PHYSICAL REVIEW E VOLUME 59, NUMBER 3 MARCH 1999

Dependence of supercooled liquid dynamics on elevation in the energy landscape

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(Received 5 October 1998)

Quenches of the Lennard-Jones unit density, $N=256$ supercooled liquid are analyzed to show that the activation energy for diffusion, E_a, increases as the energy of the associated local minimum on the potential energy landscape, U_m, decreases. Super-Arrhenius T dependence of the self-diffusion constant D, characteristic of fragile liquids, is thus a consequence of the descent of the system, with decreasing T, from a plateau of U_m values at the top of the landscape. Departure from the top occurs at a random temperature T_s but introduction of $E_a(U_m)$ allows a systematic analysis of $D(T)$. A single quench exhibits several features of the experimental glass transition. Fast cooling in prior work has isolated the supercooled ''top'' state only. The difference between strong and fragile liquids, and the fate of the quenches, is discussed in terms of the landscape and its N dependence. [S1063-651X(99)09503-3]

PACS number(s): 64.60.Ht, 64.70.Pf

I. INTRODUCTION

Perhaps the most striking feature of supercooled liquids is the increase in relaxation times τ by a factor of $\sim 10^{14}$ between room temperature and the glass transition T_g. The form of $\tau(T)$ provides [1] the basis of the classification of liquids into ''strong'' and ''fragile.'' Strong liquids exhibit Arrhenius T-dependence all the way down to T_g. In fragile liquids an Arrhenius upper T-range may be identified, but 'super-Arrhenius' behavior, with activation energy $E_a(T)$ increasing with decreasing T, sets in below some $T>T_g$.

The many proposed explanations [1] of the T-dependence have not led to a definitive theory. An appealing approach is [2] to connect $\tau(T)$ to the potential energy ''landscape,'' the topology of the potential energy surface as a function of all the atomic or molecular positions. Landscape theories have been held back by a lack of quantitative topological information. Recently, however, Sciortino *et al.* [3] have obtained $U_m(T)$, the depth of the local minimum to which the liquid will ''drain,'' in simulations of fragile supercooled orthoterphenol. Sastry, Debenedetti, and Stillinger (SDS) calculate [4] both $\tau(T)$ and $U_m(T)$ for a fragile supercooled Lennard-Jones (LJ) liquid mixture. They found Arrhenius $\tau(T)$ and constant U_m at higher T, and super-Arrhenius coinciding with a decrease in $U_m(T)$ at lower T. That is, Arrhenius and super-Arrhenius are signatures of a plateau region at the top of the landscape, and of lower-lying minima, respectively.

Mixtures and molecular liquids are favored in simulation of supercooled states for resistance to crystallization. Nonetheless the $\rho=1.00$, $N=256$ supercooled pure LJ liquid, which we have [5,6,7] extensively studied, rarely crystallizes; it should be an extremely fragile liquid. In the following we report new results on this system, in the spirit of SDS. Although most experiments are carried out at constant pressure, evidence exists [4,8] that the significant T-dependence may be observed at constant density. Reduced LJ units will be used throughout; $\rho=(N/V)\sigma^3$, σ is the collision diameter, N the number of particles, V the volume, T is in units of the well depth ε, the time unit is $t_{\mathrm{LJ}}=(m\sigma^2/\varepsilon)^{1/2}$, m is the mass, and U denotes potential energy/particle, ε/N.

We probe the supercooled liquid through quenches (meaning cooling, not energy minimization) in which an equilibrated $T=5.00$ system is first cooled below the melting temperature, $T_m\sim 1.8$, $N=256$, in one MD step. After an equilibration period and a data gathering run the system is taken in one step to the next supercooled T, equilibrated, etc. An ensemble of quenches is generated from different $T=5.00$ configurations. Single-quench averages are denoted $[\,](T)$. Invariably the potential energy $[U](T)$ is a near-linear function, denoted $[U^t](T)$, until a point T_s at which it drops sharply. Different quenches have different T_s. The upper-T behavior corresponds to an approximately constant U_m^t on a high plateau of minimum energies at the top of the landscape [9], with the dominant T-dependence arising from harmonic vibrations within the wells. The drop at T_s reflects a descent of U_m from the top along the *slope* leading to the *bottom* of the landscape [9]. Sufficiently below T_s excellent linear behavior of the low-T form $[U^b](T)$ resumes for a system trapped in a well near the bottom with energy U_m^b. We refer to top, bottom, and slope states of the finite-T system via the associated U_m. Crystallization is also possible, but occurred in only 3 out of 50 quenches in Ref. [5] (6%) and not at all in the studies to be reported below.

All $[U^t](T)$ are identical but the $[U^b](T)$ vary, with $[U^b](T=0)$ falling in a range between, and well separated from, the crystal energy and the extrapolated $[U^t](T=0)$. The upper-U_m^b bottom states possess [5] pair distribution functions $g(r)$ typical of an amorphous solid, while those with the lowest U_m^b show some polycrystalline character. Note that much can be deduced about U_m from $[U](T)$ without costly minimizations.

In our prior work [5–7] we used rapid cooling $(\sim 10^{-2}\varepsilon/t_{\mathrm{LJ}})$ to obtain T-dependent dynamic and static properties of a reproducible supercooled state down to $T=0.33$. Full averages, $\langle\,\rangle(T)$, were constructed by including all quenches with $T>T_s$. The resulting $\langle U\rangle(T)$ was approximately linear in T and is now identified as $\langle U^t\rangle(T)$, the top

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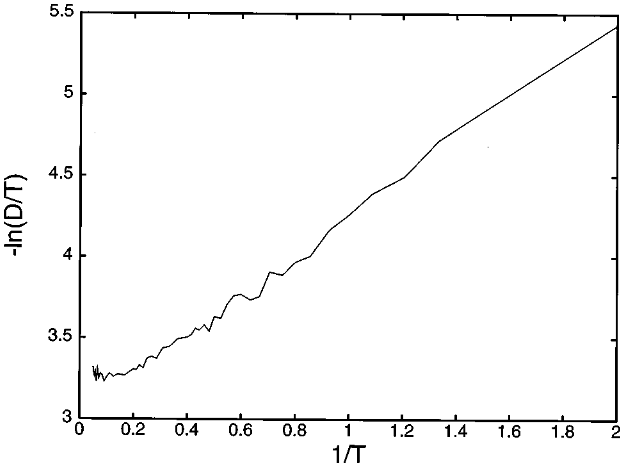

FIG. 1. Arrhenius plot for the velocity correlation time, $\tau_v = (D/T)$, in the *top* state of supercooled LJ, $20.0 > T > 0.50$.

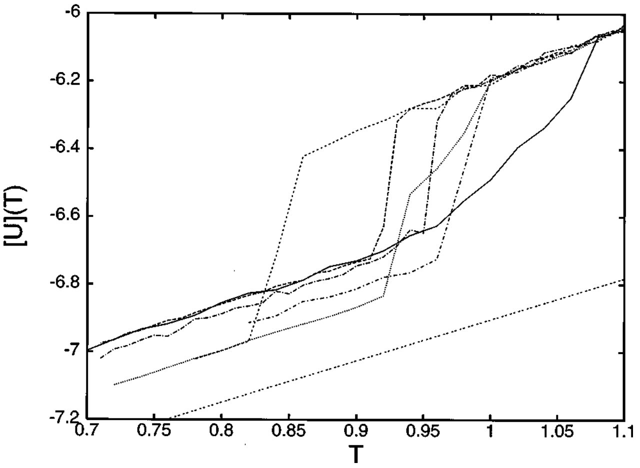

FIG. 2. Potential energy $[U](T)$ vs T for representative quenches; lower line is crystal.

state potential energy. The self-diffusion constant, $D^t(T)$, has weak T-dependence, being well described (Fig. 1) by an Arrhenius function (we actually fit the velocity correlation time $\tau_v = D/T$) with $E_a \sim 1.3$, or by a power law over much of the supercooled range. Because of the variation of T_s it is impossible to assign it a physical significance, so we did not investigate the $T \sim T_s$ region. In this Article we show that such an investigation is possible and fruitful. In agreement with SDS, we find super-Arrhenius T-dependence as U_m falls down the slope from the top and we demonstrate the correlation between U_m and E_a.

Our results suggest a new perspective on supercooling. Conventionally one selects a system and cooling rate to avoid crystallization. However, like the mixture, pure LJ, $N = 256$, is unlikely to crystallize. The important difference is that the mixture [4] falls off the top reproducibly, while the pure LJ system does not. Rapid quenches [5–7] circumvent this problem by trapping pure LJ in the top supercooled state.

II. DYNAMICS ON THE SLOPE IN QUENCHES OF PURE LJ

To study the dynamics of pure LJ on the slope we have performed slower quenches of cooling rate 3.08×10^{-4}, in the range studied by SDS. The $N = 256$, $T = 5.00$ system is cooled to $T = 1.10$ and equilibrated for 2.5 (1.25) t_{LJ}, data are gathered for 62.5 (31.25) t_{LJ}, T is decreased by $\Delta T = 0.02$ (0.01), etc. The quench terminates at $T = 0.70$, by which point the system has undergone its sharp drop in $[U](T)$ and no further information about the liquid is available. At each T we obtain $[U]$ and the mean-square-displacement $[r^2(t)]$ out to 6.25 t_{LJ}, yielding D; $[U](T)$ for six quenches (different $T = 5.00$ configurations), and $\langle U \rangle(T)$ for the crystal, are shown in Fig. 2. Roughly, $1.1 \geqslant T_s \geqslant 0.85$, while our faster quenches had [5] $0.90 \geqslant T_s \geqslant 0.40$.

Calculation of a physically meaningful averaged $D(T)$, including contributions from quenches with $T < T_s$, is problematic, since $D(T)$ drops dramatically as the system descends the slope. At the same T different quenches are in the top, slope, and bottom states, with wildly different D. Figure 3 shows $[r^2(t)]$ for nine T in a quench with $T_s \sim 0.98$; the change upon passing through T_s is evident. This is why we previously confined our studies to the top states. How, then, are we to organize our seemingly chaotic data? It develops that this can be done with the assumption that the activation energy is a function of the minimum energy, $E_a(U_m)$.

Fits to $[U^b](T) = U_m^b + TC_V^b$ yield U_m^b and the heat capacity (potential energy only) C_V^b. From 11 quenches we find $-7.85 \geqslant U_m^b \geqslant -8.05$ (crystal is -8.22) and $1.39 \geqslant C_V^b \geqslant 1.25$, $\langle C_V^b \rangle = 1.30$. Most U_m^b cluster around two values, ~ -7.9 and ~ -8.0. These probably represent distinct states; some scatter is doubtless introduced by the fits. There is a slight curvature in $[U^t](T)$, corresponding to a small upward drift of the plateau, so a linear fit depends somewhat on the T-range fitted. We choose $1.50 \geqslant T \geqslant 1.00$ and obtain $U_m^t = -7.57$, $C_V^t = 1.39$. We thus have, for every quench but the single anomaly with $C_V^b = 1.39$, $C_V^t > C_V^b$, and $\langle C_V^t \rangle > \langle C_V^b \rangle$, in agreement with experiment [1] if reaching the bottom is identified with the glass transition. Furthermore, passage of the slope will contribute a hump in C_V just above T_g, also observed [1] in some experiments.

A schematic $N = 256$ LJ landscape is shown in Fig. 4, with energies in units of the $T = 0$ crystal energy U_{xtl}. Bar-

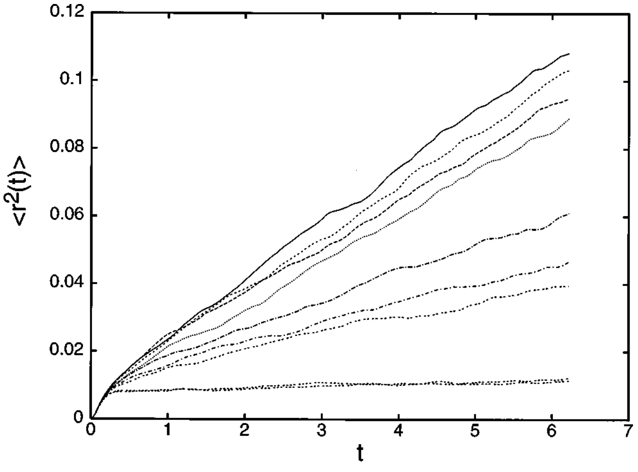

FIG. 3. Mean square displacement $[r^2(t)]$ vs t for nine T in a single quench. Top to bottom, T decreases from $T = 1.06$ by $\Delta T = 0.02$. Note the sharp decrease in slope at $T_s \sim 0.98$.

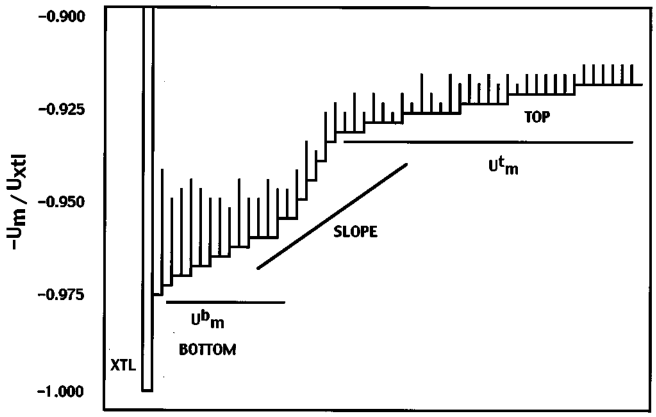

FIG. 4. Schematic landscape for $N=256$. Barrier heights are exaggerated ~10×.

riers are exaggerated ~10× but the relative increase of average height (~3×, *vide infra*) from top to bottom, and the increase in fluctuations at constant average height [7] along the top are correctly indicated. A few remarks about landscape cartoons are in order. Minimum energies are $O(N)$ and barrier energies are $O(1)$, so barriers will vanish as $N\rightarrow\infty$ if expressed in a unit of $O(N)$, e.g., U_{xtl}. Even at $N=256$ the true barriers are then too small for a useful illustration, hence the 10×. Amorphous minimum spacings, comparable to barrier energies, are also $O(1)$. With one-dimensional ''reaction coordinates'' the relevant kinetic energy for barrier crossing is just 1/2 ε, again on the $O(1)$ scale of minimum spacings and barrier heights.

When the system is plainly in a top or bottom state, $U_m=U^{t,b}_m$. To obtain U_m in intermediate cases without minimizing, we suggest that the position of U_m between U^t_m and U^b_m is the same as that of $[U](T)$ relative to $[U^t](T)$ and $[U^b](T)$,

$$(U_m-U^b_m)/(U^t_m-U^b_m)=([U](T)-[U^b](T))/([U^t](T)-[U^b](T)), \quad (1)$$

where $[U^{t,b}](T)$ are the linear fits. Minimizing is of course preferable but the interpolation, Eq. (1), is reasonable and computationally trivial. Figure 5 shows energies $U_m(T)$ from 11 quenches. The height of the plateau as seen from the bottom, $U^t_m-U^b_m$, is in the range (0.25–0.45)ε. The slope is roughly $-7.60>U_m>-7.85$, with some lower-lying points for quenches going to the deepest parts of the bottom. Slope states are not generated in a particularly efficient fashion, but a reasonable database may be easily accumulated.

Activation energies are calculated from the relation

$$E_a(T)=-T\ln[\tau_v/\tau_v(T=\infty)]; \quad (2)$$

recall that $\tau_v=D/T$ and that it varies inversely to viscosity. In fact [6] τ_v does reach a constant value of 0.038 as $T\rightarrow\infty$. Figure 1 shows, however, that the Arrhenius plot is not linear at high T. Extrapolation of the $1.50>T>1.00$ range to $(1/T)=0$ yields $\tau_v\sim0.05$, and we choose $\tau_v(T=\infty)=0.050$. Equation (2) then yields $E_a\sim1.3$ for $1.50>T>1.00$ in the top state, consistent with the Arrhenius plot. A similar method was used by SDS.

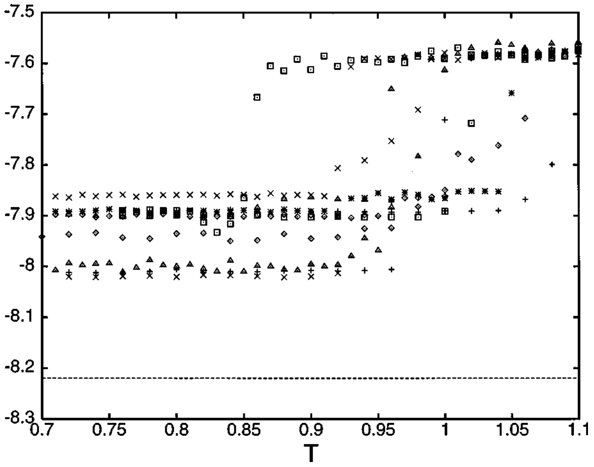

FIG. 5. Minimum energies U_m from Eq. (1) vs T for 11 quenches; horizontal line is crystal.

We now seek a relation between E_a and U_m. For each quench we take all the points in the transition region and one or two on the top closest to T_s. It is important to verify that the former are indeed liquid states, and we carefully monitor both $[r^2(t)]$ and $g(r)$. These indicators do not show the slightest hint of solidification, and slope states of quenches going to purely amorphous or polycrystalline bottom states are indistinguishable. The two quenches with the broadest transitions exhibit a smooth variation of D over two bottom points, and we keep these as well. Figure 6 is our principal result, the dependence of E_a upon U_m. *E_a is a systematic function of U_m*, rising from 1.3 on the top to >4 as the bottom is reached. Through the function $E_a(U_m)$ our ''scattershot'' data, with uncontrolled T_s, are fit into a unified framework. Figure 6 supports the contention of SDS that super-Arrhenius behavior occurs on the slope of the landscape.

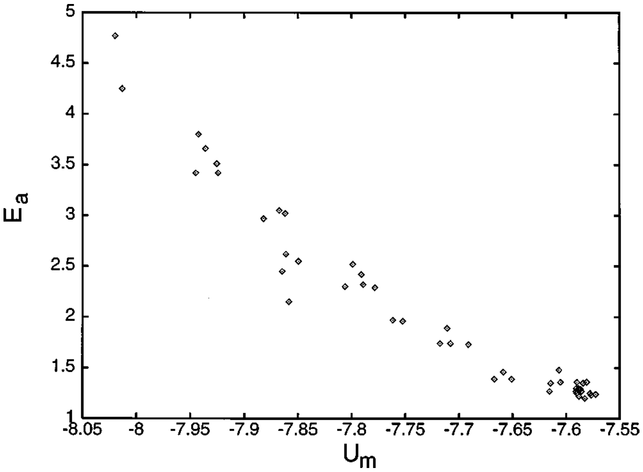

FIG. 6. Activation energy E_a as a function of minimum energy U_m for representative points taken from 11 quenches.

It is not surprising that some scatter remains in the points. Our D, and E_a, surely have some uncertainty, particularly for $E_a>3$. If E_a is scaled by λ at fixed T, D is multiplied by $[\exp(-E_a/T)]^{\lambda-1}$. Starting with values of D and $E_a=1.3$ in the top state, to conclude $E_a=4.0$ we must measure $D \sim 1.0\times10^{-3}$ ($\sim5.0\times10^{-4}$) at $T=1.00$ (0.85). More averaging is necessary for confidence in results for D of that magnitude.

III. *N* DEPENDENCE

The landscape exhibits [3,10] important N-dependence, so it is of interest to consider the role of system size in the fate of our quenches, especially given the perhaps surprising rarity of crystallization for $N=256$. Indeed crystallization is common at $N=32$; of 20 quenches, otherwise identical to those reported in Sec. II, 7 crystallized (35%). Furthermore, in the quenches which go to amorphous minima, the distinct drops in $[U](T)$ are absent. Stillinger and Weber (SW) have [10] mapped out the values of U_m visited by $N=32$ and $N=108$ systems interacting with a potential closely related to the LJ potential, but which vanishes identically at a cut-off radius. Their results may explain our N-dependent quench behavior.

SW Figs. 2 and 3 for $N=32$ show a tight band of U_m, with a deepest noncrystal minimum slightly separated at [11] $U_m/U_{xtl}=0.895$ ($U_{xtl}=-6.000$, SW potential). A detailed landscape is provided [11] by Huer, with a gently sloping top, two bottom states, and a rather sparse slope. In contrast, SW Figs. 7 and 8 for $N=108$ show the band, shifted to lower energy, plus a striking halo of much deeper amorphous minima, ranging down to $U_m/U_{xtl}\sim0.97$ (for our deepest amorphous minimum in LJ, $N=256$, $U_m/U_{xtl}\sim8.00/8.22=0.97$). The lowest halo states are bottom states, separated from the band by a relative large gap. We suggest that the remaining halo minima are slope states. Thus, the primary differences between $N=32$ and $N=108$ are (a) the top-bottom separation is larger at $N=108$, and (b) There are more slope and bottom states at $N=108$.

Suppose similar N dependence of the landscape holds for LJ. The greater gap between top and bottom for larger N (halo states) explains the presence and absence, respectively, of sharp drops in $[U](T)$ for $N=256$ and $N=32$. The trend in frequency of crystallization would follow if more and deeper non-xtl minima effectively complete with crystallization. At the risk of being extremely speculative, perhaps the existence of a spectrum of bottom states is the cause of the randomness of T_s, $N=256$.

IV. DISCUSSION

It is possible to study super-Arrhenius T-dependence and glass formation in pure LJ, given a method to deal with the variation of T_s from quench to quench. Each quench exhibits many properties of a supercooled fragile liquid. Our results support the idea [4] that the depth of the local minimum to which a finite-T system will drain determines the activation energy. Indeed, to rationally organize data from quenches with different T_s, we *require* $D\sim\exp[-E_a(U_m)/T]$. Theoretically, $D(U_m,T)$ should be determined by an average over barriers connected to minima at U_m, $\langle\exp(-E_{\text{bar}}/T)\rangle(U_m)$, and we conclude that the barrier heights increase with decreasing U_m. The average may involve [5,7] a broad distribution of E_{bar}, with the lowest barriers dominating at low T.

The behavior of $\tau(T)$ in fragile liquids follows [4,9] from the presence of a high-T plateau of U_m plus accessible states on the slope and bottom of the landscape. What, then, explains the behavior of strong liquids? Another system upon which we have performed hundreds of quenches is CS_2 which, if not an obvious strong liquid, should be stronger than LJ. We have *never* observed a drop in $[U]$ corresponding to descending the slope, and Arrhenius behavior always holds. Perhaps, as Angell suggests [9], the minima on the slope are simply too sparse to contribute in strong liquids or perhaps the extra time needed to organize the orientational degrees of freedom makes them kinetically unavailable. In the former case, we observe that strong liquids are in some ways similar to fragile liquids at small N. Further direct investigation of the landscape is essential.

Supercooling, at least at rates available in simulations, allows more than avoidance of crystallization; the system may be trapped on the top of the landscape. In supercooled top LJ $D(T)$ has [5] a weak T-dependence (Fig. 1) but other significant T-dependence may be identified. We have [5,7] analyzed the change in the instantaneous normal mode (INM) imaginary frequency density of states, concluding [7] that $\langle E_{\text{bar}}\rangle$ remains constant but the fluctuations in E_{bar} become large as T decreases (Fig. 4). This picture is supported [12] by our application of the soft potential model to liquids. The prior theories and simulations must now be understood to hold at constant U_m. We will expand them to include U_m dependence in the future. Such dependence should be included in any comprehensive theory of supercooled dynamics.

ACKNOWLEDGMENT

This work was supported by NSF Grant No. CHE9708055.

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