

Statistical Mechanics and Dynamics of a Three-Dimensional Glass-Forming System

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In the context of a classical example of glass formation in three dimensions, we exemplify how to construct a statistical-mechanical theory of the glass transition. At the heart of the approach is a simple criterion for verifying a proper choice of upscaled quasisppecies that allow the construction of a theory with a finite number of “states.” Once constructed, the theory identifies a typical scale ξ that increases rapidly with lowering the temperature and which determines the α -relaxation time τ_α as $\tau_\alpha \sim \exp(\mu\xi/T)$, with μ a typical chemical potential. The theory can predict relaxation times at temperatures that are inaccessible to numerical simulations.

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Introduction.—Among the best studied models of the glass transitions are those employing point particles with a soft binary potential. Some repeatedly studied examples are the Kob-Andersen model [1], the Shintani-Tanaka model [2], the Dzугutov model [3], and various versions of binary mixtures with purely repulsive potentials; see, for example, [4–6]. While easy to simulate on the computer, these models are challenging for theorists due to the fact that it is extremely hard to evaluate statistical-mechanical partition-function integrals in continuous coordinates. It is therefore very tempting to find a reasonable upscaling (coarse-graining) method that would define a discrete statistical mechanics with partition sums rather than integrals, with the sum running on a finite number of quasisppecies which have well characterized degeneracies and enthalpies. Indeed, in a number of examples in two dimensions (2D), it was shown that such a discrete statistical mechanics is possible [7–11] and quite advantageous [12,13] in providing a successful description of the statistics and the dynamics of systems undergoing the glass transition. In this Letter, we offer a general criterion for the selection of upscaled quasisppecies and demonstrate it, for the first time, in the context of a 3D model system undergoing a glass transition. While for 2D systems the approach discussed here could be confused with “defect” theories or kinetically constrained models [14], the present discussion in 3D shows the generality of the approach and its independence of previous methods. The novel validation scheme presented here guarantees the existence of statistical mechanics that can be used also when simulations become too slow to predict the correct relaxation times.

Model.—We employ here a version of a much studied model of a 50:50 mixture of N point particles in three dimensions ($N = 4096$ in our case), interacting via a binary potential. We refer to half of the particles as “small” and half as “large”; they interact via the potential $U(r_{ij})$:

$$U(r_{ij}) = \begin{cases} \epsilon \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^\alpha - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^\beta + a_0 \right], & r_{ij} \leq r_c(i, j), \\ 0, & r_{ij} > r_c(i, j). \end{cases} \quad (1)$$

Here ϵ is the energy scale and $\sigma_{ij} = 1.0, 1.2,$ or 1.4 for small-small, small-large, or large-large interactions, respectively. For the sake of numerical speed the potential is cut off smoothly at a distance, denoted as r_c , which is calculated by solving $\partial U / \partial r_{ij} |_{r_{ij}=r_c} = 0$ which translates to $r_c = (\alpha/\beta)^{1/\alpha-\beta} \sigma_{ij}$. The parameter a_0 is chosen to guarantee the condition $U(r_c) = 0$. Below, we use $\alpha = 8$ and $\beta = 6$, resulting in $r_c = \sqrt{8/6} \sigma_{ij}$ and $a_0 = 0.10546875$.

As in many of these models, one can quantify the slowing-down in the supercooled regime by measuring a typical correlation function. Here we measured the self part of the intermediate scattering function [5] summed over the large particles only:

$$F_k(t; T) \equiv \left\langle 2/N \sum_{i=1}^{N/2} \exp\{ik \cdot [r_i(t) - r_i(0)]\} \right\rangle. \quad (2)$$

In Fig. 1, we show these correlation functions for $k = 5.1\sigma^{-1}$ and for a range of temperatures as indicated in the figure. We see the usual rapid slowing-down that can be measured by introducing the typical time scale τ_α that is determined by the time where $F_k(t = \tau_\alpha; T) = F_k(0; T)/e \equiv 1/e$. The relaxation times are shown in the inset in Fig. 1 as a function of $1/T$ in a log-lin plot to stress the non-Arrhenius dependence at lower T .

Statistical mechanics.—Our aim is to provide a statistical-mechanical theory that captures the structural changes upon lowering the temperature such that there will pop up a typical scale that can be used to predict the relaxation time τ_α . To this aim we need to upscale (coarse-grain) from particles to quasisppecies that can be characterized by their enthalpy and degeneracy. Upscaling can be done in various ways, and there is no unique algorithm to select *a priori* a “best” upscaling. Here we offer a criterion to validate a chosen upscaling. We choose to work with particles and their nearest neighbors, where “neighbors” are defined as all of the particles j around a chosen central particle i that are within the range of inter-

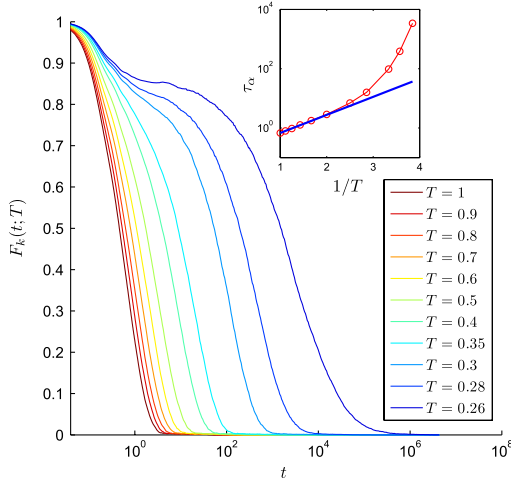


FIG. 1 (color online). Time dependence of the correlation functions (2) for a range of temperatures (decreasing from left to right) as shown in the figure. The inset shows the relaxation time τ_α in a log-lin plot vs $1/T$, compared to an Arrhenius temperature dependence.

action $r_c(i, j)$. In the interesting range of temperatures, we find 8 quasispecies with one small central particle and 3, 4, ..., 10 neighbors and 9 quasispecies with one large central particle with 6, 7, ..., 14 neighbors, all in all 17 quasispecies. Other combinations have negligible concentration ($<0.5\%$) throughout the temperature range. We denote these quasispecies as $C_s(n)$ and $C_\ell(n)$, with s and ℓ denoting the small or large central particle, respectively, while n denotes the number of neighbors. We measured the mole fractions $\langle C_s(n) \rangle(T)$ and $\langle C_\ell(n) \rangle(T)$, and the results are shown in Fig. 2.

To decide whether this upscaling provides a useful statistical mechanics, we now ask whether there exist free energies $\mathcal{F}_s(n; T)$ and $\mathcal{F}_\ell(n; T)$ such that

$$\begin{aligned} \langle C_s(n) \rangle(T) &= \frac{e^{-\mathcal{F}_s(n; T)/T}}{2 \sum_{n=3}^{10} e^{-\mathcal{F}_s(n; T)/T}}, \\ \langle C_\ell(n) \rangle(T) &= \frac{e^{-\mathcal{F}_\ell(n; T)/T}}{2 \sum_{n=6}^{14} e^{-\mathcal{F}_\ell(n; T)/T}}. \end{aligned} \quad (3)$$

The free energies are found by inverting Eqs. (3) in terms of the measured concentrations. We then plot these quantities as a function of the temperature, as demonstrated for the present case in Fig. 3. If $\mathcal{F}_s(n; T)$ and $\mathcal{F}_\ell(n; T)$ can be well approximated as linear in the temperature, we can interpret

$$\begin{aligned} \mathcal{F}_s(n; T) &\equiv H_s(n) - T \ln g_s(n), \\ \mathcal{F}_\ell(n; T) &\equiv H_\ell(n) - T \ln g_\ell(n), \end{aligned} \quad (4)$$

where now the degeneracies $g_s(n)$ and $g_\ell(n)$ (read from the slopes in Fig. 3) and enthalpies $H_s(n)$ and $H_\ell(n)$ (read from the intercepts) are *temperature independent*. This validates the choice of upscaling. In other words, the approximate linearity of the inverted free energies in the temperature

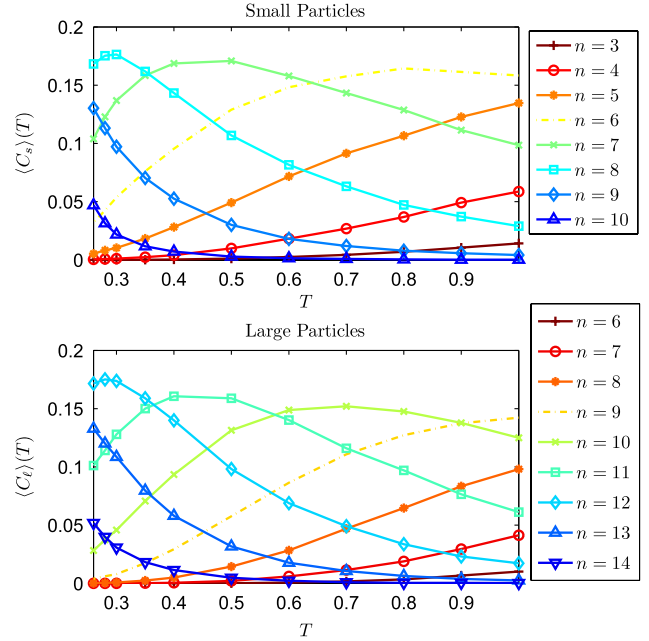


FIG. 2 (color online). Temperature dependence of the concentrations of the various quasispecies. Symbols are simulation data, and the lines are a guide to the eye.

means that we can write the concentrations as

$$\begin{aligned} \langle C_s(n) \rangle(T) &\approx \frac{g_s(n) e^{-H_s(n)/T}}{2 \sum_{n=3}^{10} g_s(n) e^{-H_s(n)/T}}, \\ \langle C_\ell(n) \rangle(T) &\approx \frac{g_\ell(n) e^{-H_\ell(n)/T}}{2 \sum_{n=6}^{14} g_\ell(n) e^{-H_\ell(n)/T}}. \end{aligned} \quad (5)$$

Then we can use these forms also as a prediction for temperatures where the simulation time is too short to observe the relaxation. The resulting degeneracies $g_s(n)$ and $g_\ell(n)$ can be easily modeled theoretically, given basically by a Gaussian distribution around the most probable number n_{mp} of nearest neighbors for small and large particles, respectively:

$$\begin{aligned} g_s(n) &\approx e^{-[(n-n_{mp}^s)^2/2\sigma_s^2]}, & n_{mp}^s &= 4.65, & \sigma_s^2 &= 1.55, \\ g_\ell(n) &\approx e^{-[(n-n_{mp}^\ell)^2/2\sigma_\ell^2]}, & n_{mp}^\ell &= 7.50, & \sigma_\ell^2 &= 2.0. \end{aligned} \quad (6)$$

The comparison of the theoretical to the measured degeneracies is shown in Fig. 4, upper panel. The same figure shows in the middle panel the enthalpies of the various quasispecies. One could model the enthalpies as a linear function in n . These results are easily interpreted; we have high enthalpies when there are large free volumes (few neighbors). The lowest enthalpies are found when there are many neighbors and there is not much costly free volume. In other words, at the present density and range of temperatures, the pV term dominates the energy in the enthalpy. Using the theoretical degeneracies and the measured enthalpies, we compute the concentrations of all of our quasispecies and compare them with the mea-

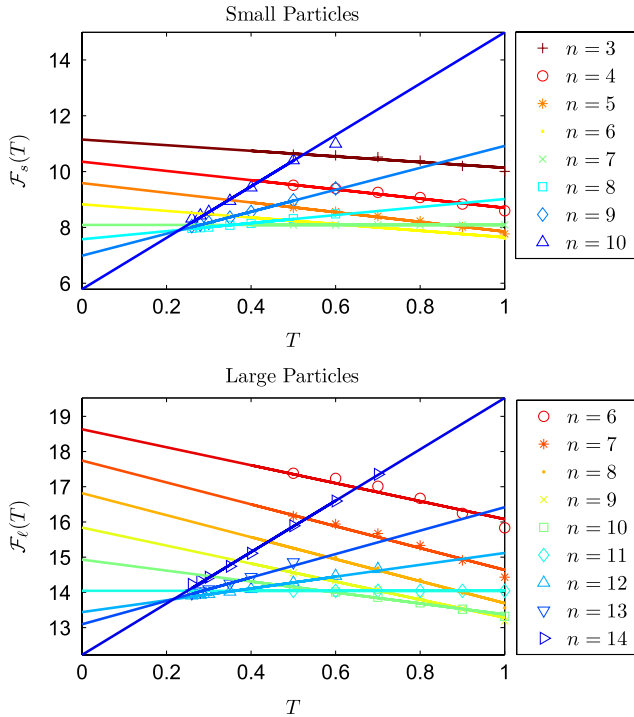


FIG. 3 (color online). The approximate linear dependence of the free energies of the chosen quasispecies on the temperature. From the slope we read the degeneracy and from the intercept the enthalpies (up to normalization); cf. Eq. (4). Note that when the free energies are large we do not have data: the concentrations become exponentially small, and in a finite simulation box they disappear completely.

surement in the lowest panel of Fig. 4. The agreement that we have, especially considering the number of quasispecies and the simplicity of the theory, is very satisfactory. Notice that the competition between degeneracy and enthalpy explains the rather intricate temperature dependence of the concentrations of the quasispecies, sometimes declining when the temperature drops, sometime rising, and sometimes having nonmonotonic behavior.

Prediction of relaxation times.—Finally, we want to connect the structural theory to the dynamical slowing-down. To this aim we note that there are a number of quasispecies whose concentration goes down exponentially (or maybe faster) when the temperature decreases and that the relaxation time shoots up at the same temperature range. We refer to these quasispecies as the “liquid” ones; in this example, the liquid concentrations are those with small particles with three and four neighbors and large particles with six, seven, and eight neighbors. We sum up these concentrations and denote the sum as $\langle C_{\text{liq}} \rangle(T)$. The dependence of $\langle C_{\text{liq}} \rangle(T)$ on the temperature is shown in Fig. 5.

This concentration is used to define a typical scale

$$\xi(T) \equiv [\rho C_{\text{liq}}(T)]^{-1/3}, \quad (7)$$

where ρ is the number density. This length scale has the

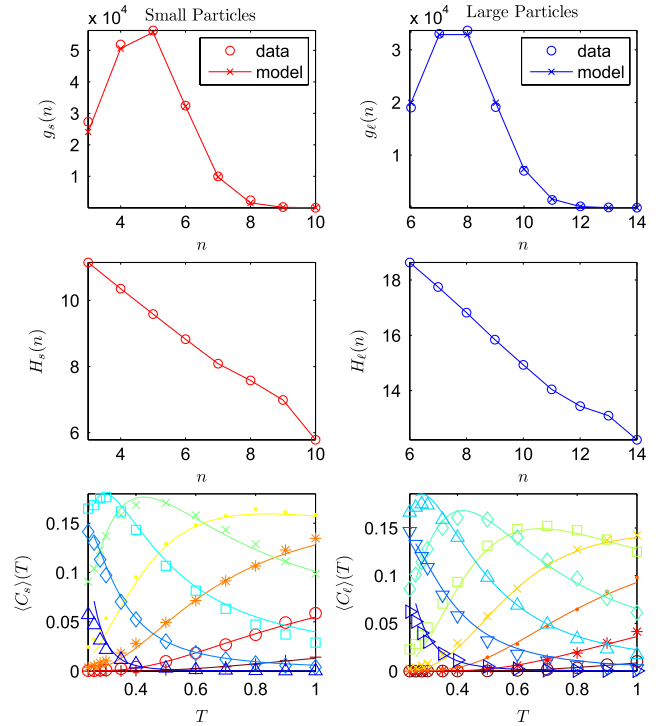


FIG. 4 (color online). Upper panel: The degeneracies $g_s(n)$ and $g_\ell(n)$ read from the slopes of Fig. 3 (in circles) and the degeneracies according to the Gaussian model Eq. (4). Middle panel: The measured enthalpies. Lower panel: Comparison of the measured concentrations of quasispecies to those calculated from Eqs. (5) using the model degeneracies and measured enthalpies. Here symbols are data, and lines are theoretical predictions.

physical interpretation of the average distance between the liquid quasispecies. It was argued before [9,10,15] that this length scale can be also interpreted as the linear size of relaxation events which include $O[\xi(T)]$ quasispecies. We

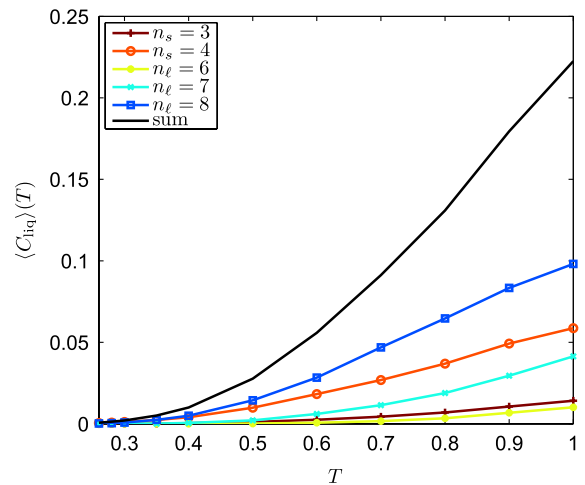


FIG. 5 (color online). The temperature dependence of $C_{\text{liq}}(T)$ is shown as the upper continuous line. The contributions of the various liquid subspecies are shown with symbols which are identified in the inset.

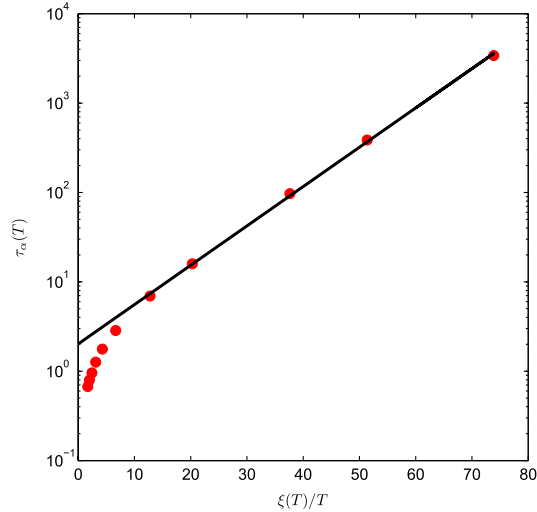


FIG. 6 (color online). The relaxation time $\tau_\alpha(T)$ in terms of the typical scale $\xi(T)$. We show the excellent fit to Eq. (8) with $\mu = 0.04$. Note that the intercept at $T \rightarrow \infty$ is of the order of unity as it must be.

can therefore estimate the growing free energy per relaxation event as $\Delta G = \mu \xi(T)$, where μ is the typical chemical potential per involved quasiespecies. This estimate, in turn, determines the relaxation time as

$$\tau_\alpha(T) = e^{\mu \xi(T)/T}. \quad (8)$$

The quality of this prediction can be gleaned from Fig. 6, where we can see that the fit is excellent, with $\mu \approx 0.04$. The intercept in Fig. 6 is of the order of unity; this is very reassuring, since this is what we expect when $T \rightarrow \infty$.

A few points should be stressed. As we expect (cf. Ref. [15]), in systems with point particles and soft potential, there is no reason to fit the relaxation time to a Vogel-Fulcher form [16] which predicts a singularity at finite temperature. In our approach, we predict that $\xi \rightarrow \infty$ only when $T \rightarrow 0$, and there is nothing singular on the way, only slower and slower relaxation. At some point, the simulation time will be too short for the system to relax, but we can use Eq. (8) to predict what should be the simulation time to allow the system to reach equilibrium.

Conclusions.—In summary, we reiterate that finite systems of point particles with soft potential are different from finite granular media or systems of hard spheres which can truly jam and lose ergodicity. Point particles with soft potential remain ergodic [15] and therefore should be amenable in their supercooled regime to statistical mechanics. To construct simple, workable statistical mechan-

ics, one needs to upscale the system and find a collection of quasiespecies with well defined enthalpies and degeneracies. In this Letter, we proposed a simple criterion to validate a choice of upscaling and demonstrated how, once the structural theory is under control, a natural length scale appears and can be used to determine the relaxation time, also for temperatures that cannot be simulated due to the fast growth of necessary relaxation time. The fact that the present approach works equally well in two and three dimensions provides good reason to believe that it has a substantial degree of generality. How to use this kind of theory to understand relaxation functions and thermodynamic properties was demonstrated before in two-dimensional examples, but there is still a large variety of related problems in two and three dimensions that can profit from this approach.

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