Inherent-structure dynamics and diffusion in liquids

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The self-diffusion constant D is expressed in terms of transitions among the local minima (*inherent structures*, IS) of the N-body potential-energy surface or *landscape*, and their correlations. The formulas are evaluated and tested against simulation in the supercooled, unit-density Lennard-Jones liquid. The approximation of uncorrelated IS-transition (IST) vectors D_0, greatly exceeds D for the highest T, but merges with simulation at reduced $T\sim 0.50$, close to the estimated mode-coupling temperature T_c. Since uncorrelated IST's are associated with a hopping mechanism, the condition $D\sim D_0$ provides a new way to identify the crossover to hopping. The results suggest that theories of diffusion in deeply supercooled liquids may be based on weakly correlated IST's.

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I. INTRODUCTION

The configuration $\mathbf{r}(t)$ of a liquid may [1] be mapped to the local minimum $\mathbf{R}(t)$, of the potential energy $U(\mathbf{r})$, to which it drains in steepest-descent minimization; both vectors denote the $3N$ coordinates of a system with N atoms. Stillinger named the minima *inherent structures* (IS) and Stillinger *et al.*, have [2] pioneered the application of this mapping to the theory of liquids. The configuration space decomposes into the basins of attraction of the IS, and so too does the configuration integral, providing a new approach to equilibrium statistical mechanics. Turning to dynamics, Stillinger and Weber [1] calculated the average T-dependent rate $\langle \omega_{is}(T)\rangle$ of *IS transitions* (IST) for an atomic liquid, obtained an activation energy comparable to that for diffusion, and discussed the connection between IST and more familiar quantities such as $U(t)$.

Goldstein [3] proposed that liquid dynamics could be understood in terms of the topology of the potential-energy surface, or *landscape*. Molecular-dynamics (MD) simulations incorporating the IS mapping, monitoring both the continuously varying $\mathbf{r}(t)$ and the discontinuous $\mathbf{R}(t)$, are well suited to explore any such connections. The most challenging area of liquid theory is the supercooled state, where the landscape paradigm is [2] widely accepted. Below a critical temperature T_c, often called the [4] mode-coupling temperature, the system is believed to remain in a basin for relatively long times, with infrequent activated hops to neighbor basins. At $T>T_c$, motion is freer and not activated, or activated with barrier heights not much greater than T. The character of dynamics has been related to [5] a sharp drop in the IS energy as T falls below T_c, and to [2] the roughness of the landscape. Nevertheless, the approach must ultimately lead to calculations of observable transport coefficients and relaxation times in landscape terms, and this has not yet been done. Here we demonstrate, in detail, the relation between the self-diffusion constant D and IST in supercooled unit-density Lennard-Jones (LJ). At the lowest attainable T, D is described accurately by a simple IST-Markov approximation. The approximation breaks down above T_c, reflecting and illuminating the corresponding change in the mechanism of diffusion.

II. DIFFUSION AND INHERENT-STRUCTURE DYNAMICS

The diffusion constant is determined by the long-time linear behavior of the mean-square displacement (MSD). Since the magnitude of the [6] *return distance* $\mathbf{u}(t)=\mathbf{r}(t)-\mathbf{R}(t)$ is bounded by the size of a single basin while the MSD increases without limit, the IS-MSD also serves $\langle[\Delta\mathbf{R}(t)]^2\rangle/6N=Dt, t\to\infty$, where $\Delta\mathbf{R}(t)=\mathbf{R}(t)-\mathbf{R}(0)$. The IS-MSD is the sum of the IST vectors, the separations of successive IS, $\Delta\mathbf{R}(t)=\Sigma_{\alpha=1}^{n(t)}\delta\mathbf{R}_\alpha$ after n transitions. Squaring, averaging for fixed n, averaging over the distribution of n at time t, and dividing by $6N$ yields

$$D=\left[\langle(\delta\mathbf{R}^2)\omega_{is}\rangle+2\sum_{\beta=1}^{\infty}\langle(\delta\mathbf{R}_\alpha\cdot\delta\mathbf{R}_{\alpha+\beta})\omega_{is}\rangle\right]\Big/6N, \tag{1}$$

where the summand is the correlation function $C(\beta)$ for β-neighbor IST vectors and we have assumed that t is much longer than the persistence time of any correlations, required for diffusive behavior. Approximations to D keeping $\beta\leqslant m$ only are denoted D_m, and the IS-Markov approximation is D_0, the first term on the right-hand side. The IST vector correlation $C(\beta)$ is somewhat analogous to the velocity correlation.

With large times and numbers of trajectories, the averages in Eq. (1) factorize into $\langle\omega_{is}\rangle$ times averages of $\delta\mathbf{R}$ only, and in particular the Markov approximation yields $D_0=\langle\delta\mathbf{R}^2\rangle\langle\omega_{is}\rangle/6N$. We use Eq. (1) as is in averaging over multiple MD runs, but our results may be understood via the factorization approximation. To see how D achieves its status as an intensive quantity consider that a liquid with short-ranged correlations may be [7] roughly divided into independent local regions. Successive IS differ [1] in the coordinates of a small number of particles and $\langle\delta\mathbf{R}^2\rangle\sim O(1)$; IST are local rearrangements. On the other hand, the number of regions is $O(N)$ and a change in any region changes the IS of the entire system, so [1] $\langle\omega_{is}\rangle\sim O(N)$ and $D\sim O(1)$.

III. SIMULATION METHODS AND RESULTS

We have previously studied [8] the unit-density supercooled LJ liquid, and use it with $N=32$, and with methods from prior work, to test the relation between IST and diffusion. System-size considerations for IS dynamics differ from those for ordinary MD. Essentially all the CPU time goes to the minimizations. The time between minimizations must be much shorter than the mean waiting time in an IS. Here this is well achieved by minimizing every five time steps. The relation $\langle \omega_{is} \rangle \sim O(N)$ indicates that IS-dynamic studies should use the smallest realistic system to avoid an intractable IST rate with no direct correspondence to a physical rate. For example, 500 particles at $T\sim 1$ would typically show a new IS at every step, making an estimate of the rate meaningless. The time step would have to be decreased to allow $\sim 15\times$ more minimizations per time. The time for a minimization scales roughly as N^2. The $15\times$ more minimizations would each take $\sim 200\times$ longer for a major computational challenge. More particles may be used if the maximum T, and thus the maximum IST rate, is lowered, but here we wish to map out behavior over a broad supercooled-T range, and exceeding 100 particles would be difficult. At $N=32$, the values obtained for D, for T_c, and for the melting T_m are close to those found at $N=108$ and 256, so we are seeing the correct qualitative physics and have expended only about one month of CPU time.

The arguments for a small system are not only computational. We believe that much supercooled dynamics may be understood [7] in terms of the cooperative local regions and we seek to characterize them. Beyond a certain point adding particles merely produces a composite with more members, from which the properties of a local region are difficult to untangle. The physically significant distribution of waiting times in a local region may not be easily extractable from the distribution for the composite, where a transition in any region causes an IST. For a nondynamical example, the IS density-of-states is an important quantity. Whatever form it may have in a local region, it will be Gaussian for large N.

Natural LJ units are used throughout, well depth ϵ for T, hard-core radius σ for distance, time unit $\tau_{\mathrm{LJ}}=(m\sigma^2/\epsilon)^{1/2}$ (2.18 ps for argon) and m is the mass; the crystal melts at $T\sim 1.6$. A hot liquid at $T=5.00$ is cooled in one step to a temperature in the 1.20–0.60 range. The system is equilibrated for 2.5 τ_{LJ}, data are gathered for 62.5 τ_{LJ}, T is decreased by 0.02, and the process is repeated 10–25 times, generating a single quench run; most quenches sampled 16 T. The cooling rate is 3.08×10^{-4}. Different $T=5.00$ configurations lead to different behavior, and thus we obtain an ensemble of quenches. At $N=32$, the abrupt drops in U signaling solidification, common at $N=256$, do not occur, but some quenches develop solidlike pair distributions and these are discarded. Results are averaged over 23 quenches at the lowest T and 30 at the highest. Quench-to-quench fluctuations are much larger than any systematic changes over $T=0.02$, so we also average results at each T with those from the next higher and lower T.

In a quench, the system stays at a given T for 141.7 ps. It would be hopeless to study the $T\sim T_c$ regime ($T_c\approx 0.50$, *vide infra*) using literally that amount of equilibration averaging time, but our simulation averages for far longer: (1) For $T\sim T_c$, towards the end of a quench, the system has already been in the supercooled state for >1 ns, equilibrating at the higher supercooled T. (2) We deliberately use multiple quenches, with shorter stays at each T, instead of single or fewer long runs to avoid broken ergodicity. Our method is equivalent to breaking up a conventional simulation of at least 3.25 ns (23 quenches$\times$141.7 ps T quench) with intervals of high-T dynamics, taking over 1 ns (point 1) to return to the desired T. The same idea is used in Ref. [9] "J-walking" and "q-jumping" Monte Carlo algorithms, which obtain superior equilibration via occasional large configurational jumps. (3) With the averaging over adjacent T, the minimum time, even ignoring points (1) and (2), is 425.1 ps not 141.7 ps. Sastry *et al.* [5] found in a LJ mixture that quenches with a cooling rate of 2.70×10^{-4}, close to ours, exhibited $\sim 75\%$ of the drop in $\langle U_{\mathrm{is}}(T)\rangle$ attained by quenching almost 100 times slower and reached an apparent bottom somewhat below T_c; this should be adequate for probing the transition regime. We believe that our results are well averaged and equilibrated down to $T\sim T_c$, and are out of equilibrium (but "well averaged" over the set of nonequilibrium configurations allowed by the quench) at the lowest T.

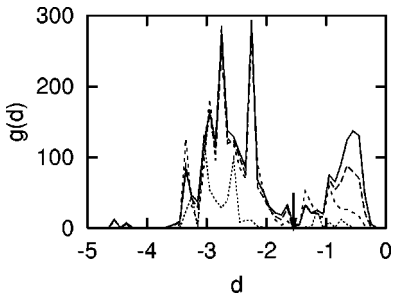

FIG. 1. Distributions of base-10 logarithms of IS-transition distances. Top to bottom at $d=-1$, $T=0.90$, 0.60, 0.50, and 0.40.

Conjugate gradient minimizations are performed every 5 time steps ($dt=0.001\,25$), or 160 minimizations/τ_{LJ}. Since the range of $\langle \omega_{\mathrm{is}}(T)\rangle$ is from 9.0 IST/τ_{LJ} at $T=1.10$ to 0.23 at $T=0.34$, this should be sufficient. The IS mapping is defined in terms of steepest-descent minimization, so we verified that, at the T of interest, CG gives the same results. The determination of whether a transition has occurred is an important, nontrivial matter. We begin [10] by calculating the distribution $g(d)$ of distances $d=\log_{10}(\{[\mathbf{R}(t)-\mathbf{R}(t-5dt)]^2/N\}^{1/2})$ between the current and prior IS, with no reference to the presence or absence of a transition. Distributions for $T=1.10$, 0.90, 0.60, and 0.40 are shown in Fig. 1. There is a large peak, not shown, around $d=-6$, which identifies the numerical uncertainty of the algorithms when the IS has not changed. Transition distances exhibit a bimodal structure, with a small feature at $d\sim -4.5$. The spikes in the larger, low-d lobe are not noise but represent specific, frequently occurring separations. They vanish abruptly between $T=0.60$ and $T=0.40$, the range in which we believe the crossover to hopping begins.

Not all IST's are associated with diffusion. A change in state of a two-level system will change the IS. Stillinger has argued [2] that motion among *megabasins* is required for

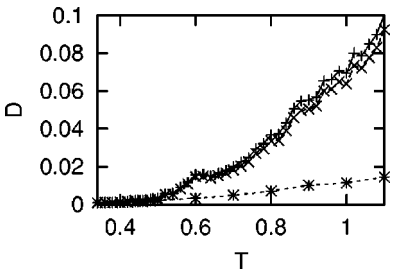

FIG. 2. Diffusion constant vs T. Top to bottom at $T=1$, D_0 (IS-Markov approximation), D_1 (adjacent IST correlations), simulation.

diffusion, with motion among the basins comprising a megabasin nondiffusive. Transition vectors with large d are most likely to reflect diffusion. Similar considerations have [11] entered the efforts to relate D to $\mathrm{Im}-\omega$ instantaneous normal modes, where *nondiffusive* modes must be discarded. Accordingly, we count an IST when d falls in the high-d lobe of $g(d)$, specifically for $d>-1.55$, marked with an arrow in Fig. 1. Our estimate of D is relatively insensitive to the choice of cutoff, because increasing $\langle\omega_{\mathrm{is}}\rangle$ by taking more small-d IST's would cause a compensating decrease in $\langle(\delta\mathbf{R}^2)\rangle$.

At each T we obtain several IST quantities, and the MSD and D as usual. Fig. 2 compares simulated D with the Markov approximation D_0 and with D_1, including the correlation of adjacent IST vectors. At $T\sim 1$, $D_0 \gg D$, which is evidence of a large negative correlation. Adjacent correlations only produce a $\sim$10% correction, so $C(\beta)$ must be ''long ranged.''

As T decreases, the situation changes strikingly. While $D_0(T)$ initially decreases much faster than $D(T)$ and would extrapolate to zero at $T\sim 0.6$, it abruptly changes slope starting at $T\sim 0.7$, and begins to merge with D at $T\sim 0.5$. This reflects that the behavior of $\langle\omega_{\mathrm{is}}\rangle$; $\langle(\delta\mathbf{R}^2)\rangle$ is roughly linear for $1.10\geqslant T\geqslant 0.34$. Figure 3 highlights the region $0.54\geqslant T \geqslant 0.34$. The joining of the curves at $T\sim 0.5$ is clear, and $D_0(T)$ and $D_1(T)$ are approaching quantitative accuracy below $T\sim 0.4$. If the lowest T are out of equilibrium, it is no less significant that the IS-Markov approximation holds; presumably it would be even more accurate in the less fluid equilibrium states. From $D(T)$, $T_c=0.52$ in this system. Around T_c $\langle U_{is}(T)\rangle$, Fig. 4, is undergoing its sharpest drop and has almost reached the bottom of the landscape, evidently [5] the underlying cause of the dynamical transition. We do not think it is a numerical coincidence that D_0 approaches D near T_c, and we propose that, in general, *dynamics is approximately a random walk among the IS for* $T<T_c$, with $D\approx D_0$, and $D\gg D_0$, $T>T_c$. Figure 4 is similar to that given [12] by Angelani *et al.* for unit-density ''modified LJ,'' $N=256$, where they estimate $T_c=0.475$. Clearly $N=32$ is not terribly different from the larger systems.

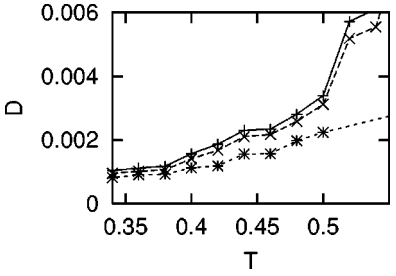

FIG. 3. Low-T region of Fig. 2. IST-Markov approximation improves with decreasing T.

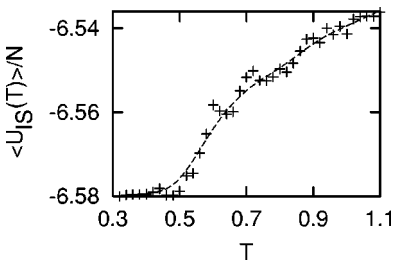

FIG. 4. Averaged IS energy vs T, points and Bezier fit. Sharp drop in U_{is} identifies T_c.

IV. DISCUSSION

In a hopping mechanism, the system is constrained by the need for an activated barrier crossing to spend a long time in a basin between hops; it is plausible that memory should be lost during the wait leading to a Markov chain of IST's. On the other hand, at higher T, the thermal energy is comparable to barrier heights and IST's are ''bookkeeping'' events as the system moves freely across IS boundaries. A burst of IST's can then [1] be generated by a small displacement through a region of closely spaced boundaries. In the language of the IST vectors, the requirement for several IST's to generate essentially no displacement is anticorrelation. Our results fit perfectly with these ideas.

At low T the relation $D\approx D_0$ strongly suggests a random walk among the IS. While theories based on the Master equation [13] require the Markov process, we give here the first evidence for its existence. Regardless of any interpretation, it is very encouraging for future work that D_0 becomes a good first approximation at low T. Of course, correlations still exist. If [2,14] the system revisits a small group of basins over and over, perhaps due to low connectivity, the corresponding IST will not cause diffusion and $C(\beta)$ must be negative. The hope is that such physical effects will be more tractable than the gross overestimate of D at high T.

At high T, $D_0 \gg D$ because the bookkeeping IST rate is unphysically large. The use of Eq. (1) then demonstrates that IST-vector correlations $C(\beta)$ are large and negative. The correlation of successive vectors is indeed negative, but not nearly large enough; thus it is further shown that correlations persist over many transitions, and they are long ranged. According to Stillinger [15], this may be explained with the essential idea that the landscape is a composite. Then even if IST's arising from changes *in a given region* have short-range correlation, they will be separated by many IST's associated with different regions, and $C(\beta)$ will persist for large β. As $N\to\infty$, the correlations will become infinitly long ranged. Again, the desirability of a small system is ap-

parent. The meaningful properties are those of the local region. Observing composite properties built up from statistical combinations of many local regions, makes both simulation and interpretation more difficult.

The crossover temperature is usually identified by fitting $D(T)$ to the [4] mode-coupling form, but we give another criterion: with decreasing T, the hopping regime, in which the dynamics is approximately a Markov chain of IST's, is entered as $D \to D_0$. Several observables reflect proximity to T_c, but we suggest that the change of IS dynamics from a highly correlated process to a random walk corresponds particularly well with the physical picture of a transition to hopping.

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