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Random energy model for dynamics in supercooled liquids: *N* dependence

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The random energy model (REM) for the critical points (saddles and minima) of the potential energy landscape of liquids is further developed. While thermodynamic properties may be calculated from the unconditional distribution of states $G(E)$, dynamics requires the distribution $G_c(E';E)$ of energies E' of neighbors connected to a state with energy E. Previously it was shown [T. Keyes, Phys. Rev. E **62**, 7905 (2000)] that an uncorrelated REM, $G_c(E';E)=G(E')$, is badly behaved in the thermodynamic limit $N\rightarrow\infty$. In the following, a simple expression is obtained for $G_c(E';E)$, which leads to reasonable N dependences. Results are obtained for the fraction f_u of imaginary-frequency instantaneous normal modes, the configuration entropy S_c, the distributions of the different-order critical points, and the rate R of escape from a state. Simulation data on $f_u(T)$ and the density of minima $\rho_0(E)$ in Lennard-Jones and CS_2 are fit with the theory, allowing a determination of some model parameters. A universal scaling form for f_u, and a consequent scheme for calculating the mode-coupling temperature T_c consistently among different materials, is demonstrated. The dependence of the self-diffusion constant D upon R and f_u is discussed, with the conclusion that $D\propto f_u$ in deeply supercooled states. The phenomenology of fragile supercooled liquids is interpreted. It is shown that the REM need not have a Kauzmann transition in the relevant temperature range, i.e., above the glass transition.

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I. INTRODUCTION

Classical thermodynamics and dynamics is ultimately governed by the potential energy surface, or landscape, defined in the $3N$-dimensional configuration space of all the atomic coordinates. With the number of atoms N diverging in the thermodynamic limit, the landscape is extremely complicated, difficult or impossible to visualize by extrapolating intuition from lower-dimensional surfaces. Random energy models [1] (REM) offer an attractive simplification for liquids and macromolecules. In 1993 [2], we suggested that the protein REM of Bryngelson and Wolynes [3] (BW) could be adapted to liquids. In that model, an amino acid—the basic unit of the system—has one ground state and ν excited states. The ground state single-unit energy is fixed and the excited state energies are random. Nearby units have a fixed interaction if they are both in the ground state, and a random interaction otherwise. In this manner the states of the entire system, and their energies, are built up from local contributions.

Currently there is considerable interest [4–8] in using the critical points or extrema of the landscape to define states of liquids. The critical points are characterized by the order K, the number of imaginary frequencies (directions of downward curvature), so that $K=0$ is a local minimum, $K=1$ a first order saddle, etc. The neighbors of a given state may be reached by moving a small number of particles, i.e., they are nearby in the configuration space; neighbor minima are connected by reaction coordinates crossing first-order saddles, etc. Transitions among neighbor states play an important role in landscape theories of dynamics. By contrast, *a priori* the REM states do not possess an order or a connectivity. BW connected the states differing by a change in a single amino acid—interconvertable by a single transition—and identified a local minimum as a state having all its connected neighbors higher in energy. We [2] proposed, in a straightforward extension, that a Kth-order saddle is a state having exactly K connected neighbors with lower energy. From this perspective, the states are identified as all the critical points. A REM may also be formulated for the minima alone [9].

The analogy to liquids is made [2] by replacing amino acids with weakly interacting local regions, possibly corresponding to the "cooperatively rearranging regions" of Adam and Gibbs [10]. We denote their number $N_r \sim O(N)$, where N is the total number of particles. A region contains $z=N/N_r\sim O(1)$ particles. The number of local "excited" states $\nu\sim O(1)$; ν is an intensive quantity, but it may be very large. Following the BW model, each state of the entire system would be connected to νN_r neighbors, the number reachable by a change in a single region. However, since not all pairs of states in a local region need to be connected, we let the number of connected neighbors, denoted as N_{cn}, equal $c\nu N_r$, anticipating that the connectivity fraction $c<1$. Both N_r and ν are temperature-independent constants but, since Adam and Gibbs' [10] main point was to associate super-Arrhenius T dependence of relaxation times with a growing cooperativity at low T, it may be necessary to make them T dependent in future work. At constant density, the condition for most simulations, any T dependent cooperativity should be weak relative to constant pressure.

Away from the critical point, or possibly the glass transition, liquids have short-ranged correlations. It would be a bad idea to convert the theory of liquids from a few-body to an N-body problem. This is avoided with the recognition that the landscape is really a composite [2] whose building blocks are the landscapes of the local regions. Thus the simplification afforded by the REM is precisely that needed to keep the landscape approach on physically sensible grounds.

The central limit theorem suggests that the REM density of states is Gaussian, and we will employ a Gaussian distribution in the following. The normalized, unconditional distribution of all the states is

$$G(E)=\frac{1}{\Delta\sqrt{2\pi}}e^{-(E-\overline{E})^2/(2\Delta^2)}, \tag{1}$$

with the center of the distribution, $\overline{E}$, and the square of the width, Δ^2, both $O(N_r)$. The unnormalized density of states is $\rho(E)=\Omega G(E)$, and the total number of states is $\Omega \sim O(e^{N_r})$. BW give explicit expressions for these quantities, which can be adapted to liquids. They also introduce an order parameter ρ, the fraction of regions in their ground state [it is hoped that the BW parameter ρ, which we mention for completeness but do not use, will not be confused with the density of states $\rho(E)$]. The distribution is then not Gaussian, but a weighted superposition of terms like Eq. (1) for each ρ. The order parameter provides the capability to predict T dependences different from those usually associated with a REM. We will defer exploitation of this generalization, suppressing the ρ dependences for now. When necessary, we will assume $\rho=0$, a simple nonparametrized Gaussian REM; then, in particular, $\Omega=\nu^{N_r}$.

In fact, the number of liquidlike states does not really fall off as a Gaussian or superposition of Gaussians at the lowest energies, exhibiting instead an abrupt cutoff, and this has consequences at very low temperature. There is no contradiction with a REM; the Gaussian approximation to a sum of random energies breaks down in the vicinity of the lowest possible energy, unless the "steps" in the sum themselves are Gaussian distributed. We will also defer discussion of this point, and so the results presented below must be viewed skeptically in the vicinity of the glass transition temperature T_g. However, we will be quite pleased to obtain a theory valid down to the "mode-coupling" temperature $T_c>T_g$, where the self-diffusion constant D extrapolates to zero from above, and the dynamical crossover from high-T to low-T dynamics is well established.

A K'th order critical point has K of its N_{cn} connected neighbors with lower energy and $N_{cn}-K$ with higher. Thus, a connection is established between the REM and the instantaneous normal modes (INM) approach [11] to the dynamics. The crucial quantity in INM theory of diffusion [11] is the fraction of imaginary-frequency or unstable modes, denoted f_u, which in this case is equivalent to the averaged fractional saddle order, $f_u=\langle K\rangle/N_{cn}\equiv\langle k\rangle$. In liquids, $f_u>\langle k\rangle$, but $\langle k\rangle$ may be regarded as a cleaned up or "diffusive" version of f_u with the contributions of nondiffusive anharmonicities removed [5–8]. A growing body of evidence [5–8,11–16] indicates that D is determined by the number of unstable diffusive modes; thus a dynamical quantity is expressed in terms of an equilibrium property, the goal of nonequilibrium statistical mechanics. The saddle fraction is intimately tied [2] to the distribution of states, but not the unconditional distribution,

$$f_u(E)=p_c^<(E)=\int_{-\infty}^{E}dE'\,G_c(E';E); \tag{2}$$

at energy E, f_u is just the probability $p_c^<(E)$ that a connected neighbor state has a lower energy, and $G_c(E';E)$ is the normalized distribution in E' of states connected to a state with energy E. The conditional, connected density of states is $\rho_c(E';E)=N_{cn}G_c(E';E)$.

In a recent paper [17], we worked out some consequences of the REM/INM theory. We obtained the relation found via simulation by La Nave *et al.* in water [14,15] and silica [16] that $\ln(f_u)$ is proportional to the configuration entropy S_c, and found further [11] confirmation that the escape rate from a state, R, is proportional to f_u. The latter result is particularly transparent for transitions to states with lower energy, since then the Boltzmann factor equals unity and the rate is just proportional to the number of destination states, proportional to $p_c^<$ or f_u [Eq (2)].

However, Ref. [17] had a glaring difficulty. BW formulated an uncorrelated REM with $G_c(E';E)=G(E')$. Since the width Δ is $O(\sqrt{N_r})$, and the thermal average energy $E^*(T)=\overline{E}-\Delta^2/T$ lies $O(N_r)$ below the center of the distribution, essentially all the connected neighbors of a thermal state are $O(N_r)$ higher in energy. By contrast, with states defined in computer simulation as minima via the inherent structure mapping [4] or as all the critical points via the saddle mapping [5–8,18], state-to-state transitions unquestionably involve energy changes $\sim O(1)$. This is because only a few particles change position. Consequently, in the uncorrelated model, both R and $f_u\sim O(e^{-N_r})$, an incorrect result in the thermodynamic limit, although relations among the badly behaved quantities are [17] reasonable and informative. Even so artifacts appeared, e.g., R has a contribution $\sim f_u^2$, which should obviously be linear.

In the following, we propose a simple approximation for $G_c(E',E)$ which properly keeps the connected neighbors of a state within an $O(1)$ energy separation. Properties of, and relations among, minima, saddles, f_u, S_c, and R result which are well behaved in the thermodynamic limit; we will highlight the order in N_r of calculated quantities. The REM/INM theory collapses simulation results for $f_u(T)$ in unit-density Lennard-Jones (LJ) and seven densities of CS_2 on a master curve, allowing a consistent estimate of the mode-coupling temperature T_c, and represents the density of minima $\rho_0(E)$ in LJ. The fits yield the model parameters. The dependence of R upon f_u, and the more complicated dependence of D upon R, are discussed. Several aspects of the characteristic T-dependent behavior [19–21] of supercooled liquids are reproduced.

II. THE DISTRIBUTION OF CONNECTED NEIGHBOR STATES

The liquid analogy to the BW model has random excited state energies in a region and random pair interactions among excited states in adjacent regions. By imagining the interaction energy to be shared between the members of the pair, the energy can be written as a sum of local contributions, $E=\Sigma_{i=1}^{N_r}\epsilon_i$. Each $\epsilon_i\sim O(1)$ is a step in a random walk in energy, which terminates at the system energy $E \sim O(N_r)$. Equation (1) will be obtained if the normalized distribution of local region energies, $g(\epsilon)$, is

$$g(\epsilon)=\frac{1}{\delta\sqrt{2\pi}}e^{-(\epsilon-\bar{\epsilon})^2/(2\delta^2)}, \tag{3}$$

where the parameters $\delta=\Delta/\sqrt{N_r}$ and $\bar{\epsilon}=\bar{E}/N_r$ are both $\sim O(1)$. We will use Eq. (3) in the following, but for future reference, recall that non-Gaussian $g(\epsilon)$ can also yield the Gaussian $G(E)$ for most of the E range, as well as a low-E cutoff.

The unconditional distribution is obtained as usual with an integral over all ϵ_i (denoted by $\{\epsilon\}$) of the product of local distributions for each region and a δ function constraining their sum to E; this amounts to a sum over trajectories leading to E,

$$G(E)=\int d\{\epsilon\}\left[\prod_{i=1}^{N_r} g(\epsilon_i)\right]\delta\left(E-\sum_{j=1}^{N_r}\epsilon_j\right). \tag{4}$$

Now consider $G_c(E';E)$. BW suggest that the connected states differ by a change in one region, and this is eminently reasonable for liquids; then the energies differ by a change in a single $\epsilon_i\sim O(1)$. To generate the states with E' connected to a state with E, start with a trajectory $\{\epsilon\}$ in the integrand of Eq. (4). Replacing any ϵ_i with a random number ϵ such that $\epsilon=(E'-E)+\epsilon_i$ will yield the indicated state, and the distribution of ϵ is $g(\epsilon)$; thus the joint probability distribution of finding connected states with E and E' is

$$G_c(E',E)=\frac{1}{N_r}\sum_{n=1}^{N_r}\int d\{\epsilon\}\left[\prod_{i=1}^{N_r} g(\epsilon_i)\right]\times\delta\left(E-\sum_{j=1}^{N_r}\epsilon_j\right)g(E'-E+\epsilon_n). \tag{5}$$

Recognizing that all terms in the sum over n are equivalent, an instructive rewriting is possible,

$$G_c(E',E)=\int d\epsilon g(E'-E+\epsilon)h(\epsilon,E), \tag{6}$$

where $h(\epsilon,E)$ is the joint distribution for finding a trajectory leading to E and a local step ϵ in that trajectory; its expression follows from a comparison of Eqs. (5) and (6).

The desired normalized conditional distribution $G_c(E';E)$ is obtained from the joint distribution by $G_c(E';E)=G_c(E',E)/G(E)$. Alternatively, it follows from Eq. (6), with $h(\epsilon,E)$ replaced by $h(\epsilon;E)=h(\epsilon,E)/G(E)$. With connectivity fraction $c<1$, not all states generated by a change in one region are connected to the original state, but that only affects the normalization N_{cn} of the conditional density of states, $\rho_c(E';E)=N_{cn}G_c(E';E)$.

For Gaussian local distributions, the integrals in Eq. (5) can be evaluated with the standard technique of introducing the representation of the Dirac δ function $\delta(x)=(1/2\pi)\int d\xi e^{i\xi x}$; thus

$$G_c(E';E)=\frac{1}{2\delta\sqrt{\pi}}e^{-[(E'-E)+(E/N_r)-\bar{\epsilon}]^2/(4\delta^2)}. \tag{7}$$

While E and E' are $O(N_r)$, Eq. (7) will constrain their difference to $O(1)$, as required. The presence of energy/region $\epsilon=E/N_r\sim O(1)$, in the argument ensures the essential property that as the energy of a state becomes more negative with decreasing T, its neighbors lie with increasing probability at higher energy. It is also easy to show that

$$h(\epsilon;E)=\frac{1}{\delta\sqrt{2\pi}}e^{-[\epsilon-(E/N_r)]^2/(2\delta^2)}; \tag{8}$$

in an N_r-step trajectory leading to E, the mean step is obviously E/N_r, and the width is unchanged from the unconditional distribution. We now explore the consequences of Eq. (7) for supercooled liquids.

III. EQUILIBRIUM PROPERTIES OF THE MODEL

The thermal average energy/region is

$$\epsilon^*=\bar{\epsilon}-\delta^2/T. \tag{9}$$

The REM has a characteristic energy at which the configuration entropy S_c vanishes, $\epsilon_{min}=\bar{\epsilon}-\delta\sqrt{2\ln(\nu)}$ (for Ref. [3], $\rho=0$), and so

$$T_{min}=\delta/\sqrt{2\ln(\nu)}. \tag{10}$$

Discussion of lower temperatures is [1,3] possible with the recognition that the states in a given realization of the REM are no longer continuously distributed. At $T<T_{min}$ [1,3], a typical realization is trapped in a state with $\epsilon\approx\epsilon_{min}$, and S_c remains ≈ 0. In liquids, T_{min} is naturally identified as the Kauzmann temperature, which is determined by extrapolation to lie below the glass transition temperature T_g. Temperatures below T_g are not accessible, so we will adopt the point of view that observable behavior must correspond to $T>T_{min}$.

1. The fraction of imaginary frequencies

Equations (2) and (7) yield

$$f_u(\epsilon)=\frac{1}{2}\left[1-\text{erf}\left(\frac{(\bar{\epsilon}-\epsilon)}{2\delta}\right)\right]. \tag{11}$$

With the well-behaved $G_c(E';E)$, as opposed [17] to the uncorrelated model, $f_u(T)=f_u(\epsilon^*(T))$ as usual, and

$$f_u(T)=\frac{1}{2}\left[1-\text{erf}\left(\frac{\delta}{2T}\right)\right]\overset{T\to 0}{\Rightarrow}\frac{T}{\delta\sqrt{2\pi}}e^{-\delta^2/(4T^2)}. \tag{12}$$

Since $T\geqslant T_{min}$, the low-T limit is not strictly reachable, but Eq. (12) demonstrates that in the REM, f_u posesses super-Arrhenius behavior with activation energy $E_{act}=\delta^2/4T$. At high T, $f_u\to 1/2$, because then the thermal energy approaches the center of the symmetric Gaussian density of states where $p^<=p^>=1/2$. The averaged saddle order $\langle K\rangle$ equals $N_{cn}f_u$. The maximum possible order of an individual saddle is N_{cn}, while the maximum of the thermal average is $N_{cn}/2$. In a liquid, the maximum possible order is the dimension of the configuration space, $3N$, but $N_{cn}=3N(c\nu/3z)\leqslant 3N$. Thus the REM incorporates a coarse graining, expressed by the factor $(c\nu/3z)$, in that only directions that lead to new states are kept. Equivalently, the nondiffusive anharmonicities that enter f_u in liquids, corresponding to false transition states that do not contribute to diffusion, are absent.

The mode-coupling temperature T_c is the temperature where $D(T)$ extrapolates to zero from above via a power law. Sciortino and Tartaglia [12] showed that T_c could also be obtained by extrapolating the fraction of diffusive ‘‘double-well’’ INM, those exhibiting a double-well potential energy profile along the eigenfunction, to zero in water. It has been demonstrated [5–8] that $\langle k(T)\rangle$ serves as well for atomic systems. Since any scheme for eliminating the nondiffusive anharmonicities makes a liquid more REM-like, we expect that all well-conceived diffusive $f_u(T)$ in liquids—including the saddle order itself—will be proportional to the REM $\langle k(T)\rangle$.

It is straightforward to make a power-law fit, $f_u=a(T-T_c)^b$, to data generated from Eq. (12). Such fits are extremely sensitive to the temperature range employed. Physically, T_c is the temperature where D would vanish if the upper supercooled dynamical mechanism only were operative; thus data from too high or too low T must be excluded. The natural temperature unit of the REM is δ, and in the following, dimensionless temperatures are understood to indicate T/δ. Starting from a lower T_L of 0.25 or higher, the estimated T_c rises and the exponent b falls as the upper limit for the fit, T_U, increases. By contrast, for $T_L=0.05$–0.15, T_c rises gently to a maximum and then declines slightly; T_c and b are remarkably independent of T_U and T_L, with $b\approx 1.50$ and $T_c/\delta\approx 0.24$ at the maximum. Intermediate behavior is seen at $T_L=0.20$, where T_c first rises with T_U but appears to be reaching a plateau of $T_c/\delta\approx 0.28$. From these observations we estimate

$$T_c\approx 0.26\delta, \tag{13}$$

which should be adequate for the semiquantitative discussion to follow. The corresponding $b=1.50$ was also found by simulation [22] in water, and is typical of the values found for other liquids.

We have [8] previously obtained $\langle K(T)\rangle$ via simulation in supercooled unit-density LJ, $N=108$, and also [13] the diffusive center-of-mass $f_u^{cm}(T)$ in supercooled CS_2, $N=108$, at seven densities 1.55 g/cc$\geqslant\rho\geqslant$1.42 g/cc, including the normal freezing density 1.46 g/cc. Equation (12) and subsequent discussion suggest that plotting $\langle K\rangle/N_{cn}$ vs T/δ will allow data on different materials to be represented by a single master curve; δ and N_{cn} are determined by fitting the number of Im$-\omega$ to N_{cn} times Eq. (12). Figure 1 demonstrates the master plot for LJ and CS_2, essentially perfect above T_c. The calculated parameters are given in Table I. With increasing density across the available range in CS_2, δ increases from 236 K to 486 K. The maximum saddle order or number of connected neighbors is remarkably constant (no rotational contributions to f_u^{cm}) between the two materials and among the different densities. Correspondingly, the ‘‘coarse-graining factor’’ $c\nu/3z=c\nu N_r/3N$ equals to 0.21 for LJ and 0.23–0.22 for CS_2; about 20% of directions lead to new states.

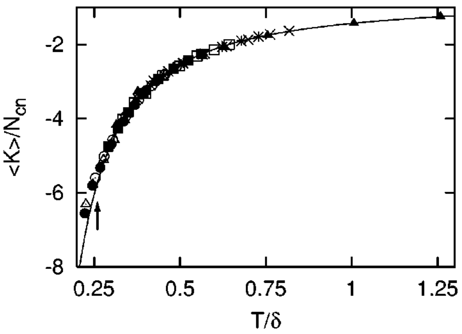

FIG. 1. Natural log–linear REM/INM master curve of fractional saddle order $\langle K\rangle/N_{cn}$ vs dimensionless temperature T/δ and simulation data, $N=108$, unit-density LJ (solid triangles), and seven densities of CS_2. Arrow denotes T_c.

The table also includes T_c from Eq. (13). For unit-density LJ, the value $T_c=0.41$ is in reasonable agreement with what we have published [8], i.e., 0.47, but somewhat lower. For CS_2, 1.46 g/cc, at 78 K is very close to our estimate [23] of 75 K. However, note that the data that gave the original T_c are represented very accurately by Eq. (12). Equation (13) is based on making the power law fit to a dataset generated from Eq. (12). Differences in T_c calculated from the original data and Eq. (13) arise only from the different temperature ranges employed for the fits, and to a lesser extent from the different spacing of the points. The higher (vs 0.41) T_c of 0.47 for LJ in Ref. [8] is a consequence primarily of starting the fit at a higher T_L and using also a higher T_U. Fitting simulation data to Eq. (12) and then taking T_c from Eq. (13) insures that equivalent fit ranges are used in all studies, since Eq. (13) resulted from a single fit to Eq. (12). We suggest that our procedure is a good way to obtain consistent T_c on different materials, from simulations covering different temperature ranges and densities.

2. Imaginary frequencies and the configuration entropy

In the uncorrelated REM, a linear relation exists [17] between the total $S_c\sim O(N_r)$ and the badly behaved $\ln(f_u)$, which is also $O(N_r)$. The essential observation is that $S_c(E)=\ln(\Omega)-(E-\overline{E})^2/(2\Delta^2)$, and the E-dependent term

TABLE I. Parameters for master plot. All systems are $N=108$, and the densities are in parentheses.

Liquid	δ	N_{cn}	$c\nu/3z$	T_c
$LJ(1\sigma^{-3})$	1.59ϵ	66	0.21	0.41ϵ
$CS_2(1.420\ g/cc)$	236 K	74	0.23	61 K
CS_2(1.440 g/cc)	265 K	71	0.22	69 K
CS_2(1.460 g/cc)	300 K	71	0.22	78 K
CS_2(1.485 g/cc)	343 K	71	0.22	89 K
CS_2(1.51 g/cc)	394 K	71	0.22	102 K
CS_2(1.534 g/cc)	448 K	71	0.22	116 K
CS_2(1.551 g/cc)	486 K	71	0.22	126 K

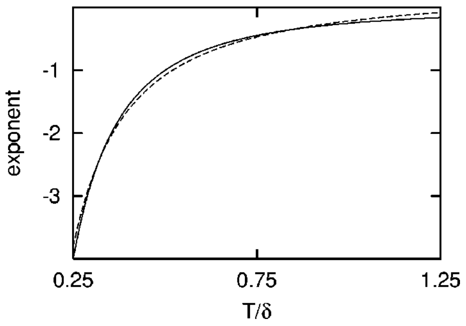

FIG. 2. Exponent of $g(\epsilon^*)$ (solid) and $0.77\ln[f_u(T)]+0.89$ vs T/δ.

may be expressed with $\ln(f_u)$, according to the asymptotic expansion of the error function. In the uncorrelated model the argument of erf is $(E-\overline{E})/(\sqrt{2}\Delta)\sim O(\sqrt{N_r})$ instead of the $O(1)$ quantity in Eq. (11).

In the current model, using the asymptotic expansion of erf and taking a thermal average by replacing ϵ by ϵ^*,

$$S_c(T)=\ln(\Omega)+2N_r[\ln(f_u(T)-\text{const}], \tag{14}$$

where const includes terms proportional to $\ln(T)$. Now, intensive entropies are reported on a per atom or per molecule basis; division by N (not N_r) will yield a factor of $1/z$ in front of $\ln(f_u)$. Rearranging to conform [14–16] to the work of La Nave *et al.*, we have

$$\ln[f_u(T)]=\frac{z}{2}[S_c(T)/N]-\text{const}', \tag{15}$$

opening the possibility that the slope of a $\ln(f_u)$ vs S_c/N plot may yield the size of the cooperative region.

Available simulations do not probe extremely low T where the asymptotic expansion must hold, and the REM is limited to $T>T_{min}$, so further analysis is required. The question is, can $\ln[f_u(T)]$ represent the exponent of $g(\epsilon^*)$ [which, multiplied by $2N_r$, gives the T-dependent part of the exponent of $G(E^*)$] at the available T? Figure 2 shows the result of fitting the exponent to $m[\ln(f_u)]+b$, varying m and b, over a temperature range typical for simulation. The representation is excellent; with best fit parameters $m=0.77$ and $b=0.89$, the slope is not terribly different from its asymptotic value of unity, and the answer to the question is affirmative. The final result for $\rho=0$ is

$$\ln[f_u(T)]=0.65z[S_c(T)/N]-[1.16+0.65\ln(\nu)]. \tag{16}$$

Both S_c and f_u are functions of the dimensionless variable T/δ, so δ does not enter Eqs. (14)–(16).

As with Eq. (12), we assume that all diffusive f_u are proportional to each other, and may be used in Eq. (16); different multiplicative constants will not change the estimate of z. Plots of diffusive $\ln(f_u)$ vs S_c/N are linear in water [14,15] and silica [16], with slopes of 0.96, $z\approx1.5$ and 16.2, $z\approx25$, respectively [24]. The obvious conclusion that silica is more collective than water is reasonable, but such a small z is puzzling for fragile water [25], which should have some collectivity. La Nave *et al.* use double-well modes for water. Perhaps all diffusive modes are not equivalent; there is some evidence [8] of this below T_c in unit-density LJ. Another consideration is that water is a molecule with (for a rigid model) six, not three, degrees of freedom/particle. Indeed, a better G_c may be indicated, but at least we know how to begin interpreting the "La Nave plots."

3. Minima and saddles

The densities of states $\rho_K(E)$ for K'th-order critical points follow from Eqs. (1) and (2), and our proposal [2] for defining a saddle in the REM,

$$\rho_K(E)=\Omega G(E)P_K(E), \tag{17}$$

$$P_K(E)=C_K^{N_{cn}}e^{N_{cn}[(1-k)\ln[1-f_u(\epsilon)]+k\ln[f_u(\epsilon)]]}, \tag{18}$$

where P_K is the probability that a state is of K'th order and C is the binomial coefficient. At low T, f_u is small and $\ln(1-f_u)\rightarrow-f_u$. The high-$T$ limit of f_u is 1/2, and $\ln(1-f_u)\rightarrow\ln(1/2)=-0.69$. The expansion of the log is no longer valid but its small f_u form nonetheless yields -0.50, which is not too far from the true value. Thus we can use the expansion for the full range of f_u in estimating properties of minima and saddles.

The case of $K=0$ (minima) is of particular interest,

$$P_0(E)\approx e^{-N_{cn}f_u(\epsilon)}. \tag{19}$$

Since even at low ϵ the smallness of f_u remains $O(1)$, P_0 vanishes as $O(e^{-N_r})$ in the thermodynamic limit. Integrating $\rho_0(E)$ approximately by making a cummulant expansion on $P_0(E)$ yields the number of minima,

$$\Omega_0\approx\Omega e^{-N_{cn}/2}. \tag{20}$$

One should note that, because the total number of states increases exponentially with N_r, ρ_0 may attain a positive entropy $\sim O(N_r)$ for some energies; nevertheless, the minima remain thermodynamically negligible. By perfect contrast, in the uncorrelated model [17], all thermally accessible states are minima. The caveat is that below ϵ_{min}, some low-lying states [1,3] will attain finite occupation probability with $P_0\neq0$, $f_u=0$. Such a transition in the occupation of the minima has been discussed [5–8] as occurring at T_c, where $\langle k(T)\rangle$ extrapolates to zero, but it would seem that the minimum-saddle transition temperature is really the unreachable T_{min} in this REM.

While we claim to have a well-behaved theory in the thermodynamic limit, the absence of minima, the essential components of much contemporary thinking, is surely controversial. A better approximation to G_c might lead to a different conclusion. On the other hand, Kivelson and Tarjus [26] have argued that all points (except the global minimum) on the landscape with the same potential energy are connected by an "equipotential ribbon" in the thermodynamic limit; then, there are no minima.

The two arguments might seem to be quite different, but there is also some similarity. Kivelson and Tarjus consider

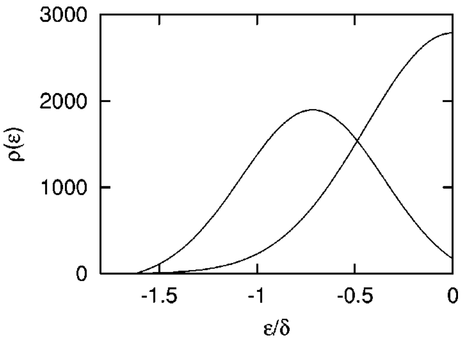

FIG. 3. Density of all states (peaked at zero) and 100 times density of minima vs dimensionless energy/region, ϵ/δ, for $N_r=5$, $\nu=5$, $c=0.4$, $\overline{\epsilon}=0$; $\epsilon_{min}=-1.79$.

that, as the number of directions in the configuration space diverges, it will always be possible to find a path that does not change the energy. In the REM, as N_{cn} diverges, and with neighbors having energy seperations $\sim O(1)$, it will always be possible to find a connected neighbor with lower energy. So both arguments depend on having a diverging number of choices for moving away from a configuration or state. It seems significant that two independent approaches point to the vanishing of the minima in the thermodynamic limit.

Figure 3 shows 100 times the density of minima and the full $\rho(E)$ for a representative small system where minima still survive. As N_r is increased, the scaling factor would also have to increase exponentially to maintain the visibility of the minima. The abrupt the vanishing of ρ_0 on the low-ϵ side is caused by the "entropy cutoff" (exponent less than unity).

Multiplying $\rho_K(E)$ by the Boltzmann factor and maximizing the exponent yields an equation for the K-dependent thermal energies,

$$(\epsilon_K^*-\overline{\epsilon})/\delta^2+c\nu G_c(E_K^*;E_K^*)\left[(1-k)-\frac{k}{f_u(\epsilon_K^*)}\right]+\frac{1}{T}=0. \tag{21}$$

A quick approximation is to replace $G_c(E_K^*;E_K^*)$ by $G_c(N_r\epsilon^*;N_r\epsilon^*)$ and $f_u(\epsilon_K^*)$ by $f_u(\epsilon^*)$, and to use the low-T approximation to f_u, yielding

$$\epsilon_K^*=\overline{\epsilon}-\frac{\delta^2}{2T}[c\nu(1-k)f_u(T)+(1-c\nu k)]. \tag{22}$$

One expects [5] that $E_{K+1}^*-E_K^*$ is comparable to the activation energy; this difference of $\sim O(N_r)$ energies must be $\sim O(1)$. We immediately obtain [recall $k=K/(c\nu N_r)$]

$$E_{K+1}^*-E_K^*=\frac{\delta^2}{2T}[1+f_u(T)]. \tag{23}$$

At low $T(f_u \ll 1)$, the REM has a super-Arrhenius activation energy $\sim\delta^2/2T$, a simple consequence of the energy spacing of the critical points of adjacent order, in agreement with the T dependence of f_u, Eq. (12).

IV. DIFFUSION AND THE ESCAPE RATE

The states of the model are all the critical points. Thus there are no barrier crossings—such a process is represented by a sequence $K\rightarrow K+1\rightarrow K$. Transitions out of a state with E to connected neighbors with E' naturally divide into those with $E'<E$ and those with $E'>E$. Cavagna [5] has discussed these as distinct mechanisms "B" and "A," respectively. BW adopt a simple Metropolis dynamical scheme, with a B transition having rate R_0, an A transition $R_0e^{-(E'-E)/T}$. It is important to note that what might be regarded as the REM—the unconditional and conditional densities of states—can be combined with *any* dynamical model, yielding different predictions for R and D. Nothing in the previous sections depends on the dynamical model, everything in this section does.

1. The escape rate R

The averaged total rate of downward transitions is, with no approximation,

$$R_B(T)=N_{cn}R_0f_u(T), \tag{24}$$

since $f_u=p_c^<$ and every connected neighbor contributes. This is the simplest possible demonstration of why rates are naturally expressed by f_u.

The averaged total rate of upward transitions is

$$R_A(T)=N_{cn}R_0\int_{-\infty}^{\infty}dEG(E)e^{-E/T}\times\int_E^{\infty}dE'e^{-(E'-E)/T}G_c(E';E)/q(T), \tag{25}$$

where

$$q(T)=\int_{-\infty}^{\infty}dEG(E)e^{-E/T}. \tag{26}$$

The factor $G(E)e^{-E/T}$ in Eq. (25) is strongly peaked at $E^*(T)$, which normally means that the integral is dominated by $E\sim E^*(T)$. The uncorrelated model [17] was not normal because of the unphysically strong N_r (and hence E') dependence of G_c. Now, evaluation of R_A is straightforward. The discussion in Sec. II shows how G_c [Eqs. (3) and (7)] keeps $(E'-E)\sim O(1)$, so the second Boltzmann factor is $\sim O(1)$ and

$$R_A(T)=\frac{1}{2}N_{cn}R_0e^{-\delta^2/4T^2}, \tag{27}$$

$$R(T)=N_{cn}R_0\left[f_u(T)+\frac{1}{2}e^{-\delta^2/4T^2}\right]\overset{T\rightarrow 0}{\Rightarrow}N_{cn}R_0f_u(T)\left(1+\sqrt{\pi}\frac{\delta}{T}\right). \tag{28}$$

Both mechanisms make equal contributions at high T, where $f_u\rightarrow 1/2$ and Boltzmann factors approach unity.

Mechanism *A* dominates at low *T*, where the lower-energy states required by mechanism *B* become unavailable, though only by a factor of (δ/T). For $T \leqslant T_{min}$, with a typical representation of the REM trapped in a minimum, presumably $f_u \equiv 0$, mechanism *B* shuts off strongly, and only activated mechanism *A* operates.

The above description captures some features of Cavagna's [5] "saddles ruled scenario." One difference is that he suggests that a rapid onset of strong super-Arrhenius could arise when the mechanism *B* turns off at a temperature where the activation energy for mechanism *A* is already large. While the REM does have mechanism *B* stop at T_{min}, both mechanisms have similar *T* dependences above T_{min}. Mechanism *B* does not require activation for a downward transition, but the number of states with $E' < E$ are vanishing in super-Arrhenius fashion.

2. The relation of diffusion to R *and* f_u

The essence of Eq. (28) is $R \propto f_u$. The next step is to relate the observable *D* to *R*, and thence to f_u. This essential link has been the subject of much of our prior work, using both INM theory [11,13] and more direct methods [27].

If the motion among the states (defined either as domains of all the critical points or of the minima) in the liquid configuration space is a random walk, with no correlation among transition vectors, then $D = \langle (\delta R)^2 \rangle \langle \omega_{tot} \rangle / (6N)$ (Ref. [27]). Here $\langle (\delta R)^2 \rangle \sim O(1)$ is the mean-square separation of successive states and $\langle \omega_{tot} \rangle \sim O(N_r)$ is the average total transition rate. Because a transition in any local region changes the state of the entire system, $\langle \omega_{tot} \rangle$ and *R* are both $O(N_r)$, making $D \sim O(1)$,

In general, $\langle \omega_{tot} \rangle$ is different from the escape rate *R*. The total rate is governed by the states in which the system waits the longest, and $\langle \omega_{tot} \rangle = 1/\langle \tau \rangle$, where $\langle \tau \rangle$ is the averaged waiting time in a state. In one dimension, $1/\langle \tau \rangle \neq R$. However, equality holds for high dimensionality, specifically if N_{cn} is large, as is so in the thermodynamic limit of the REM. Assuming that each escape pathway to state *j* with rate ω_{ji} from state *i* with energy ϵ_i contributes an independent, exponential distribution of waiting times $\omega_{ji} e^{-\omega_{ji} t}$, the probability of waiting for time *t*, and then escaping is expressed as a sum of contributions from all the connected neighbors. The average over waiting times in state *i*—not the thermal average—is $\langle \tau_i \rangle = 1/\Sigma_j \omega_{ji}$. If there are enough terms in the sum it is "self-averaging" and equal to $R(\epsilon_i)$; then, given the dominance of the thermodynamic energy, $\langle \omega_{tot} \rangle = 1/\langle \tau \rangle = R(T)$ and $D(T) = \langle (\delta R)^2 \rangle R(T)/(6N)$.

In unit-density LJ, $\langle (\delta R)^2 \rangle$ (for minima) is only weakly *T* dependent [27]. The REM does not have a length scale, but assuming that it behaves like LJ in this regard, we have

$$D(T) \propto R(T)/N_r \propto f_u(T) \tag{29}$$

for a Markov process of state-to-state transitions. Uncorrelated transitions are expected in a hopping mechanism where waiting times are long enough for the system to lose memory. Thus $T \leqslant T_c$ is indicated, and we have verified [27] that the process of minimum-to-minimum transitions then approaches a random walk in unit-density LJ. In general, "back and forth" motions in two-level systems or groups of states in deep valleys can [28] lead to correlation even below T_c. The simplicity of the dynamics depends upon an intelligent choice of states. If motion among the microscopic states is correlated, it may be a Markov process among appropriately chosen groups of states. As discussed above, the REM already includes a coarse graining. Further groupings may be made with a hierarchical REM [29], which has recently been applied to liquids by Sasai [30].

Despite these warnings, a Markov approximation in the configuration space is a reasonable approximation at the lowest available temperatures. It is also likely that the strongest *T* dependence of *D* is carried by f_u, and that a study covering many decades in a deeply supercooled liquid described by this simple REM [3] would find $D \propto f_u$. However, various relations or fits of form $D \propto f_u^{\alpha}$, with $\alpha \geqslant 1$, have been discussed [13,15,16,30] in the literature. What are the implications of nonlinear relations between *D* and f_u? What new physical information, or information about the validity of the REM, do they convey?

We believe that deviations from $D \propto f_u$ are mostly explained by deviations of true dynamics from that of the current REM. (1) With a state-to-state transition model factors of *T* related to the velocities, significant at higher temperatures, are difficult to treat. (2). Describing the escape rate to higher energy with a Boltzmann factor alone ignores the complexities of motion along a "reaction coordinate" given by, e.g., Kramers theory. Recall also that $f_u = \langle k(T) \rangle$ in the REM, but INM calculations use various schemes to obtain diffusive $\mathrm{Im}-\omega$, and some may be better than others.

Perhaps the most obvious point is that $D \propto T$ at high temperature and constant density, while f_u reaches a constant value. Normal liquid dynamics is not our interest, but its influence is still felt in upper supercooled data; simulations cannot probe the deeply supercooled states where it is negligible. Under such conditions one *must* compare D/T, not *D*, with $\langle k(T) \rangle$ or another diffusive version of $f_u(T)$. A power law fit [13,30] of $D(T)$ to $\langle k(T) \rangle^{\alpha}$ in unit-density LJ would yield $\alpha > 1$, but in fact, [8] D/T is linear in $\langle k(T) \rangle$ and the physically uninteresting interpretation would be that a factor of *T* was being represented parametrically in terms of $\langle k(T) \rangle$.

Contributions of the kinetic energy are treated properly in Zwanzig's theory [31], where *D* is calculated from the velocity correlation function assuming that escape from a minimum—defined as a structure in a local region—is what randomizes the correlation. The zero-time value of the velocity correlation is *T* in our units, and the result [11] is $D = T \langle \omega_{min}^{-2} \rangle (R/N_r)$ at low *T*, where $\langle \omega_{min}^{-2} \rangle$ is the averaged inverse-squared frequency at the minima. Consistency with the random walk picture requires that $(T \langle \omega_{min}^{-2} \rangle)$, which is something like the harmonic approximation to the mean-square displacement along a coordinate in a minimum, be proportional to the multidimensional mean-square separation of successive states, $\langle (\delta R)^2 \rangle$. This may be true, but a careful rationalization of the two approaches has not been achieved.

The Zwanzig theory is well behaved at high *T*. Combined with an INM approximation [32] to *R*, it does a reasonable job of predicting D from T_c up to $T=20$ in unit-density LJ. The change in $D(T)/T$ from sharply increasing at low T to a plateau [32] is already beginning in the upper supercooled regime $T\sim 1.6$. In terms of the chain of transitions among the states, the theory is properly handling the correlations that are important at finite T. Thus expressing D/T instead of D with f_u is to some extent accounting for correlated transitions, which [27] cause D to increase more slowly than R.

Second, R can be much more complex than the simple Metropolis anzatz. INM-plus-Kramers theory [11,13] has been used to relate the escape rate from the minima to f_u. The transition-state theory limit gives

$$R^{tst}=\frac{N_{cn}\langle\omega_u\rangle f_u}{2\pi(f_u^{mx}-f_u)}, \tag{30}$$

while the low-friction limit [13] is

$$R^{low}=\frac{N_{cn}\langle\omega_u\rangle E_{act}\zeta f_u}{\langle\omega_{min}\rangle(f_u^{mx}-f_u)T}, \tag{31}$$

where $\langle\omega_u\rangle$ is the averaged unstable frequency, f_u^{mx} is the maximum high-T value (1/2 in the REM), and ζ is the microscopic friction. The REM states are all the critical points, not just the minima, and Eqs. (30) and (31) apply to R_A only. Nonetheless, it is seen that textbook theories of activated dynamics yield expressions for R containing T-dependent quantities, which are not even defined in the current REM.

In Ref. [13], we argued that the low-friction limit applied in deeply supercooled liquids, and that that the most important T dependence of Eq. (31) was $R\propto\langle\omega_u\rangle f_u/T$. The low-$T$ limit of Zwanzig's [31] theory then gives $D\propto\langle\omega_u\rangle f_u$, if the T dependence of $\langle\omega_{min}^{-2}\rangle$ is negligible. For the seven densities and eight temperatures [13] of supercooled CS_2 used in Fig. 1, a fit $D=a(\langle\omega_u^{cm}\rangle f_u^{cm})^\alpha$ gave α within 1% of unity for the three lowest densities, and close to 0.90 for the four highest. In fact, $D=\langle\omega_u^{cm}\rangle f_u^{cm}$ was very accurate for all 56 states (a close to unity also), supporting the proposition that the center-of-mass modes, free of rotational anharmonicity, are good diffusive modes. On the other hand, at the lowest density, a fit $D=a(f_u)^\alpha$ yields $\alpha=1.41$. This $\alpha>1$ results from ignoring the factor $\langle\omega_u^{cm}\rangle$. It indicates the need for a better dynamical model, not a better description of the states of supercooled liquids.

Besides our work on LJ [8] and CS_2 [13], Ribeiro and Madden [33] found $D\propto f_u$ in molten salts and La Nave *et al.* (using their diffusive modes, Sec. III 2) have $D/T\propto f_u^{1.3}$ in SiO_2 [16] and [15] $D\propto f_u^2$ in water. All these could be explained with different dynamical schemes, retaining the simple REM energy distributions. Perhaps in the case of water, a T-dependent connectivity, expressed with a hierarchical REM as explained by Sasai [30], is also playing a role.

V. THE REM AND THE PHENOMENOLOGY OF SUPERCOOLED LIQUIDS

An extensive literature [19–21] attempts to characterize the T-dependent properties of supercooled liquids. Perhaps the most obvious connection to the REM is via δ, the width of the local density of states. A large δ increases the configurational heat capacity $C_V/N_r=d\epsilon^*/dT=\delta^2/T^2$, corresponding [19] to greater fragility. The configurational entropy does not vanish above T_g, but an extrapolated $T_{min}<T_g$ can be identified. The ratio T_g/T_{min} is closest to unity in fragile liquids [34], again connecting large δ to fragility, as S_c drops more strongly to vanish at a higher T_{min}. The δ-fragility association is not unreasonable, although Sastry [9], considering minima only, has shown that the "vibrational free energy" of the states $F_{vib}(T,\epsilon)$ must also be considered. There is no F_{vib} in the current REM.

It must also be noted that δ is the natural temperature unit, so in many ways changing δ simply rescales the temperature and varying the states/region, ν, is more important. Equations (10) and (13) indicate that T_{min} depends on the number of states per region, ν, while T_c does not. They are equal at $\nu=1630$, and

$$T_c>T_{min}, \quad \nu>1630, \tag{32}$$

$$T_c<T_{min}, \quad \nu<1630. \tag{33}$$

The complex dynamics [19–21] of fragile liquids, including the super-Arrhenius T dependence, is most pronounced below T_c and, of course, above $T_{min}=T_K$; a necessary condition for the REM to describe a fragile liquid, then, is $\nu>1630$.

Strong [19] or "nonfragile" [25] liquids exhibit Arrhenius, and otherwise simple, behavior all the way down to the glass transition. It is still possible to calculate T_c for a strong liquid, but it may not be very interesting, so $T_c<T_{min}$ might be acceptable. However the only hope for obtaining *any* Arrhenius T dependence is to have $T<T_{min}$, with the system confined for long periods in low-lying states with $\epsilon\approx\epsilon_{min}$, and T_{min} must be considered inaccessible. Thus, the simple REM is fundamentally a model for fragile liquids, and will describe more and more of the interesting temperature range as ν and T_{min} increase above 1630 and decrease below T_c, respectively. Fortunately, a large number of states is a known [20,21] attribute of fragile systems.

Any discussion on the dynamics must recognize that the activation energy is irrelevant if $T>E_{act}$. Fragile behavior is often associated with higher and more irregular barriers at lower T. If the accessible landscape changes over a temperature range where $T>E_{act}$, however, there will be minimal consequences. Defining T_{act} such that for $T<T_{act}$, activation is required, i.e., $E_{act}>T$, we have [discussion following Eq. (12)] $T_{act}=0.5\delta$; activation sets in at just below twice T_c. The condition for activation at T_{min} is $\nu\geqslant e^2\approx 7$. A system with fewer than seven states/regions, if such exists, would exhibit "high-T dynamics" for all available T [which would only (*vide infra*) span a small dynamic range].

Above T_{min}, the viscosity η should obey

$$[\eta(T)/\eta_{ref}]\approx e^{\delta^2/4T^2}, \tag{34}$$

where η_{ref} is a reference normal liquid value, and so

$$[\eta(T_{min})/\eta_{ref}]\approx\sqrt{\nu}. \tag{35}$$

One definition of the glass transition [34] is $[\eta(T_g)/\eta_{ref}]=10^{16}$. It follows that the REM *will not have a Kauzmann transition above T_g, if $\nu\geqslant10^{32}$*. It is often stated that the REM must have a Kauzmann transition, which is true, but one occurring below T_g is quite a different matter. The REM will then give a reasonable representation of a fragile liquid for all $T\geqslant T_g$, with $T_g=0.082\delta$. Angell [22] estimated $T_c/T_g\approx1.2$ in fragile materials. Our result is much higher, indicating a need to refine the model.

The predictions of the REM depend crucially upon ν. Its estimation, and that of the other REM parameters, is of first importance. There are several possible approaches. First, consider that the total number of states (assuming $\rho=0$) is

$$\Omega=e^{N_r\ln(\nu)}=e^{[\ln(\nu)/z]N}. \tag{36}$$

The number of distinct minima in several systems has been found to obey the relation $\Omega_0=e^{\alpha N}$ [35–37], with estimates of α (unfortunately α has already been used to denote the power in $D\propto f_u^{\alpha}$ but we hope the power law in question will be clear from the context.) ranging from 0.019 (lower bound, general arguments) [35] to 0.8 (data on various simple systems) [37], to 13.14 (thermodynamic data on very fragile OTP) [36]. As part of an ongoing mapping of the landscape of unit-density LJ, $N=32$, we have a preliminary distribution $\rho_0(E)$ with $\Omega_0=8780$ liquidlike minima corresponding to $\alpha=0.28$. The position of LJ on the fragility scale has been unclear. With an α of 0.28 vs 13.4 for OTP, it certainly appears nonfragile (fewer states) compared to OTP, consistent with the arguments of Ferrer *et al.* [25].

If the REM states were minima, Eq. (36) would imply $\ln(\nu)/z=\alpha$, and the condition to avoid a Kauzmann transition would be $z\geqslant2.303(32/\alpha)$. Then the minimal z is 6 for $\alpha=13.14$, 92 for $\alpha=0.8$, 264 for $\alpha=0.28$, and 3878 for $\alpha=0.019$. However, the states are all the critical points, not just the minima. For unit-density LJ, $N=32$, fitting $\langle k(T)\rangle$ [8] to Eq. (12) yields $N_{cn}=18.8$ and $\delta=1.54$ (encouragingly identical to 1.59, $N=108$); Eq. (20) then yields $\Omega/\Omega_0=1.2\times10^4$. Even if the vanishing of the minima in the thermodynamic limit found here is an artifact, there are in general more states than minima. If the large α of OTP is typical of fragile liquids, it is evident that they satisfy $T_{min}<T_g$ counting minima alone and are perfect candidates for an REM description. Even nonfragile liquids with fewer states and smaller α could meet the condition with reasonable values of z, although the REM would not treat their Arrhenius T dependence properly. Nonetheless, Eq. (12) gave a good representation of $\langle k(T)\rangle$ for LJ. The data were well above T_c, where exponential T dependence in LJ is weak [25], and we have some hope for a description of less fragile systems under such conditions.

Second, fitting $f_u(T)$ with Eq. (12) yields $c\nu N_r$, and an estimate of $z=N/N_r$ allows determination of $c\nu$. We suggested [18] that $3z$ could be identified with the participation ratio of the vector connecting successive local minima to which the system is mapped [4]. For unit-density LJ, $N=108$, this yields $z\approx7$—cooperative regions of seven atoms—or $N_r=15.4$, $c\nu=4.3$. However, c and ν remain unknown.

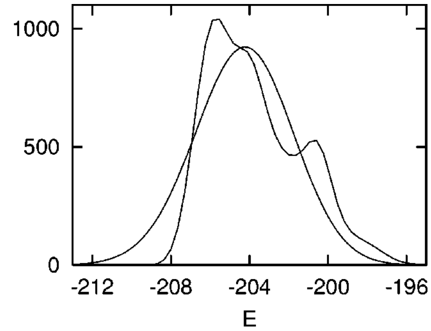

FIG. 4. REM theory and simulation data (irregular curve) for density of minima, ρ_0, vs energy E (LJ units), unit-density LJ, and $N=32$.

Third, the theory of ρ_0 contains the parameters N_r,ν,Δ,c, and $\overline{E}$, and one can try to determine them by a fit. The relation $\Delta^2/\delta^2=N_r$, with δ estimated from Eq. (12), provides another route to N_r or z. A five-parameter fit to our preliminary ρ_0 for unit-density LJ, $N=32$, gives representations of similar quality for widely different parameter sets, and is not useful. The number of free parameters may be reduced to three. Thus we hold $c\nu N_r=18.8$ fixed and use $N_r=\Delta^2/1.54^2$ while varying ν, Δ, and $\overline{E}$. The result is shown in Fig. 4, with $\nu=30.69$, $\Delta=3.390$ and $\overline{E}=-196.3$. It follows that $N_r=4.84$, $z=6.61$ in excellent agreement with our other estimate of ≈7, and $c=0.12$. With ν, z and Ω_0 in hand we may calculate $\Omega/\Omega_0=e^{7.0}$, compared to $e^{9.4}$ from Eq. (20). Note that $\overline{E}$, the center of the distribution of all the states, is calculated to lie well above the peak in the distribution of minima.

Unit-density LJ then has $T_{min}=0.38\delta>T_c$, or 0.58 in LJ units. It is not an ideal system for a REM description, but most of our supercooled data do fall in the $T>T_{min}$ range. The representation of $\langle k(T)\rangle$ and the internally consistent fit to $\rho_0(E)$ indicate that the REM is performing better than one might hope in a nonfragile system.

VI. SUMMARY AND DISCUSSION

Our prior attempts to combine the INM approach with the REM [2], and to apply [17] the resulting theory to liquids, suffered from the unphysical N_r dependences of the uncorrelated model. In this paper, with a simple approximation to the connected distribution of states $G_c(E';E)$, we have obtained a well-behaved REM/INM theory that incorporates some of the important phenomenology of fragile supercooled liquids. With fits to simulation data, a beginning has been made at estimating model parameters for several materials. If the number of states/regions, ν, is sufficiently large, the Kauzmann transition is avoided and the REM exhibits super-Arrhenius behavior down to $T_g=0.082\delta$; δ sets the temperature scale. The mode-coupling temperature T_c is $\approx0.26\delta$. In contrast to the uncorrelated model where all states are minima in the thermodynamic limit, the probability P_0 that a state is a minimum is now seen to vanish in the limit. This finding is consistent with the arguments of Kivelson and Tarjus [26].

The REM expression for $f_u(T)$, which we consider comparable to the fraction of diffusive Im$-\omega$ INM in liquids, suggests that data for different materials can be plotted on the same master curve by introducing the reduced temperature T/δ. Using the master curve also allows a consistent determination of T_c from different studies on different systems. The method is demonstrated for unit-density LJ and seven densities of CS_2.

A good fit is obtained to the density of minima, $\rho_0(E)$, in unit-density LJ, confirming our prior estimate [27] of seven atoms in a local region and yielding a value of ≈ 30 states/regions. Consequently, $T_{min}=0.58$ LJ units, and the REM description does not extend to the deeply supercooled regime, but works surprisingly well at higher temperatures. Perhaps this is because LJ, while nonfragile, has weak Arrhenius T dependence [25], with an activation energy less than the melting temperature. The REM could not possibly reproduce strong Arrhenius behavior.

The slope of $\ln(f_u)$ vs S_c/N is somewhat greater than $z/2$ for $T \gtrsim T_c$. Comparing with the work of La Nave *et al.* [14–16,24] gives $z \approx 25$ in SiO_2 and $z \approx 1.5$ in water. The former is reasonable while the latter may point to deficiencies in the theory.

The escape rate from a state, R, naturally divides into an activated (mechanism [5] A) contribution R_A for upward transitions and nonactivated R_B for transitions to lower energies. Even so the two mechanisms have similar T dependences, since the number of states with lower energy contributing to R_B decreases strongly with decreasing T. The total rate R is proportional to f_u.

In deeply supercooled liquids, the model predicts, with plausible assumptions, $D \propto R \propto f_u$. Some simulations [13,15,16] show $D \propto f_u^{\alpha}$, with $\alpha > 1$. It was argued that the cause is probably the presence of factors with relatively weak (compared to a Boltzmann factor) T dependence, arising from dynamical details not included in the REM. Such factors are important when fitting over the limited ranges available to computer simulation. Replacing the simple BW [3] Metropolis anzatz with something more correct for liquids is an essential improvement. Here it should be possible to borrow what has already been done [11,13] for INM theory. In water, the relatively large $\alpha=2$ and the small value of z from Eq. (16) may indicate the need for a better REM.

While the master curve and the representation of ρ_0 clearly show that the REM can be a valuable tool in the theory of liquids, the work has only begun. The idea of dividing a liquid into independent local regions is still vague, despite having been discussed at least since Adam and Gibbs [10], and must be implemented quantitatively. Fitting simulated properties of the landscape to the model for more substances should make an important contribution to this task, determining the parameters and their possible T dependences. Use of the order parameter ρ [3] will add new flexibility to the theory. For example, while currently $C_V/N_r = \delta^2/T^2$, more generally

$$C_V/N_r = -\frac{d}{dT}[\delta^2(\langle\rho(T)\rangle)/T], \tag{37}$$

which need not have the parabolic form commonly associated with the REM.

Our proposed $G_c(E';E)$ is physically motivated and fixes the obvious shortcomings of the uncorrelated model. However, even given our assumptions it is approximate. A Gaussian distribution of local energies is a simplification which cannot describe all systems—e.g., one suspects, water—and more work is required to represent liquids in detail. The status of the minima remains unclear. The uncorrelated model and the current model represent two extremes, with all minima and no minima, respectively, in the thermodynamic limit. Nonwithstanding the arguments of Kivelson and Tarjus [26], it may be that the current theory goes too far in eliminating the bias of the neighbor distribution towards $\overline{E}$.

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