The random first order transition theory of the dynamics of supercooled liquids is extended to treat aging phenomena in nonequilibrium structural glasses. A reformulation of the idea of “entropic droplets” in terms of libraries of local energy landscapes is introduced which treats in a uniform way the supercooled liquid (reproducing earlier results) and glassy regimes. The resulting microscopic theory of aging makes contact with the Nayaranaswamy-Moynihan-Tool nonlinear relaxation formalism and the Hodge-Scherer extrapolation of the Adam-Gibbs formula, but deviations from both approaches are predicted and shown to be consistent with experiment. The nonlinearity of glassy relaxation is shown to quantitatively correlate with liquid fragility. The residual non-Arrhenius temperature dependence of relaxation observed in quenched glasses is explained. The broadening of relaxation spectra in the nonequilibrium glass with decreasing temperature is quantitatively predicted. The theory leads to the prediction of spatially fluctuating fictive temperatures in the long-aged glassy state, which have non-Gaussian statistics. This can give rise to “ultra-slow” relaxations in systems after deep quenches.

PACS numbers:

I. INTRODUCTION

The energy landscape metaphor has turned theorists towards viewing the global geometry of the phase space of complex systems. When these systems are mesoscopic in size, for example, small proteins [1] or gas phase clusters [2], a more or less complete mathematical formulation of the idea, called treating kinetics and thermodynamics, can be made using statistical tools to characterize minima and saddle points of the entire system. Yet for macroscopic systems, most transitions rearrange particles only locally. This essential aspect of the dynamics is brought home forcefully by noting that a liter of liquid water will move from one energy minimum to another in $10^{-39}$ sec. Such a short time scale cannot be directly relevant to any laboratory measurement on this system! The necessity for using a local description is clearly recognized in the modern theory of supercooled liquids and glasses which is based on the statistical mechanics of random first order transitions [3]-[5]. In the deeply supercooled liquid regime this theory explains not only the phenomenological features of the dynamics [6] but quantitatively predicts, on a microscopic basis, the size of cooperative lengths, the precise non-Arrhenius behavior of typical relaxation times [6, 5] and the non-exponentiality of relaxation [6]. A quantized version of the theory explains the low temperature thermodynamics of amorphous substances, usually interpreted in terms of two level systems [3] and the more energetic Boson peak excitations [7]. The crucial manifestation of the locality concept in this theory (which has many mean field, global, aspects) is the notion that “entropic droplets” drive the large-scale activated notions in glass forming liquids [1,2,3,4] and give both liquids and glasses an intrinsic “dynamical mosaic” structure.

The main purpose of this paper is to describe the predictions of the RFOT theory for the behavior of glasses that have fallen out of equilibrium because of being rapidly cooled from the melt. Dynamics does not cease in rapidly quenched liquids that become glasses; rather motions persist but are frustratingly slow and hard to study experimentally. This slow, far-from-equilibrium dynamics, called “aging”, is not only of fundamental interest for statistical mechanics [11] but also is of great practical interest since so many amorphous materials are used in everyday life for times exceeding their preparation time [12]. Sometimes even small changes of properties upon aging are crucial to engineering performance.

Like the quantum theory of the low temperature properties of glasses, the description of the nonequilibrium aging regime requires the explicit construction and study of the energy landscape of local regions of the glass. This local energy landscape description turns out to be a microcanonical ensemble reformulation of the entropic droplet concept that was formulated originally in the canonical ensemble. We have found this microcanonical description to be more vivid and somewhat easier to communicate than the original canonical formulation. After introducing this formulation we will show that it indeed reproduces the results for the dynamics of equilibrated supercooled liquids already obtained using the random first order transition theory. More important, this local energy landscape theory makes several very striking predictions about the aging regime and how the aging dynamics in the nonequilibrium glass is related to the kinetics and thermodynamics of the equilibrated liquid. The predictions are consonant with all experiments known to us and make contact with, but are formally distinct from, the phenomenological approaches commonly used to de-
scribe aging in structural glasses \cite{13, 14, 15, 16, 17}. The present theory, for example, makes a specific prediction of the so-called nonlinearity parameter, $x_{NMT}$, in the Narayanaswamy-Moynihan-Tool, formalism \cite{13, 14, 15}. In addition, the degree of nonexponentiality of relaxation characterized by a $\beta$ exponent is predicted. $\beta$ turns out to be neither precisely fixed at $T_g$ nor does it precisely scale like the $\beta$ for an equilibrated liquid with $T$, another assumption often made. The predicted variation of $\beta$ with quench temperature is however modest until very low temperatures are reached. Likewise the Adam-Gibbs expression \cite{15} has been extended phenomenologically notably by Hodge and Scherer into the aging regime below $T_g$ by assuming the configurational entropy to be frozen at $T_g$. While above $T_g$, an Adam-Gibbs like form of the temperature dependence of relaxation time is found from the present theory, below $T_g$, the local energy landscape approach gives a different expression for the relaxation rate in an aging glass. Quantitatively this expression gives relaxation rates close to the Hodge-Scherer-Adam-Gibbs (HSAG) latter extrapolation but the local energy landscape theory predicts a deviation from that formula. This deviation would be interpreted within the HSAG framework as a quench temperature dependence of the apparent configurational entropy. Such a deviation has been found by Alegria et al. in their careful work on aging of polymers \cite{19}.

Our most explicit results are obtained for the idealized situation of the aging initially found after a cooling history with a single rapid quench of modest depth. We will also quantitatively discuss modifications of the simple theory expected for very deep quenches. We also discuss the behavior of systems that have significantly relaxed in the quenched state. While, our analysis suggests that, to a first approximation, introducing a single fictive temperature should serve well to describe many quench histories, the local energy landscape theory shows that using a single fictive temperature is not exact. We suggest possible modifications of the usual aging kinematics based on the present theory.

The organization of the paper is as follows: we first describe how the local energy landscape view of entropic droplets can be visualized and show how a library of local energy landscapes can be constructed. We next show how to derive in this framework the (previously obtained) Vogel-Fulcher behavior above $T_g$. We then present the results for typical relaxation rate for rapidly quenched, aging glasses and compare these predictions with experimental results. We then discuss the predictions for the stretching exponent both above and below $T_g$. Following this, the generalizations needed for very deeply quenched glasses and glasses that have undergone significant relaxation in the aging state are discussed. Finally we summarize our theory and suggest some further experimental tests of it.

II. THE LOCAL ENERGY LANDSCAPE CONSTRUCTION

The energy landscape language is usually applied to a small system (protein or cluster). It is also used for a thermodynamically large system described by mean field theory \cite{21, 22}. In the first situation, the barriers between states are, of course, finite because the system is finite, but barriers may be formally infinite for the mean field system. The “states” for a cluster or a protein are often taken to be the basins surrounding minima of the potential energy \cite{22}. These are well defined and no transitions can occur, classically, between them at absolute zero. The “states” of a mean field system are tied to minima of free energy and again, owing to the $O(N)$ barriers, no transition can occur between them (even at finite $T$).

In a supercooled liquid the observed plateau in the time dependent neutron scattering correlation function \cite{23} shows that most molecules spend a great deal of time vibrating about a given location. At least deep in the supercooled regime (where the plateau is well developed) we can, therefore, conceptually imagine constructing an average location for any particle about which it vibrates (for times less than the plateau). The three dimensional structure based on these average locations will be quite close to a potential energy minimum found by removing kinetic energy from the system with infinite speed (“steepest descent” to an “inherent structure”). A mean field theory of the glass transition can be obtained by constructing a free energy functional dependent on the (plateau time averaged) density and then noting that this functional has minima for density patterns localized around such inherent structures \cite{21, 22, 24}. In this way a vibrational component of the free energy can be defined and can be added to the average energy of such a state to give a free energy which determines the thermal probability of being in this state through the Boltzmann law.

Free energy functionals only have such aperiodic minima below a temperature $T_A$. This temperature has been shown (within a simple approximation) to be equivalent to the mode coupling dynamical transition temperature \cite{3}. The transition has the character of a spinodal for a first order phase transition \cite{4}. Above $T_A$ even simple vibrational motions will take the system from one minimum to another, but below $T_A$, the plateau in the time dependent structure factor indicates the persistence of such states and therefore their relevance to dynamics. In fact, as a first approximation, the persistence of these states allows them to act as a “basis set” for describing supercooled liquid dynamics. Thus we say a free energy landscape emerges at $T_A$. $T_A$ has been evaluated both for simple liquids \cite{24, 25} and for models of network forming liquids with repulsive force \cite{26} from first principles. The physical meaning of the temperature $T_A$ is simple. When supercooled below its melting temperature $T_m$, the liquid is, of course, in a metastable state as a whole, and therefore must be metastable locally. $T_A$ can be conve-
niently interpreted, for example, as a temperature below which every two molecules will spend a particular number (say, 300) of vibrational periods together between the first encounter and the final departure.

As part of our programme to describe the microscopics of liquid relaxations, we will show that transitions between the metastable configurations of the liquid as a whole consists of transitions between local metastable configurations. We will employ a microcanonical procedure in which only local regions are considered and will find that beyond a certain (relatively small) size $N^*$, the thermal and relaxational properties of the liquid do not depend on the size of the sample. Alternatively said, all liquid properties of interest can be deduced by focusing on a liquid region of size $N^*$ and completely disregarding what the rest of the liquid is doing. This is the essence of the locality of the liquid free energy landscape. The microcanonical procedure is a necessary step in establishing such locality; it is however rarely used, so let us first train our intuition on the very familiar example of a harmonic lattice. Imagine being inside an extremely large, cubic, and purely harmonic lattice and being given the ability to do arbitrary thermodynamic measurement locally. You are further assigned to explain, within a formal model, those thermal measurements, but are allowed to visually inspect and mechanically test the bonds with an arbitrarily large, but finite region, limited by how fast you can perform the inspection. Upon checking that all individual bonds are truly harmonic and the lattice is cubic within a certain region (of size $L$), you write down a simple hamiltonian but are left with the issue of the conditions at the boundary - strictly speaking, the assignment is undoable! Being an optimist, you say: let me assume for today that the rest of the sample is totally rigid (fixed boundary conditions) or does not exist at all (open boundary condition) and diagonalize the resulting Hamiltonian; tomorrow I can expand my horizon, repeat the procedure and see what happens. The first day proves frustrating though, because the Hamiltonian has an energy gap (proportional to $\pi/L$), while the thermal measurements clearly show very low frequency excitations are present. Fortunately, since (unbeknownst to you) the lattice was harmonic and periodic, your consecutive inspections and diagonalizations will yield a smaller and smaller gap. Clearly, the landscape of a regular harmonic lattice is non-local and the microcanonical procedure offers a definitive test of non-locality. Consider yet another elementary notion: Suppose you have a product of two Hilbert spaces $A \otimes B$ (possibly interacting via $V_{A,B}$ with an energy $\epsilon_{iA,jB}$ assigned to configurations $iA$ and $jB$ of the subspaces $A$ and $B$. Consider the partition function $\sum_{iA,jB} e^{-\beta \epsilon_{iA,jB}} = \sum_{iA} e^{-\phi_{iA}}$, where $e^{-\phi_{iA}} = \sum_{jB} e^{-\beta \epsilon_{iA,jB}}$. If $A$ and $B$ are independent: $V_{A,B} = 0 \Rightarrow \epsilon_{iA,jB} = \epsilon_{iA} + \epsilon_{jB}$, one may further simplify $\phi_{iA} = \epsilon_{iA,jB} - TS_B$. In either case, $\phi_{iA}$'s are free energies of the degree of freedom $B$, but can still be (with advantage) regarded as an energy, as far as the $A$ degree of freedom is concerned. For example, one is allowed to build a microcanonical construction using $\phi_{iA}$'s as the label. In the following, we will use a $\phi_{iA}$-like quantity to describe all the degree of freedom in the supercooled (or quenched) liquid in excess of the lowest energy crystalline structure corresponding to this substance (at this temperature). (For a polymer that does not form a crystal our results will still apply qualitatively.) While the "integrated out" degrees of freedom $B$ are clearly related to the vibrations of the corresponding crystal structure, they are easy to conceptualize only in the mean field limit, where they are indeed harmonic vibrations (see shortly). Otherwise, the "$B$" motions are strongly anharmonic.

We are now ready construct a library of free energy minima for a very large sample of a liquid (or glass). This spectrum is shown schematically in the first column of Figure 1 as a function of the free energy of a state $i$, $\phi^{ib}_i$ which we take as the sum of an energy $\epsilon_i$ and an entropic contribution from vibrations within the basin $-T S_{ib,i}$. Because the system is very large this global library of states has an exceedingly dense spectrum, whose density dramatically increases with free energy. Let us imagine the system is presently in one of these basins with

![FIG. 1: In the upper panel on the left a global configuration is shown, chosen out of a global energy landscape. A region of $N = 5$ particles in this configuration is rearranged in the center illustration. The original particle positions are indicated with dashed lines. A larger rearranged region involving $N = 7$ particles is connected dynamically to these states and is shown on the right. In the lower panel, the left most figure shows the huge density of states that is possible initially. The density of states found in the local library originating from a given initial state with 5 particles being allowed to move locally is shown in the second diagram. These energies are generally higher than the original state owing to the mismatch at the borders. The larger density of states where 7 particles are allowed to move is shown in the right most part of this panel. As the library grows in size, the states as a whole are still found at higher energies but the width of the distribution grows. Eventually with growing $N$, a state within thermal reach of the initial state will be found. At this value of $N^*$ we expect a region to be able to equilibrate.](image-url)
(free) energy $\phi_i^{\text{lib}}$. We can now construct a set of local libraries of states. To do this, imagine mentally cutting out a region around a location $R$ containing $N$ particles, where $N$ is much less than the total number of particles in the sample. Call this region $D(R, N)$. Next, freeze the molecules outside this region but allow molecules within $D$ to move. (Unlike in the cubic crystal analogy, a supercooled structure has built-in stress, so using open boundary condition is not useful.) With the frozen environment one could (by quenching the potential energy or a free energy functional) find a new set of inherent structures that involve only reconfiguring the particles in $D$. Actually such a set of structures (apart from strains near the surface of $D$) will locally resemble a subset of the original global library. If $N$ is small, however, we expect the subset of the states so sampled to be selected on average from a higher energy part of the global spectrum than where the original $\phi_i^{\text{lib}}$ was found. Essentially this is because the density of states rapidly increases with $\phi$ and there is less freedom to readjust particles in the constrained minimization problem because of the fixed environment. In absolute terms, we expect the discrepancy in energy of the mean energy of the states in any local library from the starting state to increase with $N$ since it is the particles at the borders that must be most strained.

When $N$ is small the local library is sparse but it grows denser and spreads out over a larger range of free energy as the size of the region increases. The set of such libraries centered around $R$ is shown also in Figure 4 for $N = 1$ up to a large value of $N$. The number of states in the library at free energy $\phi_i$ determines the configurational entropy $\Omega_c(\phi_i^{\text{lib}}) = e^S_c(\phi_i^{\text{lib}})/k_B$, where $k_B$ is the Boltzmann constant. The competition between the average energy growth and the spreading of the range of energies with size of the region means that there is a characteristic size $N^*$ where a state will finally be found within thermal energy of the starting state. $N^*$ turns out to be the size of a dynamically correlated region in the liquid or glass. Since the new configuration is within $k_BT$ of the starting state, a transition of such a region from its original configuration to the new state can occur with reasonable probability. The region after reconfiguration will be characterized by a temperature $T$. Elementary transitions in the liquid must leave most of the molecules near their old locations - this is the dynamical essence of locality. Therefore the local landscape libraries are locally connected to each other: in order to re-arrange a large region, smaller regions located in the same place must first be rearranged. The specific law connecting states in neighboring libraries must obey detailed balance (at the vibrational temperature $T$) but otherwise will depend specifically on molecular details for each system. The additional activation energy, for a downhill move in such a library should only be a few times the energy needed to heat a particle to $T_A$, the dynamical transition temperature.

Irrespective of the detailed motions allowed, the locality of the dynamics, however, guarantees that the transitions from the initial state to one of the thermally allowed states in the library for $D(R, N^*)$ will nevertheless be slow: owing to the initial rise of the average energy there will be a bottleneck in the probability flux at an intermediate value of $N$, namely $N^4$. The activation free energy for reaching this bottleneck state determines the escape rate from the initial configuration by motions in the vicinity of $R$.

While the local libraries can be constructed explicitly given sufficient computational resources, the RFOT theory suggests a useful set of approximations to the statistics of these libraries when $N^*$ and $N^4$ are moderately large. We now describe these approximations: We ascribe to each state $j$ of the library for a region $D(R, N)$ a so-called bulk free energy $\Phi_j^{\text{bulk}}(R, N)$. Naively this would be the sum of the vibrational entropies and internal energies of each molecule in $D$ and the pair interactions between the molecules within $D$. (Rigor here would require ensuring the appropriate finite ranges of interactions and some precisely specified ways of partitioning vibrational entropies: entanglement entropies of the interface are too subtle for consideration at present). Note that in a system with a globally correlated landscape, such as the harmonic lattice considered earlier, a description in terms of local libraries will not provide the full list of configurations available to the system as a whole.

In a similar way we would define a bulk free energy of the initial state relevant to this region $\Phi_{\text{in}}^{\text{bulk}}(R, N)$. The actual energy of the complete sample when the state $j$ is inserted in region $D(R, N)$ will not just reflect the difference in the bulk energies corresponding to the state $j$ and the initial state; instead, it will be higher by an amount $\Gamma_{j,\text{in}}$:

$$\phi_j^{\text{lib}} - \phi_i^{\text{lib}} = \Phi_j^{\text{bulk}}(R, N) - \Phi_{\text{in}}^{\text{bulk}}(R, N) + \Gamma_{j,\text{in}}. \quad (1)$$

As mentioned earlier, the new local structure labelled by $\phi_j^{\text{lib}}$ is likely to be higher in energy than the initial configuration. Our construction thus suggests $\Gamma_{j,\text{in}}$ will usually be positive and will at most scale with the interface area. We will write $\Gamma_{j,\text{in}} = \gamma_j N^x$. As we shall see later the estimate for the exponent $x = 2/3$ in 3 dimensions, based solely on the interface area, is probably naive near $T_g$.

We now wish to calculate the equilibration rate of the region $D(R, N^*)$. If the environment remains frozen, this rate is the escape rate from $N = 0$ to $N = N^*$. The probability flux to increase $N$ falls until the bottleneck value $N^4$ is reached. After $N^4$, even though the average energy of states in the libraries increases, the growth of the number of states with increasing library size is sufficient so that a rapid path to a thermally equilibrated state at size $N^*$ can be found. Let the typical downhill microscopic rearrangement have a rate $\tau_{\text{micro}}^{-1}$. This rate will only be weakly activated. The flux to any state at a size
$N$ smaller than $N^*$ will be

$$k = \tau_{\text{micro}}^{-1} \int (d\phi_{\text{eq}}^{ib} / c_\phi) e^{S_c(\phi_{\text{eq}}^{ib})/k_B T} e^{-(\phi_{\text{eq}}^{ib} - \phi_{\text{eq}})/k_B T}$$

$$\simeq \tau_{\text{micro}}^{-1} e^{S_c(\phi_{\text{eq}}^{ib})/k_B T} e^{-(\phi_{\text{eq}}^{ib} - \phi_{\text{eq}})/k_B T},$$

(2)

where $\phi_{\text{eq}}$ maximizes the integrand and $c_\phi$ is some constant of units energy. The quantities $\phi_{\text{eq}}^{ib}$ and $\Phi_{\text{eq}}^{bulk}$ are related through Eq. (1). This maximization means $\phi_{\text{eq}}$ will be the internal free energy characteristic of the system at the ambient (i.e. vibrational) temperature $T$.

That is, $\phi_{\text{eq}}$ is the sum of the energetic and vibrational entropic contributions appropriate to equilibrium at $T$. In essence, the equation above is nothing more than the rate of escape through a transition state with non-zero entropy, hence a structure resembling the canonical ensemble. Aside from a numerical factor, the integration in Eq. (2) is indeed a canonical summation in terms of $\phi_j$, which should be regarded as the non-mean-field analog of the free energy of the so called “pure” state. The concept of the pure state is well developed in the context of frustrated mean-field spin systems [22]. In the mean-field limit, the pure states are separated by infinite barriers and thus the vibrations around the metastable free energy minima are purely harmonic. The quantity $\phi_{\text{eq}}^{ib}$ is non-mean-field because it can be defined only locally (after paying the “price” of the surface energy $\gamma_{j,in}$). It is the degrees of freedom due to transitions between those (non-meanfield) “pure” states of the liquid that give rise to the (measurable) configurational entropy. Note also that owing to the intense and strongly anharmonic motions in the liquid (at this finite $T$), a local liquid state labelled by a particular value of $\phi$ is not a single inherent structure [22], but rather is a weighted superposition of many inherent structures, with more or less harmonic vibrations on top.

Note, $\phi_{\text{eq}}$ is a function of $T$ and $N$. Since $\Phi_{\text{eq}}^{bulk}$ is the equilibrium bulk free energy at temperature $T$, one may replace $S_c(\phi_{\text{eq}}^{ib})$ by its equilibrium value at that temperature $S_c(N,T)$. Thus we get for the escape rate to $N$ the result

$$k(N) = \tau_{\text{micro}}^{-1} \exp \left\{ S_c(N,T) - \phi_{\text{eq}}^{ib} + \phi_{\text{eq}}^{ib}/k_B T \right\}. \quad (3)$$

The location of the bottleneck is determined by the minimum of this expression over $N$. We can thus define an activation free energy

$$F^\dagger(N) = \phi_{\text{eq}} - \phi_{\text{eq}}^{ib} - TS_c(N,T), \quad (4)$$

whose maximum defines the bottleneck location. Notice this activation barrier depends on the total free energy of having any target state at size $N$ and the initial nonequilibrated particular state free energy $\phi_{\text{eq}}^{ib}$ in which we only include a vibrational contribution and no configurational entropy. This function is shown in Fig. 2. Introducing Eq. (1) into Eq. (4) yields:

$$F^\dagger(N) = F_{\text{eq}}^{bulk}(N,T) - \Phi_{\text{eq}}^{bulk}(N,T) + \gamma N x, \quad (5)$$

where $F_{\text{eq}}^{bulk}(N,T) = \Phi_{\text{eq}}^{bulk} - TS_c(N,T)$ is the total equilibrium free energy that includes both the configurational entropy of the region of size $N$ and the internal bulk free energy with its vibrational contribution. In this expression we have substituted the average mismatch energy coefficient $\gamma$, for the state specific values. For dynamically connected states $F_{\text{eq}}^{bulk}(N,T)$, $\Phi_{\text{eq}}^{bulk}(N,T)$, and $S_c(N,T)$ grow linearly with $N$. There will also be $\delta F$, an additional fluctuation that typically scales as $N^{1/2}$. Thus we write

$$F^\dagger(N) = \left[ F_{\text{eq}}(T) - \phi_{\text{eq}}(T) \right] N + \gamma N x + \delta F, \quad (6)$$

where $F_{\text{eq}}(T) = F_{\text{eq}}^{bulk}(N,T)/N$ is the total bulk free energy per particle of the final state at temperature $T$ and $\phi_{\text{eq}}(T) = \Phi_{\text{eq}}^{bulk}(N,T)/N$ is the internal free energy per particle of the initial state. In the following, we will omit the fluctuation term $\delta F$, whenever computing the most probable barrier, but will consider it explicitly when estimating the degree of non-exponentiality of the relaxation, which is directly related to the barrier fluctuations. Note, the expression above is simply what would be prescribed by a regular nucleation theory for the free energy barrier of conversion from a (usually non-equilibrium) initial state to the other (usually equilibrium) state. Clearly, when the initial state is at equilibrium: $\Phi_{\text{eq}}^{bulk} = \Phi^{bulk}$, - the “free energy” driving force $F_{\text{eq}}(T) - \phi_{\text{eq}}(T)$ is equal to $-TS_c$, i.e. there is still relaxation in the supercooled liquid, as driven by conversion between alternative (local) aperiodic packings of the liquid. In general, the maximum of the typical $F^\dagger$ occurs at $N^\dagger$ such that $\partial F^\dagger / \partial N|_{N=N^\dagger}$ vanishes giving

$$N^\dagger = \left( \phi_{\text{eq}} - f_{\text{eq}} \right) / x \gamma \quad \Rightarrow \quad (7)$$

and a typical (most probable) rate

$$k = \tau_{\text{micro}}^{-1} \exp \left\{ -\gamma \left( \phi_{\text{eq}} - f_{\text{eq}} \right) / x \gamma \right\} \left( 1 - x \right). \quad (8)$$

FIG. 2: The free energy to reconfigure the initial configuration is shown as a function of the size of the locally rearranged region. There will be fluctuations in the shape owing to the detailed packing found in the initial configuration but on the average the profile is given by equation 6 in the text. The dashed curve shows the profile for an initial state which is much higher than the equilibrium energy at $T$, while the solid curve is the free energy profile for an initially equilibrated state.
We finish this Section by elaborating on why the relaxations occurring with the rate from Eq. (5) can occur with a zero free energy gap thus leading to a local free energy landscape. Consider first a supercooled liquid at equilibrium (i.e., not quenched): $f_{eq} - \phi_{in} = -T s_c$. Clearly the size $N^*$ at which $F^T(N^*) = 0$ corresponds to the same liquid state, therefore a region of size $N^*$ can survey all liquid configurations typical of this temperature. An isoenergetic state exists because the system resides in a metastable state much higher than the lowest energy crystalline arrangement, as reflected in non-zero configurational entropy $s_c$, and the very high density of states $e^{S_c(\phi)}$. (Note, this notion underlies the existence of residual structural degrees of freedom in glasses even at cryogenic temperatures \(\star\).) If the liquid is quenched and aging, the driving force $f_{eq} - \phi_{in}$ is still negative (it will be computed shortly), so both quantities $N^\dagger$ and $N^*$ exist and are comparable to their equilibrium values, although $N^*$ no longer signifies straightforwardly the degree of the landscape locality (consistent with the system being out of equilibrium in the first place). Regardless, relaxations are local during aging too.

III. RELAXATION IN THE EQUILIBRATED SUPERCOOLED LIQUID

Examining the expressions for the relaxation rate for an equilibrium sample makes explicit the connection to the earlier form of the entropic droplet idea. In the equilibrated sample case, the internal vibrational free energies of the initial and final states are the same so the driving force to distinct equilibrated configurations comes only from the configurational entropy contribution available at the equilibrium temperature. People are sometimes confused how configurational entropy, which is never made explicit in the equilibrium temperature. People are sometimes confused how configurational entropy, which is never made available in a strict mean field scenario, can drive a transition event. This is because of the locality of the landscape in the droplet analysis, which goes beyond mean-field thinking. Locally, for a region of space $D(R, N^*)$ there is a “funnel” of states leading away from the initial configuration to other equally equilibrated configurations. Configurational entropy drives the activated motions of the local regions of a glass in the same way the entropy arising from the large number of denatured configurations of a protein drives the unfolding of a folded native protein even though the denatured states are individually higher in energy \(\dagger\). Any individual escape path is likely to find a big barrier but this barrier is partially cancelled by the growth of the number of escape routes. The free energies along each path fluctuate thus increasing the likelihood of finding a low energy path, when a large number of paths is available. As the entropy per particle, $s_c(T)$ gets smaller the driving force to re-equilibrate falls so the critically activated region of the glass necessary for re-equilibration grows larger and the rate falls, owing to the larger activation barrier from the mismatch contribution. The precise way this happens depends on the mismatch energy and its exponent $x$.

Therefore, before proceeding to study the nonequilibrium situation, we digress to discuss aspects of the average mismatch energy $\Gamma$ which we have approximated as $\gamma N^x z$. First it is clear that the form of $\gamma N^x z$ is only a crude approximation to the mismatch energy when $N$ is small. In principle, recall, the mismatch energy could be explicitly computed by carrying out the local library construction on a computer. The only problem is obtaining initial configurations equilibrated to the appropriate low temperatures. Finding such equilibrated configurations deep in the landscape currently requires heroic computer resources. Therefore the mismatch energy must presently be inferred by analytical considerations.

The simplest free energy functional calculations of the mismatch energy gives an energy proportional to the interface area and therefore gives the mismatch exponent $x = 2/3$. Such simplified calculations also give an explicit value of the prefactor of the scaling relation, $\gamma_0$ at the ideal glass transition temperature, $T_K$. At this temperature, the lost interaction terms of a sharp interface have to balance the entropy cost of localizing each particle to its cage. This gives, at $T_K$ \(\dagger\) \(\dagger\),

$$\gamma_0 = \frac{2\sqrt{3}a}{k_B T_K} \ln \left[ \frac{(a/d_L)^2}{\pi e} \right], \tag{9}$$

where $d_L$ is the mean square fluctuations of particles in a given basin \(\dagger\) and $a$ is the interparticle spacing. The ratio $d_L/a$ is about 0.1 for glassy configurations, just as it is in the Lindemann criterion for melting. Calculations based on free energy functional show that $\gamma$ vanishes as $T_A$ is approached from below \(\dagger\). This is because $T_A$ resembles a spinodal. From these estimates, $\gamma(T)$ can be obtained \(\dagger\). These naive mean field estimates would give an activation barrier varying as $s_c z$, as first detailed by Kirkpatrick and Wolynes \(\dagger\) and later discussed by Parisi \(\dagger\).

Kirkpatrick, Thirumalai and Wolynes pointed out an effect left out in the naive estimate of the mismatch energy \(\dagger\): One must acknowledge there are numerous solutions of the mean field equations describing minima of the free energy functional, these precisely correspond to our local energy landscape libraries. In principle some of these other configurations can be interpolated between the internal target state to which the region is relaxing and its fixed environment in order to lower the mismatch energy. This interpolation is called “wetting”.

Such wetting only can be rigorously defined for very large $N$. Wetting is a dynamical process that takes some time to develop. We should therefore for greater accuracy ascribe a frequency dependence to the mismatch surface tension $\gamma(T, \omega)$. The mapping between the free energy functional and the random field Ising model allows us to invoke an argument of Villain \(\dagger\), that gives a curvature dependence to the surface tension coefficient $\gamma = \gamma_0 (a/R)^{1/2}$ in three dimensions where $a$ is the microscopic length where the surface tension $\gamma_0$ is established
\( R^d \propto N \). Accounting for this wetting correction leads to the exponent \( x = 1/2 \). When this exponent is used in Eq. 3, we see that the relaxation rate in the equilibrium system has exactly the Adam-Gibbs form

\[
k = \tau_{\text{micro}}^{-1} e^{-A/s_c}, \tag{10}
\]

where \( s_c \) is the configurational entropy per particle. If we assume that \( s_c \) vanishes linearly at an ideal glass transition temperature \( T_K \), this rate agrees with the Vogel-Fulcher law. Distinct from the AG argument, however, in the RFOT theory the critical size \( N^* \) scales as \( s_c^{-2} \) not \( s_c^{-1} \) and the dynamical correlation length is much bigger than the AG picture implies, but if the simple estimate of \( \gamma_0 \) based on the vibrational free energy cost is used, explicit values of the typical barrier height are obtained in addition to the experimental scaling of rates, as found by the RFOT theory \( 8 \). The surface tension \( \gamma_0/T_g \), being a logarithmic function of the vibrational amplitude in the glass, depends little on the atomic make up of the glass. Therefore if we use the Vogel-Fulcher expression

\[
k = k_0 \exp\{-DT_g/(T - T_K)\}, \tag{11}
\]

the \( D \) is predicted to depend inversely on \( \Delta c_p \) - the change in heat capacity upon vitrification. Specifically one finds

\[
D = 32k_B/\Delta c_p \tag{12}
\]

The resulting correlation of barrier heights (measured by \( D \)) and glass thermodynamics is excellent \( 8 \). The softening of \( \gamma \) near \( T_A \) also explains very well the deviations from the VTF laws that are observed as the temperature is raised to \( T_A \) where there is a crossover to collisional dynamics \( 8 \). We will use the same “wetted” form of the surface energy term without softening in the body of the paper to follow. We must note however even at \( T_g \), these microscopic calculations give \( N^* \) only of the order of hundreds of particles (consistent with experiment \( 31 \)), so we are far from asymptopia and other “ultimate” scalings (closer to \( T_K \)) are conceivable.

The local library and mismatch energy concepts let us discuss \textit{en passant} various “defect” pictures of glassy dynamics in landscape terms. Many theories of the glassy state imagine there is a basic undefected structure at the heart of the phenomenon (an “\textit{ur-structure}”). Doubtless for many systems, the periodic crystal itself is one such basic “\textit{ur-structure}”. For big enough \( N^* \) the periodic crystal will indeed be a member of the local landscape library but it will not be entropically favored and as long as the surface tension between liquid and crystal remains sufficient it will not be a major target state. Certainly “devitrification” can and does occur in the laboratory but we will leave the study of this transformation for future discussion. Other \textit{ur-structures} have been discussed as dominating glassy dynamics such as icosahedral crystals \( 31 \) or other “avoided crystalline phases” \( 32 \). Deep in the local energy landscape, these structures and their defected forms must be found. The dimension of the defects supported by these \textit{ur-structures} will determine the mismatch energy and thus how the rate will depend on the driving entropy, in the present picture. Point defects such as interstitial-vacancy pairs have an energy cost independent of the region site i.e. giving an exponent \( x = 0 \) and would give a relaxation rate independent of \( s_c \). Non-Arrhenius behavior based on point defects usually must rely on special kinetic constraints, which must be encoded in the transition rules \( 33 \). By construction, the quasi-equilibrium estimate of the rate made above would fail for such models. Of course if there were only a few “dead-end” states these could be explicitly subtracted out in the estimates. Such a situation may apply for entangled polymers.

Simple estimates of the free energies of such point defects puts their energy cost near to the limit seen in ordinary laboratory glass transitions \( 34 \). At low temperature they may conceivably short-circuit the generic transitions proposed here. Line-like defects enter prominently into the constellation of approaches based on frustrated icosahedral order \( 31 \), and presumably should occur also when other types of frustrated regular ordered systems act as \textit{ur-structures}. Nussinov has argued that hamiltonians for uniformly frustrated systems should exhibit random first order transitions in the mean field approximation \( 35 \). It is likely correct to view the states accessible in the high density of states region relevant for real glasses in this way even for models based on frustrated order.

Recall, in assessing the relevance of defect based models, that the measured configurational entropy per particle at the laboratory \( T_g \) is about 1 \( k_B \). This means we are usually far from the low defect density regime.

At low defect density, nevertheless, line-like defects may either traverse the correlated region directly or wander across the region like a Brownian path. The line length in the first case of “ballistic” traversal should scale like \( N^{1/3} \) while in the Brownian case the length is proportional to square of the traversed distance so we expect the mismatch energy to scale like \( N^{2/3} \), resembling the mean field result without wetting. It is interesting that an interpolation between the ballistic and Brownian scalings would be hard to distinguish from the result we use \( \Gamma \sim N^{1/2} \). Even at \( T_g \), \( N^* \) is only about 150 so all these power laws (with the exception of the point defect case) could likely be fitted to a detailed mismatch construction with similar accuracy for liquids in the laboratory.

**IV. RELAXATION IN THE IMMEDIATELY QUENCHED GLASS**

The microcanonical local landscape arguments allow us to estimate the relaxation rates once the statistics of the energies of the local regions in the initial nonequilibrium state are known. Once the system has fallen out of equilibrium, in general, these statistics depend
on the detailed quenching history of the sample. The complete aging theory should determine these statistics self-consistently. In the present and following sections we will assume the quench involves simple straightforward cooling and that little time has elapsed since the glass transition was passed. In this case the statistics of the initial energies are taken to be those of an equilibrium system at a temperature $T_g$. Presumably $T_g$ will be temperature of the midpoint of the dynamic heat capacity drop upon cooling. Thus we take $\phi_{eq}(T)$ to be the bulk energy at $T_g$ augmented by the vibrational part of the free energy at the ambient temperature $T$. The fluctuations of the internal energy of regions, which determine the nonexponentiality of relaxation in the glass will also be taken to be the same as the equilibrium fluctuations at $T_g$, and therefore to be determined by $\Delta c_g(T_g)$.

Using the mismatch exponent $x = 1/2$ in equations \(7\) and \(8\) we obtained fairly simple results for the critical cluster size

$$N^c = \left[ 2(\phi_g - f_{eq}) / x \gamma \right]^{-2}$$  \hspace{1cm} \text{(13)}$$

and the typical rate

$$k = \tau_{\text{micro}}^{-1} \exp \left\{ -\frac{\gamma^2}{4k_B T(\phi_g - f_{eq})} \right\}.$$  \hspace{1cm} \text{(14)}$$

The initial and final states are at the same vibrational temperature but not at the same configurational temperature. The initial state is typical of a $T_g$ configuration but the activated state is “equilibrated” to the temperature $T$ both in vibrational terms and in locally configurational terms. Because of this the driving force for reconfiguration is not purely entropic in the nonequilibrated case. Thus there is a big conceptual difference from the usual extrapolation of the Adam Gibbs formula. In addition, the rates predicted by Eq. \(14\) differ from the Adam-Gibbs formula extrapolated with a fixed configurational entropy $s_c(T_g)$.

At $T_g$, clearly the rates predicted by the equilibrated formula \(10\) and Eq. \(14\) are the same. Upon further cooling the nonequilibrium rate while decreasing, however, is substantially higher than it would be at equilibrium. This is because the driving force for reconfiguration not only includes the configurational entropy at the ambient temperature but also an energy increment of the initial state $\Delta \epsilon = \epsilon_g - \epsilon_{eq}(T)$. (We assume vibrational free energy contributions are nearly the same in inherent structures typical of $T_g$ and the ambient temperature $T$.) Just such a change of slope is observed in the laboratory: the apparent activation energy in the nonequilibrium glassy state is smaller than the extrapolated value from the equilibrated supercooled liquid. This change is usually quantified in the Nayaranaswamy-Moynihan-Tool framework through the expression

$$k_{n.e.} = k_0 \exp \left\{ -x_{NMT} \frac{\Delta E^*_g}{k_B T} - (1 - x_{NMT}) \frac{\Delta E^*}{k_B T_f} \right\}.$$  \hspace{1cm} \text{(15)}$$

where $E^*$ is the equilibrated apparent activation energy at $T_g$ and $x_{NMT}$ lies between 0 and 1. To compare with our initial quench result we would take $T_f = T_g$, again noting in a realistic cooling history $T_f$ would need to be self-consistently determined. We note that equation \(14\) gives a gradual transition to Arrhenius behavior. We can find $x_{NMT}$ most easily at low temperatures (near $T_K$), where the typical relaxation rate will follow an Arrhenius law according to Eq. \(14\). The Arrhenius behavior applies because, for ordinary liquids near to $T_K$ we expect the mismatch free energy to largely be energetic so we take it as a constant. By the definition of the Kauzmann temperature $f_{eq}(T_K) = \phi_K$ is also mostly energetic since the configurational entropy vanishes. The vibrational components of $f_{eq}$ and $\phi_g$ are assumed to cancel so the activation energy is in the nonequilibrium very low temperature regime

$$\Delta E^\dagger_{n.e.L.T.} = \frac{\gamma(T_K)^2}{4(\epsilon_g - \epsilon_K)}$$  \hspace{1cm} \text{(16)}$$

where $\epsilon_g$ is the energy per particle of the frozen glassy state, as prepared, and $\epsilon_K$ is the energy per particle in the putative ideal glassy ground state equilibrated at the Kauzmann temperature. The energy difference $\epsilon_g - \epsilon_K$ is determined by the configurational part of the heat capacity $\Delta c_p(T)$ for intermediate values of $T$ such that $T_g > T > T_K$. The apparent activation energy in the nonequilibrated glass at low temperatures turns out to be comparable to the equilibrium activation free energy, $\Delta F^\dagger$ at $T_g$. It therefore should not vary much from substance to substance but depends on the quenching time scale $t_Q$ through the relation

$$t_Q = \tau_{\text{micro}} \exp \left( \frac{\Delta F^\dagger_{n.e.L.T.}}{k_B T} \right).$$  \hspace{1cm} \text{(17)}$$

To obtain this result of the near equality of $\Delta F^\dagger_{n.e.L.T.}$ and $\Delta F^\dagger_{n.e.L.T.}$, let us take the configurational heat capacity to have the form $\Delta c_p = \Delta c_p(T_g)T_g/T_g$, as suggested by Angell. This form is based on good laboratory estimates. We can now find by integrating and insert this into Eq. \(16\) to give:

$$\Delta E^\dagger_{n.e.L.T.} = \frac{\gamma(T_K)^2}{4\Delta c_p(T_g)k_B T_g \ln(T_g/T_K)}.$$  \hspace{1cm} \text{(18)}$$

The activation free energy at $T_g$, on the other hand is obtained by finding $s_c$ from the integration of $\Delta c_p/T$ and using this in the equilibrium rate expression to give:

$$\Delta F^\dagger_g = \frac{\gamma(T_g)^2}{4\Delta c_p(T_g)k_B T_g(T_g/T_K - 1)}.$$  \hspace{1cm} \text{(19)}$$

The ratio of the activation energy in the glass to the equilibrated free energy barrier at $T_g$ is therefore

$$\frac{\Delta E^\dagger_{n.e.L.T.}}{\Delta F^\dagger_g} = \left[ \frac{\gamma(T_K)^2}{\gamma(T_g)^2} \right] \frac{(T_g/T_K - 1)}{\ln(T_g/T_K)}.$$  \hspace{1cm} \text{(20)}$$
If $T_K$ and $T_A$ are close, as they are for “fragile” systems expanding the logarithm gives a ratio close to one. Even for the strong liquid SiO$_2$ the ratio of $T_g$ (1480K) to $T_K$ (876K) is only 1.7, which gives $\Delta E_{n.e.L.T.}^\dagger / \Delta E_g^\dagger = 0.8$, if we neglect any temperature dependence of $\gamma$. For a laboratory glass transition on the one hour time scale we should find universally to a good approximation (1 hour quench) 32 to 39 $k_B T_g$. To compare with the NTM phenomenology we note that the RFOT theory predicts $\alpha$ transition temperature appropriate to 1 hr, so $\Delta g_{\text{app}}$. Assuming the $\gamma$ ratio is near one and using the glass transition temperature appropriate to 1 hr, so $\Delta E_g^\dagger / k_B T_g = \ln 10^{17} \simeq 39$, and a generic $T_g / T_K = 1.26$ [8], we obtain $m \simeq \frac{19}{x}$. (26)

This relation is plotted in Figure 4 along with data for several systems. We see that the estimate agrees reasonably well with experiment. In this estimate we have neglected the $T$ dependence of $\gamma$. The microscopic treatment from RFOT shows however that $\gamma_0$ depends both on the proximity to $T_K$ and to $T_A$, as discussed in our paper on the barrier softening effect [8]. Thus we will generally have both an entropic and an energetic contribution to $\gamma_0$ which may explain some of the scatter in the curves. Indeed we see more fragile systems lie systematically above the curve as is expected since $T_K$ and $T_A$ are closer leading to the longer barrier softening effect.

According to the RFOT theory the typical relaxation time in the nonequilibrium quenched state does not immediately become Arrhenius in temperature dependence below the laboratory glass transition. Thus there should be deviations from the NMT formalism, which might be crudely fit by allowing the nonlinearity parameter to be $T$ dependent. Indeed some of the scatter in Fig 4 probably arises also from this cause. Below $T_g$, the expected nonArrhenius behavior from RFOT theory is much weaker than the divergently nonArrhenius behavior found above $T_g$. Within the Adam-Gibbs nonequilibrium extrapolation advocated by Hodge and Scherer [17] and Scherer-Adam-Gibbs extrapolation. In one way to express this connection is to compare $\Delta E_{n.e.L.T.}^\dagger$ to its value at $T_g$. The inverse of this ratio would be the apparent configurational entropy in a Hodge and Scherer-Adam-Gibbs extrapolation. In
of the NTM nonlinearity parameter $x_{NMT}$. The curve is predicted by the RFOT theory when the temperature variation of $\gamma_0$ is neglected. The data are taken from Ref. [39]. A few substances (PVAc = polyvinyl acetate, PVC = polyvinyl chloride, PS = polystyrene, $B_2O_3$, and $As_2Se_3$) are labeled. Notice some measured values are not consistent on multiple measurements; this may reflect a breakdown of phenomenology for the history dependence discussed in the text or different material preparation. The more fragile substances lie above the prediction without barrier softening, which has no adjustable parameters.

view of Eq. (14), the inverse ratio is given by:

$$
\left[ \frac{\Delta F^\gamma_{n.e.}(T)}{\Delta F^\gamma_{c}} \right]^{-1} = \left[ \frac{\phi_g - f_{eq}(T)}{T_g s_{eq}(T_g)} \right] \left[ \frac{\gamma(T_g)}{\gamma(T)} \right]^{2}
$$

$$
= \left\{ \frac{T - T_K}{T_g - T_K} \left[ 1 + \ln(T/T_g) \right] \right\} \left[ \frac{\gamma(T_g)}{\gamma(T)} \right]^{2},
$$

where the second equality is found by computing $f_{eq}$ with the help of the Angell’s form of $\Delta c_p(T)$ (see the Appendix). We plot the ratio above in Fig. 4. We point out that although we have highlighted the connection with more traditional treatments of aging phenomenology, neither of the earlier approaches is exactly commensurate with our theory. On the other hand we have shown the expression for the nonequilibrium rate is very explicit once the average energy of the sample is known. It therefore would not be terribly difficult to use the full expression in a dynamic treatment with the nonequilibrium energy as the indicator of the “fictive” temperature. We do not carry out this analysis here because it involves detailed numerical fitting for each system and the quench history of each particular experiment.

$$
\Delta F_{n.e.}^\gamma = \frac{\gamma^2}{4(\phi_{in} - f_{eq} + \delta \phi_{in})},
$$

If $\delta \phi_{in}$ is small, we find the fluctuations in the barrier
height

\[ \delta \Delta F_{\text{n.e.}}^2 = \frac{\gamma^2(-\delta \phi_{\text{eq}})}{4[\phi_{\text{eq}} - f_{\text{eq}}]^2} = \frac{\Delta F_{\text{n.e.}}^2(-\delta \phi_{\text{eq}})}{\phi_{\text{eq}} - \phi_{\text{eq}} + T s_c(T)}. \]  

(30)

Since the structure is frozen at \( T_g \) the typical fluctuation in \( \phi \) is the same as at \( T_g \) and is determined by \( \Delta c_p \) at \( T_g \). We see the ratio of the size of the \( \Delta F^1 \) fluctuations in the frozen, cooled state \( \delta \Delta F_{\text{n.e.}}^1 \) to those found at \( T_g \), \( \delta \Delta F_g^1 \) is

\[ \frac{\delta \Delta F_{\text{n.e.}}^1}{\delta \Delta F_g^1} = \frac{\Delta F_{\text{n.e.}}^1}{\Delta F_g^1} \frac{T g s_c(T_g)}{\phi_{\text{eq}} - \phi_{\text{eq}} + T s_c(T)}. \]  

(31)

Both factors in this expression increase rather slowly below \( T_g \), and saturate at \( T_K \).

How do these fluctuations translate into stretching exponents? Roughly speaking, the relaxation function for a Gaussian distribution of barriers is approximated by a stretched exponential with a value given by \( \beta \): \[ \beta \simeq \left[ 1 + (\delta \Delta F^1/k_b T) \right]^{-1/2}. \]  

(32)

If the liquid is “strong”, \( \Delta c_p \) is small so there are small energy fluctuations leading to small \( \delta \Delta F^1 \). Thus for strongly liquids \( \beta \) remains near 1 until rather low temperatures. If the fluctuations in \( \phi \) are large (as they are for very fragile systems) we would find instead

\[ \beta \simeq \frac{k_b T}{\delta \Delta F^1}. \]  

(33)

This formula should thus give an overestimate for the variation of \( \beta \) with temperature. Using this estimate along with Eqs. (29) and (31), we find

\[ \frac{\beta_{\text{n.e.}}(T)}{\beta(T_g)} = \frac{T}{T_g} \left[ \frac{\Delta F_{\text{n.e.}}^1(T)}{\Delta F_g^1} \right]^{-2} \left[ \frac{\gamma(T)}{\gamma(T_g)} \right]^2. \]  

(34)

A plot of this expression is shown in Fig. 5 (note the \( \Delta F_{\text{n.e.}}^1/\Delta F_g^1 \) ratio has already been computed in Eq. (28)). At \( T_K \) and below the term in parenthesis saturates and so, we find a simple expression

\[ \frac{\beta_{\text{n.e.}}(T)}{\beta(T_g)} = \frac{T}{T_g} \left[ \frac{\Delta F_{\text{n.e.}}^1(T_K)}{\Delta F_g^1} \right]^{-2} \left[ \frac{\gamma(T_K)}{\gamma(T_g)} \right]^2. \]  

(35)

Thus we see in general \( \beta \) should fall as we cool but the effect remains modest in the range where \( T \) is greater than \( T_K \). This modestly cooled range is where the most detailed aging studies have been reported. Although \( \beta \) falls, indeed, the rate of fall slows from its \( T \) dependence above \( T_g \) for fragile substances, since according to the simple RFOT approximation of Xia and Wolynes the equilibrium \( \beta \) would vanish at \( T_K \), while this (approximate) nonequilibrium vanishes only at absolute zero. In contrast, \( \beta \) for strong substances, that was near unity and \( T \)-independent above \( T_g \), is predicted to show more pronounced temperature dependence below the glass transition (see the inset of Fig. 5). Thus we see the form of the relaxation is not the same as the equilibrium relaxation at any “fictive” temperature. For fragile liquids \( T_K/T_g \sim 0.8 \), so if \( \gamma \) is temperature independent, a 40% reduction is expected until \( T_K \) is reached. Often relaxation data in the aging regime have been fit with the approximation \( \beta \sim \beta(T_g) \). Alegria et al. suggest \( \beta \) remains constant below \( T_g \). The RFOT indicates this is a reasonable zero order approximation. Alegria et al. have measured \( \beta \) in the regime \( T_g > T > T_K \). These are difficult measurements and there is scatter in the data.

We must bear in mind that the theoretical \( \beta \) assumes that measurements can scan over the complete relaxation process (even below \( T_g \)) but part of the relaxation is missed in experiment. Since the glass only partly relaxes, in most experiments \( \beta \) will appear to be closer than if the full relaxation could be followed. This effect of missing part of the distribution gives a positive increment to \( \beta \) at the glass transition, as pointed out by Alegria et al. Such an increment on cooling is found.

After this artifactual increment in \( \beta \), Alegria et al. actually do find \( \beta \) to slightly decrease upon cooling. We must emphasize that the arguments leading to Eq. (34) generally give an overestimate of the variation of with temperature in the glass state. First and most simply the approximation made in going from Eq. (32) to Eq. (14) causes an underestimate. Second, but more important, as discussed by Xia and Wolynes \( \beta \), the zeroth order Gaussian approximation for the barrier distribution

FIG. 5: The variation with temperature of the nonequilibrium \( \beta \) in comparison with \( \beta(T_g) \) is shown as a dashed line for a substance with \( T_K/T_g \) (1 hr.) = 0.8, characteristic of a fragile system and a solid line for a strong system with \( T_K/T_g = 0.5 \). The two other lines indicates how the equilibrium would vary with \( T \). The approximate estimates from Eq. (34), which exaggerate the variation are plotted as the very thin lines, which nearly coincide with the more accurate expression Eq. (32). The inset shows a magnified view of the region near \( T_g \), where only factual \( \beta \)’s, depicted by thick lines in the main graph, are given.
is not quantitative because the simple argument leading to that result assumes the environment of a reconfiguring domain is temporally fixed. Clearly if the domains surrounding a region that may re-configure have themselves already changed before the reconfiguration event, the library construction’s premise of having a fixed environment to the mosaic cell fails. This change of environment effect might be called a “facilitation”. In any case this effect means the barrier height distribution will be cut off on the high barrier side. A simple cutoff distribution follows from the idea that domains slower than the most probable rate would actually re-configure when their environmental neighbors have changed; thus they actually will re-configure at nearly the most probable rate, which has already been predicted by the RFOT theory. The resulting cutoff distribution for activation barrier:

\[ P(\Delta F^\dagger) = \begin{cases} P_f(\Delta F^\dagger), & \text{for } \Delta F^\dagger < \Delta F^\dagger_0 \\ C\delta(\Delta F^\dagger - \Delta F^\dagger_0) & \end{cases} \]  \tag{36}

- has been shown to reproduce the variation of the equilibrium at \( T_g \) with composition quite well. It also reproduces the temperature dependence of \( \beta \) in the equilibrium supercooled liquid. The weight \( C \) ensures the normalization of the distribution. Clearly the cutoff again acts to dampen the variation of with temperature, below \( T_g \). Explicit calculations using Eqs. (36) and (31) for the fluctuation can be used to study the detailed \( T \) variation of \( \beta \) in the nonequilibrium glass, which may be relevant for deep quenches.

VI. RELAXATION IN QUENCHES BELOW \( T_K \)

We have emphasized dynamics in the glassy regime just below \( T_g \) and ranging down to \( T_K \). In this regime dynamics is fast enough so that significant relaxation is still accessible to detailed experiments. The results we have obtained should hold to considerably lower temperatures at least before much aging has actually occurred. Essentially the average rate will become Arrhenius below \( T_K \) while the breadth of relaxation times will continue to increase as \( T \) approaches the absolute zero. Quantitatively several effects may intervene that are worthy of further study, however. These effects are 1) secondary relaxations, 2) fluctuations in mismatch energies and changes in the “wetting” mechanism, and 3) quantum effects. We comment on these in turn.

1) As a practical matter, less and less of the range of relaxation times can be accessed on deep cooling during a typical laboratory experiment - at the lowest temperatures only the fast end of the relaxation time distribution can be accessed. This part of the distribution is caused by regions of high energy that correspond to a small domain size. At the shorter length scale several effects that are system specific, will occur.

This region of the relaxation time spectrum is often called the \( \beta \)-relaxation. The term \( \beta \)-relaxation tends to bring to mind universal characteristics and indeed the RFOT theory does for example suggests a scale for the maximum rate corresponding to the cost of overturning a single molecular unit; essentially this is \( \gamma_0 \). On the other hand most glass formers have internal structure and these inner parts or side-chains of the molecule will have multiple conformations that can relax, in a specific ways as well those predictable from RFOT alone. These “rapid” relaxations, also will slow with temperature, and might come into the measurement window. Dyre has argued that just such a “contamination” of the main \( \alpha \) aging process by a \( \beta \) relaxation may explain some of the Leheny-Nagel measurements on glycerol.

2) Well below \( T_K \) the mismatch energies may change their scaling with size. The “wetting” mechanism relies on there being a multiplicity of states to interpolate through the interface. Such a multiplicity exists at \( T_K \) but becomes less important with decreasing \( T \). This leads to a “hardening” of the interface (increase in \( \gamma \)) or perhaps a crossover from \( N^{1/2} \) scaling to \( N^{2/3} \) scaling of the mismatch energy. At the same time, rare fluctuations of the barriers may allow some regions to relax more rapidly than expected. Plotkin and Wolyynes have analyzed just this sort of effect in the context of “buffing” of energy landscapes in protein and Lubchenko and Wolynes have studied a similar effect in the quantum regime which allows a tail of resonant tunneling states to appear. Also well below \( T_K \) - small regions may reconfigure by crystallizing - an effect we ignore in the present paper.

3) Eventually below \( T_K \) classical barrier crossing will be supplanted by quantum tunneling. This gives rise eventually to two level systems and the Boson peak which we have discussed in detail elsewhere.

VII. AGING AND HISTORY DEPENDENCE

The local energy landscape theory put forward in this paper predicts the relaxation of a system where the statistics of the energies in the local energy landscape libraries of the sample is assumed to be known at any instant. The explicit formula for the typical relaxation rate depends on the mean bulk energy of the cooperative regions and the explicit formula for the stretching exponent \( \beta \) also contains the variance of these energies. In the quenched sample we have assumed these statistics are characteristic of an equilibrium system at the temperature \( T_g \) where the system “fell out of equilibrium”. Since the cooperative regions are large it is natural to assume these statistics are Gaussian as we have done. In simple quench histories \( T_g \) can be estimated by the temperature where the apparent heat capacity most rapidly falls during cooling. But more complicated thermal histories are possible and even in a simple quench \( T_g \) really must be determined self-consistently by the dynamics of the system, itself. In general the statistics of the local landscape libraries for a nonequilibrium system will be determined by the system’s dynamics and its detailed past thermal history.

The most general description of the nonequilibrium
energies equilibrate quickly by thermal conduction.

\[ \rho_t \]

at a temperature \( T \) be taken as that characteristic of an equilibrium system which in turn depends on the variance of energies of the β only depends on

\[ T \]

a patchwork of equilibrated and nonequilibrated mosaic cells (see Figure 6). The nature of the new statistics, after some transitions occur and substantial aging has progressed, depends on how big is the difference between the typical current energy of a region and the target equilibrium energy. If the gap is big, a two peaked structure in the distribution of local bulk energies will develop and the statistics will be far from Gaussian: some regions that are newly equilibrated will relax further at a (slower) rate characteristic of equilibrium at \( T \), while the other, not yet transformed regions will still relax at the faster nonequilibrium rate discussed already. Such a situation, if it arises, might account for “ultra-slow” relaxations which have occasionally been reported in aging studies 

FIG. 6: After a considerable period of aging well below \( T_g \) a patchwork of equilibrated and nonequilibrated mosaic cells will be found. If the equilibrium energy at \( T \) is more than a standard deviation of the configurational energies at \( T_g \), the distribution of energies will be noticeably bimodal and the idea of a single fictive temperature will break down. The unimodal distribution with a single fictive temperature should be quite safe if \( \Delta T = T_g - T < \sqrt{\frac{k_B T^2}{\Delta \rho} N^*} = \delta T^* \). For \( T_g \) relevant to 1 hr. quenches this gives \( \delta T^*/T_g \simeq 0.07 \). Most of the Alegria et al. data lie in this modest quenching range, while “hyperquenched” samples (with \( \Delta T \gg \delta T^* \)) will often fall outside the allowed range of using a single fictive temperature. When a sample has a two peaked distribution of local energies, an ultra-slow component of relaxation will arise. Notice that an equilibrated region at the temperature \( T \simeq T_g - \delta T^* \) will relax on the tens to hundreds of hours scale (using the relation that \( \Delta F_{n,e,L.T}^f \simeq \Delta F_{n,e,L.T}^g \)) if \( \tau_g \) is taken to be one hour. Percolation of the ultra slow regions will lead to the possibility of observing multiple length scales.

statistics is quite complex since the bulk energies of any region can be considered functions over the shape and size of domains. These functions might be described as a set of fluctuating bulk energy fields, but the resulting construction is complex. When the system is cooling, high energy regions of size \( N^* \) will be replaced by regions equilibrated to the ambient temperature \( T \). Thus there will be a patchwork of equilibrated and nonequilibrated mosaic cells (see Figure 6). The nature of the new statistics, after some transitions occur and substantial aging has progressed, depends on how big is the difference between the typical current energy of a region and the target equilibrium energy. If the gap is big, a two peaked structure in the distribution of local bulk energies will develop and the statistics will be far from Gaussian: some regions that are newly equilibrated will relax further at a (slower) rate characteristic of equilibrium at \( T \), while the other, not yet transformed regions will still relax at the faster nonequilibrium rate discussed already. Such a situation, if it arises, might account for “ultra-slow” relaxations which have occasionally been reported in aging studies 

where \( \rho \) is the relaxation function when the statistics of libraries are known and fixed by \( \bar{\epsilon}(t_1) \), \( T(t_1) \) is the ambient temperature at time \( t_1 \) - we assume vibrational energies equilibrate quickly by thermal conduction. \( \rho \) not only depends on \( T(t_1) \) and \( \bar{\epsilon} \) but contains the parameter \( \beta \) which in turn depends on the variance of energies of the local region. As a first approximation the variance can be taken as that characteristic of an equilibrium system at a temperature \( T^* \) such that

\[ \epsilon_{eq}(T^*) = \bar{\epsilon}. \]  

(38)

\[ \bar{\epsilon} \]

In this approximation, we may use Eq. (35) for

\[ \beta = \beta_{in}[T(t), \bar{\epsilon}]. \]  

(39)

We see that if the shape of the distribution of local libraries does not change much, the RFOT picture leads to a situation where a single parameter \( \bar{\epsilon} \) suffices to characterize the system. \( T^*(\bar{\epsilon}) \) thus essentially fixes the “fictive temperature” \( T_f \) in the NTM phenomenology, albeit with different expressions for \( \tau(T, T_f) \) and \( \beta = \beta(T, T_f) \). The non-Gaussian statistics alluded to earlier, however suggests the use of a single fictive temperature is only approximate and that a more complete characterization

\[ \bar{\epsilon} \]

\[ \rho \]

\[ T \]
of the statistics may be needed. Multiple fictive temperatures defining the higher moments could in principle be defined. In addition spatial fluctuations of fictive temperatures are needed to capture the co-existence of equilibrated and nonequilibrated domains in the mosaic structure. At least for moderate quenches it may be possible to ignore the spatial inhomogeneity and merely monitor the fluctuations in energies of domains as a secondary variable.

VIII. SUMMARY

We described a local energy landscape theory of the dynamics of supercooled liquids and glasses. In the equilibrated supercooled regime this theory is just a microcanonical ensemble reformulation of the random first order transition theory and its notion of entropic droplets. New results are obtained in the aging regime of nonequilibrium quenched glasses. The key equation is (14) which shows it is the difference between the equilibrated free energy at the quench temperature and the initial free energy of the particular frozen state that drives motions. The theory approximately reproduces the phenomenology of Narayanaswamy and Moynihan and Tool. Thus the nonlinearity parameter in NMT theory can be calculated. This parameter is shown to be correlated with the supercooled liquid’s fragility in agreement with experiment. This correlation is quantitatively very similar to that obtained by the Hodge-Scherer-Adam-Gibbs extrapolation that assumes configurational entropy is fixed at \( T_g \). Deviations from that extrapolation which assumes Arrhenius behavior in the glassy state are predicted however. The previously puzzling, modest non-Arrhenius temperature dependence of relaxation observed within the glassy state is explained by the RFOT theory, although it is a small effect. The variations of nonexponentiality of relaxation in the glassy state are predicted but are also rather small in the moderately quenched regime. The comparison of nonexponentiality with experiment is less conclusive than the comparison of mean relaxation rates however, owing to the difficulty of accessing the complete relaxation behavior during the quench.

One advantage of the aging theory based on RFOT theory is that in principle the behavior upon very deep quenches is predicted. Most importantly \( \beta \) is predicted to continue to decrease with quench temperature. We hope that more experiments in this regime will be done. We have noted however that some non-universal effects may enter for such quenches. Also the kinematics of deep quenches may be complex owing to spatial fluctuations of fictive temperature predicted by our theory.

Although the present approach justifies to some extent the use of a single fictive temperature to characterize the glassy state the limitations of this idea have been made clear. A straightforward extension of the usual formulation to include fluctuations in the moderately cooled regime more fully was proposed. In the strongly cooled regime, the theory predicts patches of especially slowly relaxing regions will appear. This prediction may be tested by single molecule imaging approaches [10, 17].

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APPENDIX

Several auxiliary results are derived in this Appendix (here, \( k_B = 1 \)). First, we derive formula (25) from the main text. Using \( s = -\partial f/\partial T \), one has (neglecting differences in vibrational entropy)

\[
feq(T) = \phi_K - \int_{T_K}^{T} sdT = \phi_K - \Delta c_p(T_g) T_g \left( \frac{T - T_K}{T_K} - \ln \frac{T}{T_K} \right), \quad (A.1)
\]

where we have used Angell’s empirical form \( \Phi \) for the configurational entropy, also used in the main text: \( s_c(T) = \Delta c_p(T_g) T_g (1/T_K - 1/T) \), \( \Delta c_p(T) = \Delta c_p(T_g) (T_g/T) \). Noting that \( feq(T_g) = \phi_g - T_g s_c(T_g) \) fixes the ideal glass state energy \( \phi_g \): \( \phi_K = \phi_g - \Delta c_p(T_g) T_g \ln(T_g/T_K) \). (A.2)

Eqs. (A.1) and (A.2) immediately yield Eq. (25).

Next, we derive the more accurate expression for the \( \beta_{n,e}(T)/\beta(T_g) \), as follows from Eq. (28). We also provide the equilibrium value \( \beta_{eq} \) of the non-exponentiality parameter \( \beta \), previously obtained by Xia and Wolynes [3], in terms of experimental parameters \( T_K/T_g \) and \( \ln(\tau_Q/\tau_{micro}) \), used throughout this paper.

First we derive \( \beta_{eq} \). According to Ref. [3], the barrier fluctuations are directly related to the local fluctuations in the configurational entropy at the scale \( N^* \) corresponding to a local equilibrium unit, of which the global composite landscape is comprised: \( \delta F^{eq}/F^{eq} = \delta S_c/S_c = \sqrt{\Delta c_p N^*} / s_c N^* \). This yields:

\[
\frac{\delta F^{eq}}{F^{eq}} = \frac{\sqrt{\Delta c_p}}{s_c \sqrt{N^*}}. \quad (A.3)
\]

It directly follows from \( F^{eq}(N) = \gamma \sqrt{N} - T s_c N \), \( (\partial F/\partial N)_{N=N^*} = 0 \), and \( F(N^*) = 0 \) that

\[
\frac{\Delta F^{eq}}{F^{eq}} = \frac{\gamma/T}{4 s_c} \quad (A.4)
\]

and

\[
\sqrt{N^*} = \frac{\gamma/T}{s_c}. \quad (A.5)
\]

Using Eq. (17), Eq. (A.4) and the temperature independence of the \( \gamma/T \) ratio in equilibrium [3], one gets

\[
(\gamma/T)_{T=T_g} = 2 \sqrt{s_c(T_g) \ln(\tau_Q/\tau_{micro})}. \quad (A.6)
\]
With the help of the equations above and Angell’s empirical form for the configurational entropy one easily obtains that
\[
\frac{\delta \Delta F}{T} = \frac{\sqrt{\ln(\tau_Q/\tau_{\text{micro}})} \sqrt{1/T_K - 1/T_g}}{\sqrt{T(1/T_K - 1/T)}}. \quad (A.7)
\]
This and Eq. (28) can be used to compute the \(\beta_{eq}(T)/\beta(T_g)\) ratio.

The non-equilibrium \(\beta\) requires even less effort. Using Eq. (31), one gets
\[
\frac{\delta \Delta F}{\delta \Delta F_g} = \left[ \frac{F_{n,e}^\dagger(T)}{F_g^\dagger} \right]^2 \left[ \frac{\gamma(T_g)}{\gamma(T)} \right]^2. \quad (A.8)
\]
Hence,
\[
\beta_{n,e.}(T) = \left[ 1 + \left( \frac{\delta \Delta F}{\delta \Delta F_g} \right)^2 \frac{F_{n,e}^\dagger(T)}{F_g^\dagger} \right]^{1/4} \frac{\gamma(T_g)}{\gamma(T)} \right]^{-1/2}. \quad (A.9)
\]
The ratio \(F_{n,e.}^\dagger(T)/F_g^\dagger\) was computed in the beginning of the Appendix and given in the main text as Eq. (28); \(\delta \Delta F^\dagger(T_g)\) is obtained from Eq. (A.7) at \(T = T_g\).

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