of length 10-100 times the structural relaxation time, τ_α, were collected and analyzed. For these simulations, τ_α is the time for the self-intermediate scattering function at wavevector π to reach $1/e$ of its initial value. We define a reduced temperature, T, as $-\ln(1-\rho) \equiv 1/T$. For additional computational details, see [12].

The structural relaxation time in the fragile (2)-TLG scales as a double exponential in inverse temperature and the strong (1)-TLG scales as a single exponential in inverse temperature [12, 15]. We therefore anticipate the following behavior for the crossover model. For a value of b between 0 and 1, we expect the system to relax as if it were the fragile TLG at high temperatures. This is because the time needed for relaxation via the fragile TLG dynamics is faster than waiting a time proportional to $1/b$ to relax via strong dynamics, despite the fact that strong relaxation is faster. At some point as temperature is lowered, the time required to wait for a strong move becomes comparable to the fragile relaxation time and the system crosses over to strong behavaior. This behavior is clearly seen in FIG. 1. For every value of b between 0 and 1, the structural relaxation time initially follows the (2)-TLG curve at high temperatures and then, at some lower temperature, $T_{\rm X}$, it crosses over to (1)-TLG behavior. As we would expect, $T_{\rm X}$ increases, as b increases.

We now turn to relaxation at larger lengthscales where a similar crossover behavior is observed in the self-diffusion constant, $D_{\rm S}$. See FIG. 1. In a dynamically homogeneous system, one would expect the product $D_{\rm S}\tau_\alpha$ to be a constant independent of temperature. That is, one expects mean field relations such as the Stokes-Einstein (SE) relation to be valid. In dynamically heterogeneous systems such as glasses, these mean field relations are dramatically violated: relaxation at long lengthscales decouples from relaxation at shorter lengthscales [11, 16, 17, 18]. In fragile glassformers, $D_{\rm S}\tau_\alpha$ has been found to increase several orders of magnitude as temperature is lowered below some onset temperature, T_o, where the dynamics starts becoming heterogeneous [11, 18]. The same is true for the (2)-TLG where the SE violation is particularly precipitous: $D_{\rm S} \sim \tau_\alpha^{-\xi}$ below $T_{\rm O}$, where $\xi \approx 0.58$ [12]. Strong glassformers, on the other hand, are anticipated to have only a weak SE violation in 2 and 3 dimensions [16]. This is again true for the (1)-TLG where, depending on the definition of τ_α, ξ is between 0.88 and 1 [12].

Therefore, for the interpolated crossover model, as T is lowered, $D_{\rm S}\tau_\alpha$ may vary non-monotonically. Indeed, this behavior is seen in FIG. 2. Moreover, the smaller the value of b, the larger the extremum. Since b varies in the same way as $T_{\rm X}$, this implies that systems with

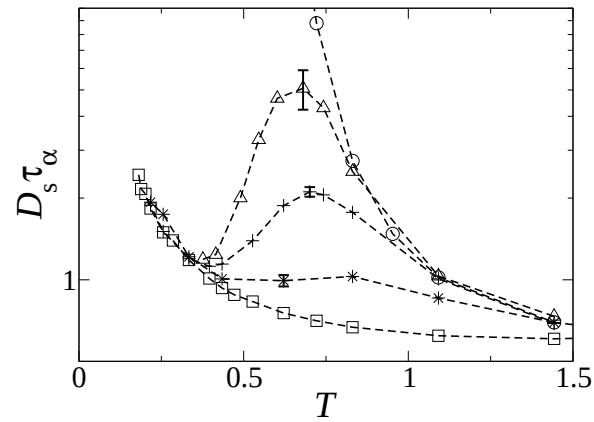

FIG. 2: The product of the self-diffusion constant, $D_{\rm S}$, and structural relaxation time, τ_α, as a function of temperature at various values of the asymmetry parameter, b. Symbols as in FIG. 1.

lower crossover temperatures will exhibit a larger decoupling extremum during a fragile-to-strong transition. Of course, this trend is only strictly true if strong glassformers did not themselves violate SE, which is approximately true for strong glassformers in 2 and 3 dimensions. The analysis of Ref. [6] suggests that salol has a fragile to strong crossover at $T_x \approx 1.1\ T_{\rm g}$. It is at this temperature where salol also shows non-monotonic decoupling [11]. In the models we study here, we have the same coincidence of fragile-to-strong crossover and non-monotonic decoupling.

Finally, we present results on the growth of dynamic heterogeneity lengthscales during a fragile-to-strong transition. We can study dynamical lengthscales by observing a trajectory over a time Δt and considering the binary field $n_{\mathbf{r}}(t;\Delta t) = p_{\mathbf{r}}(t)[1 - p_{\mathbf{r}}(t+\Delta t)]$. Here, $p_{\mathbf{r}}(t)$ is 1 if there is a particle at lattice site $\mathbf{r}$ at time t and 0 otherwise. The field, $n_{\mathbf{r}}(t;\Delta t)$, gives

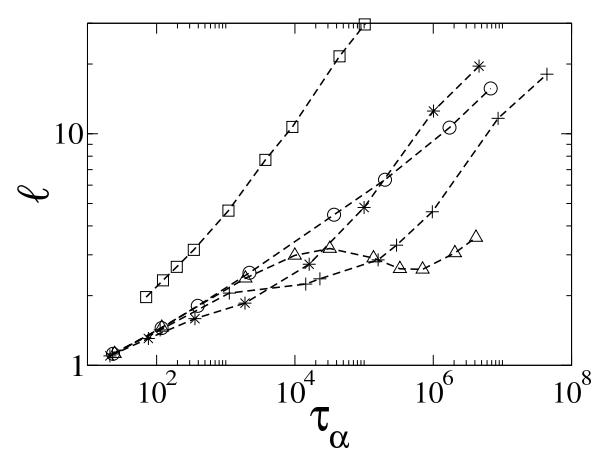

FIG. 3: Growth of dynamical heterogeneity length as a function of structural relaxation time for different values of b. Symbols as in FIG. 1.

a signal only when there is particle motion at $\mathbf{r}$ over the range of time between t and $t + \Delta t$. We then extract a dynamical lengthscale, $\ell(\Delta t)$, as the inverse of the first moment of the structure factors of the mobile particles [6, 12, 20, 21, 22]. These structure factors are four point functions: they measure a correlation function which depends on two points in time, t and $t + \Delta t$, and two points in space, $\mathbf{r}$ and $\mathbf{r}'$. The growth of the dynamic heterogeneity lengthscale with structural relaxation time also exhibits crossover behavior. At some crossover lengthscale, ℓ_{X}, the growth changes from fragile growth to strong growth. This behavior is consistent with [6], where it is argued that generally the relaxation of all fragile systems will obey strong dynamics at large enough lengthscales. We predict, at least for systems exhibiting entropic crossovers [23] like the one studied here, that lower crossover temperatures, T_{X}, will give rise to larger decoupling extremum as temperature is lowered through the crossover region.

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