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Inherent structure switching patterns for glass-forming liquids [1]

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Abstract

Gradient-descent mapping on the potential energy hypersurface locates the relevant inherent structures (local minima) during the course of MC or MD simulation runs for continuum models. Observing temporal sequences of such inherent structures is proposed as a way to clarify relaxation processes near the glass transition. Also, the importance to execute parallel MC and MD runs on the same glass model is stressed to establish a quantitative time scaling for the two to permit comparison of relaxation results.

The impact of powerful computers on condensed-matter physics and materials science has been enormous. Fundamental glass science has shared in this success, particularly through the ability to investigate well-posed molecular models by Monte Carlo (MC) and molecular dynamics (MD) simulation. But many basic questions about the glass transition remain unanswered. It is the purpose of this short essay to recommend a possibly useful simulation strategy to answer some of those questions.

We confine attention to continuum models, with interaction potentials Φ that are continuous and differentiable functions of the particle coordinates $\boldsymbol{r}_1 \cdots \boldsymbol{r}_N$ (except possibly when nuclear positions coincide). All of the principal classes of glass-forming materials (atomic, ionic, molecular, covalent, polymeric) can be realistically modeled this way with appropriate Φ's. In any given case, the multi-dimensional configuration space of particle coordinates can be exhaustively partitioned into basins of attraction for each of the local Φ minima (the "inherent structures" for the system) by means of a gradient-descent mapping [1]. Note that inherent structures are free of the distracting deformations due to particle vibrations and librations.

The number of substantially distinct inherent structures, that is those not related by permutation of identical particles, rises exponentially with N. For the study of liquids and glasses it is useful to classify the inherent structures by an obvious order parameter,

$$\phi \equiv \Phi/N,$$

their potential energy on a per-particle basis. Under this classification, the asymptotic distribution of distinct inherent structures is also exponential in N [2],

$$\exp[\sigma(\phi)N],$$

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where $\sigma(\phi)$ is independent of N. Out of this enormous collection of possible particle arrangements, thermal equilibrium at temperature T selects a narrow fraction centered, say, at $\phi^*(T)$.

Above the melting point, at least for simple liquids, ϕ^* is surprisingly insensitive to T [3]. If T declines below the melting point T_m, by rights ϕ^* should jump discontinuously to a low crystal value. But if nucleation and crystal growth can be avoided (a frequent simulational experience), ϕ^* smoothly declines with decreasing T through T_m. In fact for fragile glass formers, this decline accelerates markedly to produce the typical heat-capacity enhancement over that of the crystal.

A running record of the inherent structures during any MC or MD run can be prepared by subjecting every nth step configuration of that run to the gradient-descent mapping [1–3]. The resulting collection of ϕ values have ϕ^* as their average of course; time autocorrelation functions

$$C(t) = \langle [\phi(t_0) - \phi^*][\phi(t_0 + t) - \phi^*] \rangle$$

should reveal the relaxation spectrum, but apparently have not yet been exploited in this connection.

The running basin depth function $\phi(t)$ for an MD simulation will be piecewise constant. The points of discontinuity represent times at which the system's configuration point crossed the boundary between contiguous basins, i.e. underwent an elementary structural transition. These switches become less and less frequent as T is reduced, and in the low-T limit of the glass are confined to localized low-barrier motions of small particle groups, the so-called two-level systems [4].

Sequences of elementary interbasin transitions provide the mechanism for a drop in T to produce a drop in ϕ^*. If T is already close to the glass transition temperature T_g, ϕ^* corresponds to rare low-potential-energy amorphous significant structures, i.e. $\sigma(\phi^*)$ is small. In order for the system to discover even deeper and rarer basins, it must cover on average a large distance in the configuration space. This process evidently must entail a lengthy sequence of elementary transitions, and has been likened to transport from the bottom of one crater in the Φ hypersurface, across rugged intervening terrain, and into an even deeper crater [5]. Currently a strong need exists to put this concept on a firm quantitative footing, and a systematic simulational study should have the capacity to do exactly that.

To be specific, it is desirable to use a simple model for a relatively fragile glass former, and to couple frequent gradient-descent mappings to low temperature MD runs to produce the piecewise constant $\phi(t)$. The corresponding autocorrelation function $C(t)$ introduced above should exhibit the presence of both short-time and long-time relaxation processes, conventionally designated β and α, respectively. These should correspond to elementary interbasin transitions, and to the lengthy intercrater transition sequences. The power of properly designed calculations of this sort is that geometric details of particle displacements, and their chronological sequences, can be examined graphically for transitions from one inherent structure to the next.

One expects the long-time behavior of $C(t)$ to conform to the experimentally famous KWW stretched exponential form,

$$C(t) \sim C_0 \exp\left[-(t/\tau)^p\right],$$

$$0 < p < 1.$$

An explanation for this type of result has been advanced [6] in terms of mobile defects in the glassy medium that execute dispersive Levy walks. In principle this intriguing picture is amenable to verification by the above procedure, if indeed the observed sequences of elementary interbasin transitions can be consistently classified as defect jumps. Again, careful simulational study, coupled to mapping onto inherent structures, is clearly warranted.

It is possible that mobile defects, or their clusters in space and in time, might underlie the recently observed translation–rotation paradox for fragile glass-forming liquids. This phenomenon involves a marked enhancement near T_g of the translational diffusion rate compared to the Stokes–Einstein prediction, while the rotational diffusion rate continues to adhere to the corresponding Stokes–Einstein–Debye result [7]. An explanation has been proposed that postu-

lates relatively large and long-lived "fluidized domains" in an otherwise substantially rigid glassy medium [7]. Tracking transitions between successively visited inherent structures in a suitably selected MD simulation might have the capacity to pin down this mechanism, or to supplant it with a more suitable alternative.

Finally, the importance of comparing MC and MD time scales needs to be stressed. Whatever transition rules are selected for the former, it is desirable to carry out series of runs by both simulational techniques at identical temperatures for a common model. Upon examining a given autocorrelation function for both, time ratios can be established for one MC step versus one MD step. Ideally, this would remain constant throughout the supercooling range and across the glass transition. However, the ratio may be significantly temperature dependent, which would tend to obscure comparisons between results from these alternative approaches. It is even possible that distinct relaxation modes are treated with variable efficiency in MC and MD, which at a given T could produce distinct KWW stretching exponents.

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