Dynamical Heterogeneity of the Glassy State

by

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ABSTRACT

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The understanding and the complete description of the glass transition are impeded by the complexity of nature of the glass. Parts of this complexity come from the emergence of long-lived inherent structures of a liquid at a temperature below which the activated reconfiguration events play a dominant role. Molecules in a glass change their locations through the activated process at a rate which varies throughout the glass owing to these local and aperiodic structures. Motions in one location also cause or relieve constrains, thereby altering the rate of transitions of neighboring regions. The key to understanding this problem is the interplay between the activated events that generate mobility and the transport of mobility. In the following we explore fluctuating mobility generation and transport in glasses to understand the dynamics of the glassy state within the framework of the random first order transition theory of glass. Fluctuating mobility generation and transport in the glass that arise from there being a distribution of local stability and thus effective temperature are treated by numerically solving stochastic continuum equations for mobility and fictive temperature fields. Fluctuating spatiotemporal structures in aging and rejuvenating glasses lead to dynamical heterogeneity in glasses with characteristics that are distinct from those found in the equilibrium liquid. We illustrate in this thesis how the heterogeneity in glasses gives rises of a non-Gaussian distribution of
activation free energies, the stretching exponent $\beta$, and the growth of characteristic lengths. These are studied along with the four-point dynamic correlation function. Asymmetric thermodynamic responses upon heating and cooling are also predicted to be the results of the heterogeneity and the out-of-equilibrium behavior of glasses below the glass transition temperature $T_g$. Moreover the dynamical heterogeneity can lead to a growth front of mobility in rejuvenating glasses that emanates from the surface where stable glasses are heated. Noticeably bimodal distributions of local fictive temperatures in aging glasses are also investigate. This result explains recent experimental observations that have been interpreted as coming from these being two distinct equilibration mechanisms in glasses.

Finally we study the mechanical properties of glasses. The remarkable strength of glasses is examined using the random first order transition theory. The theory predicts that the strength not only depends on the elastic modulus but also depends on the amount of configurational energy frozen in when the glass is prepared. The stress catalysis of cooperative rearrangements of the same type as those responsible for the supercooled liquid’s high viscosity account quantitatively for the measured strength of a range of metallic glasses, silica and a polymer glass.
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Chapter 1

Introduction

The ultimate goal of a theory of glass and of the glass transition is to understand why glasses have amorphous structure like liquids but behave rigidly like solids. The rigidity of the glasses comes from the difficulty of rearranging particles, thereby allowing flow. The flow of glasses is nearly imperceptible. One of the most common ways of making a glass is by lowering temperature of a liquid with a rate fast enough to avoid a first order transition to a crystal at the melting temperature $T_m$ [1, 2]. In this way the liquid enters into a thermodynamic metastable phase known as a supercooled liquid. As the temperature decreases and the density increases further the liquid shows a remarkable variation in dynamical behaviors within a rather narrow range of temperature [3]. The viscosity of the liquid, for example, rises extremely fast and can be well fit by the so-called Vogel-Fulcher (VF) law $\eta = \eta_0 \exp (DT_0/(T - T_0))$, where the material-dependent quantity $D$ is called the liquid’s fragility [4, 5]. Clearly the viscosity, which is proportional to the structural relaxation time, obtained from the VF law diverges as the ambient temperature $T$ approaches a material characteristic temperature $T_0$. In practice, if this law holds, we could never cool the liquid all the way down to the temperature $T_0$ and keep the liquid in equilibrium. Thus the liquid falls out of equilibrium near the laboratory glass transition temperature, $T_g$ [2]. Upon lowering the temperature $T$, the vibrational entropy of the liquid decreases but the molecules in the glass are frozen in various configurations corresponding to stable local environments. Extrapolating below the glass transition temperature $T_g$,
the excess configurational entropy which counts the number of such configurations, $S_c \equiv S_{\text{liquid}} - S_{\text{crystal}}$, appears to vanish at a temperature $T_K$, called the Kauzmann temperature. If this situation were to continue below $T_K$, the entropy of the liquid would be less than the entropy of the thermodynamic stable state of crystal and indeed might eventually violate the third law of thermodynamics itself. This is the entropy crisis which was highlighted by Kauzmann in 1948 [6]. One of the remarkable aspects of the original VF equation is that the fitting constant in the kinetic law $T_0$ is found to be very close to the thermodynamic quantity $T_K$ for all glass formers (typically $0.9 < T_K/T_0 < 1.1$) [3, 7]. This coincidence suggests a relationship between the VF fitting function and in the extrapolation of thermodynamic quantity leading to $T_K$. Adam, Gibbs, and Di Marzio had been inspired by this coincidence [8, 9]. They suggested the vanishing of the configurational entropy drives the increasing viscosity. They proposed that the molecular motion in the glass occurs cooperatively with an activation barrier proportional to the volume of the mobile region. In particular, a formula of Adam and Gibbs provided a relation between the viscosity and the configurational entropy of the glass $S_c(T)$ given by $\eta = \eta_0 \exp(A/T S_c(T))$ where $A$ is a material constant. Their model gave no hint as to how the parameter $A$ can be understood in terms of molecular properties or intermolecular forces. More importantly the properties of the glass vary from local region to region and depend on the cooling/heating history. Each molecule in the glass experiences distinct local environments because of the aperiodic nature of the structure. This leads to very strongly heterogeneous dynamics and makes even the phenomenology a problem of glasses challenging.
1.1 Random First Order Transition Theory

In late 1980s, Kirkpatrick, Thirumalai, and Wolynes proposed the random first order transition (RFOT) theory [10, 11, 12, 13]. Further developments by Wolynes and coworkers show how the theory can provide a unified quantitative description of many aspects of glass problem [2]. The original aim of the early work was to investigate relationship between a mean field theory of glass formation and a thermodynamic theory of p-spin glasses [13]. Within mean field theory the p-spin glass can be solved exactly. This exact solution of the thermodynamics shows a static transition at $T_s$, while the dynamical equations corresponding to the model however show that time scales diverge and ergodicity broken at $T_d > T_s$. At $T_d$ an exponentially large number of metastable states emerges below the dynamic transition. On the other hand for $T > T_s$ metastable states have negligible thermodynamic weight with respect to the paramagnetic phase and are therefore invisible in the mean field thermodynamic calculation. The configurational entropy, $S_c$, vanishes at $T_s$ where the number of states becomes sub-exponential. In mean field systems metastable states have infinite barriers and ergodicity is broken below $T_d$, while in finite range systems the transition at $T_d$ is expanded to become merely a dynamic crossover and the relaxation time must remain finite until $T_s$. The strict broken ergodicity of mean field theory reflects the fact that metastable states are separated by infinite free energy barriers in mean field, but it will be restored by locally activated transition in finite dimensions.

In mean field theory, the lifetime of a given aperiodic structure is infinite. However, in a finite system below $T_d$ where there are many states to escape to, the system become trapped in metastable configurations only for finite periods of time. Different portions of the system can be found in different local glassy states. Each state reconfigures to a new glassy state through the activated events and the cal-
culation of viscosity can be reduced to finding the free energy barrier height that one state needs to overcome to reconfigure to another one. In order to create a metastable state there is mismatch energy at the interface separating the two states, and thus a surface tension. This term is renormalized according to \( \sigma(r) = \sigma_0 (r/a)^{1/2} \), where the surface tension coefficient at the molecular length scale the “bead size” is \( \sigma_0 = \frac{2}{3} (k_B T/a^2) \ln \left( (a/d_l)^2 / \pi e \right) \) \[14, 15\]. The Lindemann length, \( d_l \), is the size of thermal vibrations of a molecule required to break up a frozen crystal structure and is equal to \( d_l \approx 0.1 \) of inter-particle spacing \( a \) (for all substances) \[16, 17\]. The thermodynamic drive to rearrange a domain of radius \( r \) is provided by the fact that such a region has an exponentially large number of available states to which it can escape. There is an entropic cost that must be paid by the region to keep them staying in just one of these many states, and this entropic cost can be released if the rearrangement takes place \[18\]. This term equals \(- (4\pi/3) r^3 T S_c(T)\). The difference in free energy between the final state and the initial state yields

\[
F(r) = 4\pi \sigma(r) r^2 - \frac{4\pi}{3} (r/a)^3 T S_c. \tag{1.1}
\]

Note that the free energy profile in equation 1.1 resembles classical nucleation theory \[19\], but is quite distinct in the sense that the final state after reconfiguration event is not different phase of the substance. Both initially and finally the configuration are members of the liquid state ensemble. The free energy profile also demonstrates that a system prepared in a specific metastable state will be unstable and will be broken up into a droplet size \( r^* \) determined from \( F(r^*) = 0 \) \[20\]. Ergodicity is restored in the finite dimension by activated processes. The time scale of this process is dominated by the bottleneck in the droplet growth and is equal to \( \tau = \tau_0 \exp(F^*/k_B T) \) where
the free energy barrier is given by

$$\frac{F^+}{T} = \frac{3\pi}{S_c} \left[ \frac{3/4 \ln((a/d_i)^2\pi e)^2}{S_c} \right] \approx \frac{32}{S_c}.$$  \tag{1.2}

The configuration entropy can be approximated near $T_K$ from the the heat capacity jump $\Delta C_p$, $S_c(T) \approx \Delta C_p(T - T_K)/T_K$. Thus we see one recovers the empirical VF law: $\tau = \tau_0 e^{D_T(T - T_K)/T_K}$ with a simple relationship between the liquid’s fragility $D$ and the heat capacity jump $\Delta C_p$ per independently movable unit: $D \approx 32/\Delta C_p$ [14].

### 1.2 Mode Coupling Theory

The glass transition in a simple liquid can also be studied by using a self-consistent mode coupling theory [21]. This theory studies the connection between dynamics at different wave-vectors. In this theory the glass transition is an intermediate wave-number phenomenon that eventually causes the slowing down dynamics of the liquid near the glass transition temperature [22, 23]. Derivation of the theory relies on the projection operator formalism which exploits the idea of constructing reduced descriptions: separate the variables into slow and fast dynamics and integrate out the fast variables [24]. This yields an effective theory in terms of slow dynamic variables. MCT has achieved many qualitative and and quantitative successes in various experiments, however, the theory fails at the temperature below the predicted $T_d$ because the system experimentally is still in a liquid phase and $T_d > T_g$ [25].

Many liquids, when cooled fast enough, freeze in to an amorphous state. We may think for example to a system of hard spheres interacting via a Lennard-Jones potential. In the glass, the density profile is not uniform and the particles prefer to stay close to a set of sites that is not periodic like crystalline structures. In this case the density correlation function, $\phi(k, t)$, can be expressed as $\phi(k, t) = \frac{1}{N} \langle \rho_{-k}(0)\rho_k(t) \rangle = $
\[ \frac{1}{N} \sum_{ij} \langle e^{-i k \cdot r_i(0)} e^{i k \cdot r_j(t)} \rangle. \]

Note that at \( t = 0 \) the function \( \phi(k, t) \) reduces to the static structure factor of the liquid \( \phi(k, t = 0) = \frac{1}{N} \langle \rho_{-k}(0) \rho_k(0) \rangle \equiv S(k) \). In the idealized MCT, the equation of motion for the dynamical structure factor \( \phi(k, t) \) can be written as [25]

\[
\ddot{\phi}(q, t) + \frac{q^2 k_B T}{m S(q)} \phi(q, t) + \int_0^t d\tau K(q, t - \tau) \frac{\partial \phi(q, t)}{\partial \tau} = 0 \quad (1.3)
\]

where \( K(q, t) \) is a memory function that is determined from wave-number-dependent mode-coupling amplitudes. The memory function has the form:

\[
K(q, t) = \frac{\rho k_B T}{16 \pi^3 m} \int dk |\tilde{V}_{-q-k, k}|^2 \phi(k, t) \phi(|k-q|, t). \quad (1.4)
\]

The vertex function \( V_{q-k, k} \) can be expressed as a function of two wavevector: \( V_{q-k, k} = \frac{i k_B T}{2mN} \left\{ \hat{q} \cdot k + \hat{q} \cdot (q-k) \right\} \), where the direct correlation function \( c(k) \equiv (1/\rho)(1-1/S(k)) \). This integro-differential equation has an unusual structure but its solution, the density-density correlation function, can be obtained numerically and is shown in figure 1.1. The correlation function measures how quickly correlations within the system decay in time. At very high temperature we expect a very short-time ballistic regime where particles move freely without mutual interaction. As the temperature is lowered a second plateau of the correlation function emerges. This evidence suggests that persistent motion of particles occurs and the particles spend longer time near each other in this intermediate time scale. The decay is no longer purely exponential. In mode coupling theory circles the decay on the short time scale is referred to as the \( \beta \)-relaxation and that for the long time scale as the \( \alpha \)-relaxation. The most striking feature of the solution is that there is a sharp transition to a completely non-ergodic phase as \( T \) approaching \( T_{MCT} \) (equivalent to \( T_d \)). This implies that MCT predicts kinetic arrest to a non-ergodic phase at temperatures where the system is still ergodic and liquid.
Figure 1.1: Two step relaxation: the dynamic correlation function $C(t)$ as a function of time for several temperatures approaching $T_{MCT}$. The curves show the appearance of a two-step decay [26].

Above the dynamical temperature, MCT rationalizes many experimental results [27, 28], but below $T_d$ the MCT picture of continuous diffusion fails eventually. This breakdown is due to activated dynamics which become the dominant mode of transport [29]. Bhattacharyya, Bagchi, and Wolynes (BBW) proposed a way to bridge the gap between the activated regime of RFOT theory and MCT by including an activated event vertex into the standard MCT vertex [30, 31, 32]. The resulting construction yields an extended mode coupling theory containing activated events and the equation of motion for $\phi(t)$ can be written as

$$\ddot{\phi}(t) + (\gamma + K_{hop})\dot{\phi}(t) + (\gamma K_{hop} + \Omega_0^2)\phi(t) + K_{hop}\delta(t) + 4\lambda\Omega_0^2 \int_0^t dt'\phi^2(t')[\dot{\phi}(t-t') + K_{hop}\phi(t-t')] = 0$$

where $K_{MCT} \equiv 4\lambda\Omega_0^2\phi^2(t')$ is the memory kernel from the idealized MCT equation, the activated-dynamic memory kernel $K_{hop}$ accounts for hopping motion. Figure 1.2 compares the numerical solutions from the idealized MCT and the extended MCT with activated dynamics. We see that although the idealized MCT result saturates to a plateau value, the extended theory exhibits a hopping induced decay that follows...
Figure 1.2: The solutions from the idealized MCT result and the extended MCT with activated dynamics have been plotted against log(t) for various values of $K_{hop}$ [30].

the idealized MCT plateau.

### 1.3 Organization of the Thesis

Aside from questions about the underlying mechanism of glass formalism even the phenomenological description of the glass transition is nontrivial. The nonergodic behavior in the glassy state implies that the measured properties of a glass not only depend on time but also on the sample’s history. Moreover dynamics of the glass is different in different places in the glass and this causes heterogeneity in both space and time. In Chapter 2 we explore in detail the dynamical heterogeneity of the glassy state. We extend BBW’s work to obtain a field theory that takes into account of spatiotemperoral structure of the dynamics in supercooled liquids and glasses. This resulting theory is able to show that asymmetric thermodynamic behavior of observables on heating and cooling and the bimodal distribution of relaxation times are the result of the heterogeneity of the glass.
Understanding dynamical heterogeneity in the glass is important in many situations, especially in the case of “rejuvenating” glasses that are heated after falling out of equilibrium upon cooling or synthesis in some other way. In the rejuvenating glass a region that is more mobile (or high mobility) catalyzes the motions of its neighbors that are less mobile (or low mobility) allowing them to reconfigure presently. A high mobility region initiates and accelerates the transformation of stable glasses into supercooled liquids. Evidence for this has recently been obtained by Ediger and coworkers in their studies of ultrastable glasses prepared by vapor deposition method [33, 34, 35]. We will discuss this phenomena and show numerical results from our theory in Chapter 3.

In chapter 4 the remarkable strength of glasses is examined using the random first order transition theory of the glass transition. The theory is able to predict that strength not only depends on elastic modulus but also depends on the configurational energy frozen in when the glass is prepared. The stress catalysis of cooperative rearrangements of the type responsible for the supercooled liquid’s high viscosity account quantitatively for the measured strength of a range of metallic glasses, silica, and a polymer glass.
Chapter 2

Dynamical Heterogeneity of the Glass State

2.1 Introduction

The complexity of glass forming systems is most apparent in the unusual nonexponential relaxation dynamics found both in the supercooled fluid and in the glassy state. After a supercooled liquid falls out of equilibrium on cooling the resulting glass initially can be thought of as frozen snapshot of the liquid state just before it fell out-of-equilibrium [36]. Thus initially there is no long-range spatial order. Since the glass is out-of-equilibrium, however, it continues to evolve, albeit slowly, as the system ages and new but subtle spatial structure emerges. On experimental timescales ergodicity is broken below the glass transition so time averages no longer equal full-ensemble averages. Furthermore, properties in the glass vary from region to region and the sensitivity of activation barrier heights to local properties leads to very strongly heterogeneous dynamics. In this article we explore the inhomogeneous dynamical structure formed within the glassy state using a framework based on the random first order transition (RFOT) theory [37, 38, 12, 39].

The random first order transition theory of glass has already provided a unified quantitative description of many aspects of supercooled liquids and structural glasses [18]. The theory has its origins in bringing together two seemingly distinct mean field theories of glass formation, one being the dynamical, ideal mode coupling theory [21], the other being a thermodynamic theory of freezing into aperiodic structures [12]. A
variety of mean-field like approximations most elegantly formulated via the replica approach deal with the self-generated long-lived randomness in structural glasses [40]. Within mean field theories there is a special temperature $T_d$, below which an exponentially large number of frozen states emerge [38, 39]. It was however easy to see via droplet arguments that beyond the pure mean-field description which gives infinite long lived metastable stats that such many metastable states will be destroyed by locally activated transitions if they are exponentially large in number[39, 41]. When ergodicity is restored thereby, in finite dimensions, the dynamical transition at $T_d$ is smeared out. Nevertheless at a lower temperature $T_K$ where the configurational entropy of the mean field states would appear to vanish, this argument suggests a true thermodynamic transition could finally appear [6]. Thermally activated motions would cease at such a thermodynamic transition if the entropy crisis occurs rather than being intercepted by some other mechanism. Eastwood and Wolynes have presented an argument that suggests while the droplets themselves could provide such a mechanism of cutting off a transition, on normal time scales, the droplet entropy correction is quantitatively unimportant [42]. Droplets provide the key feature of RFOT theory, an activated mechanism of mobility generation. Nevertheless, because of its shared origin with mode coupling theory, RFOT theory allows mobility once generated below $T_d$ to be transported giving a microscopic basis for the notion of facilitation [43, 44]. Facilitation, in its simplest incarnation, can be thought of as defect diffusion, which in low dimensional systems by itself can lead to nonexponentiality [45, 46]. In the quantitative analysis of non exponential relaxation using the RFOT theory the mobility transport effect was shown to be an essential feature that diminishes the effects of the instantaneous heterogeneity in activation barriers which otherwise would lead to a broader distribution of relaxation times than observed [15].
The entropy driven activated events in RFOT theory allow one to connect a broad range of experimental measurements on dynamics in glasses with their thermodynamics. Examples included the predictions of the fragility index $D$ [14], the fragility parameter $m$ [47], the stretching exponent in the supercooled liquid $\beta$ [15], the correlation length [20] and the yield strength [48]. All these predictions require only thermodynamic data as input, while they are all decidedly kinetic observables.

Aside from questions about underlying mechanism even the phenomenological description of dynamics in the glassy state is nontrivial. The nonergodic behavior in the glassy state implies that measured properties not only depend on time but also are dependent in detail on the sample’s history of preparation. The need to describe experimental protocols makes even communicating experimental results a challenge let alone predicting results theoretically [2]. The fictive temperature concept was introduced as a single additional number globally characterizing the instantaneously non-equilibrium state of the glass in the phenomenological description of Narayanaswamy, Moynihan and Tool (NMT). This is not enough. Lubchenko and Wolynes have, however, argued within the RFOT framework that every patch of glass can be described as having a fictive temperature locally [18]. In this framework extending the local fictive temperature concept to describe the global level requires dynamically coupling regions together i.e. it requires combining the mobility generation mechanism that acts locally in RFOT with mode coupling that transports mobility. Bhattacharyya, Bagchi, and Wolynes (BBW) [30, 32, 31] have shown how combine these by including an activated event vertex into the standard MCT vertex. The spatial variations in activated dynamics were not made explicit in their calculations. The theory has been extended to obtain a field theory that takes into account of spatiotemporal structure of dynamics in supercooled liquids and glasses by expanding the mode coupling
memory kernels using a Taylor series in terms of its gradients thus defining a mobility field $\mu$ having explicit space and time dependence [36]. This expansion yields a continuum equation for the mobility field in which mobility can be both generated from activated events or transported from highly mobile regions to less mobile areas through mode coupling facilitation effects. To account for the random nature of mobility generation and transport the equations for the mobility field also contain generation and transport noises. We have already used these equations to describe the front like transformation of stable glass into supercooled liquids discovered by Ediger et. al [33, 35]. The numerical solutions of the continuum equations predict the transformation front speed in quantitative agreement with the experiments [49].

While our previous work detailed the spatiotemporal character of the transformation of stable glasses into equilibrium liquids where the mean mobility differs by many orders of magnitude across the sample, even dynamics in the bulk glass alone exhibits heterogeneity in both space and time [50, 51]. This heterogeneity is an intrinsic characteristic in all glassy systems and is evident in non-exponential relaxation [52]. The RFOT theory has already explained quantitatively the dynamical heterogeneity in equilibrated supercooled liquids. Using RFOT theory, Xia and Wolynes argued that due to facilitation the free energy barriers will not be Gaussian distributed, but will have a distribution with significant skewness [15]. They showed that the non-exponential parameter depends on width of the distribution of the free energy through a static stretching exponent $\beta_0 = 1/\sqrt{1+(\delta \Delta F/k_B T)^2}$. Here we will show that the continuum equations of a fluctuating mobility field and fluctuating fictive temperature which have been derived describes more completely the dynamical heterogeneity and directly leads to a distribution of the free energy having a long tail on the low energy barrier side as Xia and Wolynes suggested. By following the complete
evolution of the mobility field, calculations of the four-point correlation function in the glassy state prove possible [53, 54].

Dynamical heterogeneity in space and time results in non-trivial out-of-equilibrium signatures in calorimetric experiments which are hysteretic and not symmetric between what happens when glasses are cooled down or are heated up. As explained earlier [18, 36], upon cooling, some previously high mobility regions will rapidly equilibrate to a low fictive temperature near that of the ambient temperature, while other regions, initially more stable, will maintain their higher initial fictive temperature [36]. Since the prematurely equilibrated regions now have a low mobility one should find in the partially aged glass a bimodal rate distribution. Mobility transport to the low fictive temperature regions also slows approach to equilibrium in their neighborhoods. In contrast, upon heating, the glasses after the first reconfiguration events, regions near to the first reconfigurating regions equilibrate faster than they would have in the original equilibrated sample. The initially reconfigured regions of high mobility now catalyze the rearrangement of their low-mobility neighbors leading to a radially propagating front of mobility. The numerical solution of the continuum equations of mobility field and the fictive temperature that we are going to present in the next section quantitatively captures these predicted phenomena.

The organization of this article is as follows. In section II we provide a more explicit derivation of the continuum equations for the mobility field driven by activated events with mobility fluctuations than was given before. We then explore the inhomogeneous dynamical structure of the glass in section III where we analyze the free-energy distribution, the four-point correlation function, and the stretching exponent for \( \alpha \)-relaxation. In section IV, we use the equations to model calorimetric experiments on several glasses and compare predictions with experimental data. In
section V, we investigate the kinetics of long-aged glasses and show that the bimodal dynamic heterogeneity which emerges will appear in the laboratory as “ultraslow” relaxations like those experimentally observed [55] and recently highlighted [56]. Section IV summarizes our study and discusses possible extensions of this work.

2.2 The Continuum Equations of Mobility and Fictive Temperature

In the following we describe in some detail the microscopic basis of the continuum equations of mobility field with fluctuating generation and transport described earlier by one of us [36]. These equations were previously studied numerically by us [49] in the context of mobility front propagation in which an ultrastable glass prepared by vapor deposition “melts” into an equilibrated liquid from the free surfaces which are predicted by RFOT theory to have higher mobility than the bulk. RFOT theory near an interface predicts $\tau_{\text{surface}} = \sqrt{\tau_0 \tau_{\text{bulk}}}$ where $\tau_0$ is the microscopic time, $\tau_{\text{bulk}}$ is the relaxation in the three dimensional bulk and $\tau_{\text{surface}}$ is the relaxation time of the surface layer [57].

In the equilibrium supercooled liquid, particles spend relatively brief times near each other, collide and then move freely and go on further to collide with others in a weakly correlated way. As the temperature decreases or the density increases further, groups of correlated collisions between particles in the same spatial region occur more and more frequently. Persistent structures therefore emerge. Individual particles continue to move and vibrate, but now reside within a nearly fixed cage. Once in awhile, particles nevertheless manage to move from one cage to another through activated processes which are actually many particle events. Thus confined
motion followed by hops becomes the dominant dynamical feature at temperatures below $T_d$. Extending mode coupling theory through more elaborate perturbative expansions that only keep track of a finite number of correlated collisions will miss the activated process which is an essential singularity in the temperature (and therefore fluctuation strength) expansion. This is why any simple perturbation extension at finite order in MCT or in static replica methods is problematic, at best. This formal difficulty exists also in the theory of ordinary first order transitions [58] and in the quantum chromodynamics of the nucleon [59].

The standard mode-coupling theory gives an equation of motion for the system average correlation function that decays from a constant value to zero in the long time limit above the dynamical transition temperature. The decay of the correlations depends on the history of the system in the past. The nature of the decay is mathematically encoded in the memory kernel [60]. This kernel can be expanded perturbatively in terms of higher order correlation functions, but can be approximated self-consistently as products of two-point correlation functions [21]. The resummed perturbative mode coupling theory works perfectly well at temperatures, above $T_d$, [25] but the theory breaks down at the temperature below $T_d$ as it shows an infinite plateau in the two-point correlation function [61], which is not allowed in finite dimension above $T_K$, i.e. the cages are permanent in mode coupling theory. Instead of complete freezing the system actually goes from collision dominated transport to transport driven by activated processes as it crosses the dynamical temperature $T_d$ [2].

Being essential singularities the activated dynamics must be incorporated into the MCT directly. As shown by BBW[30], activated processes give an extra decay channel for the correlation function. When the activated events are included, the
memory kernel consists of two distinct contributions one coming from idealized MCT kernel $M_{\text{mct}}(k; t, t')$ and one described by an additional hopping kernel $M_{\text{hop}}(k; t, t')$

$$M_{\text{total}}(k; t, t') = M_{\text{mct}}(k; t, t') + M_{\text{hop}}(k; t, t'). \quad (2.1)$$

The mode coupling memory kernel has a complicated structure involving coupling to density fluctuation modes with other wave vectors, but it is dominated by density modes with wave vector $k$ near the value corresponding to the first peak of the structure factor, since Fourier density modes of the wavelength decay the slowest due to de Gennes narrowing [62]. This simplification leads to the so-called schematic mode coupling theory.

A mobility field can be defined as the longtime rate at which particles reconfigure through activated dynamics. This field can thus be formulated in real space as a Fourier transform in space of that memory kernel and is an integral of that kernel over elapsed time $t'$.

$$\mu(r, t) = \int_{-\infty}^{t} dt' \int_{-\infty}^{\infty} dke^{-ik\cdot r} M_{\text{total}}(k; t, t').$$

The total mobility field will contain two components one from the activated dynamics and one from the idealized MCT part

$$\mu(r, t) = \mu_{\text{hop}}(r, t) + \mu_{\text{mct}}(r, t), \quad (2.2)$$

where

$$\mu_{\text{hop}}(r, t) = \int_{-\infty}^{t} dt' \int_{-\infty}^{\infty} dke^{-ik\cdot r} M_{\text{hop}}(k; t, t')$$

and

$$\mu_{\text{mct}}(r, t) = \int_{-\infty}^{t} dt' \int_{-\infty}^{\infty} dke^{-ik\cdot r} M_{\text{total}}(k; t, t')$$

$$= \int_{-\infty}^{t} dt' M_{\text{mct}} \left( x + \frac{\delta R}{2}, x - \frac{\delta R}{2}; t, t' \right).$$
We assume that the part of the mobility coming from hopping dynamics $\mu_{\text{hop}}$ instantaneously re-adjusts to depend on the local fictive temperature $T_f$ and the ambient temperature $T$. The MCT memory kernel is determined by the full dynamic density correlation function $\phi(k, t) \approx \phi_{\text{MCT}}(k, t)\phi_{\text{hop}}(k, t)$,

$$M_{\text{mct}}(r, r'; t, t') \sim \int dk \int dk_1 e^{-ik\cdot(r-r')}V(k, k_1; t, t')\cdot \phi(k, t')\phi(|k - k_1|; t'),$$  \hspace{1cm} (2.3)

where $V(k; t, t')$ is the usual vertex function in the standard MCT.

Ultimately the mobility field differs from one region to another because the local mobility has inherited local fluctuating structure from the liquid state. Particles residing in the cage also have different activated relaxation times depending on the local fictive temperature which itself varies in space and time. These effects both lead to the mobility being inhomogeneous in space and time. In the approximation that these quantities do not change too rapidly from one place to neighboring regions, we can expand the mobility field in a Taylor’s series around $x$ and $t$. Doing this leads to an equation of motion for $\mu_{\text{mct}}$. To see this, note the correlation function $\phi(k, t)$ itself depends on the memory kernel which again varies in space and time because mobility does. Now if we expand $\phi(k, \mu(x', t'))$ about $\mu(x, t)$ we find that

$$\phi(k, \mu(x', t')) \approx \phi \left(k, \mu(x, t) + (x' - x)\nabla \mu + \frac{(x' - x)^2}{2}\nabla^2 \mu(x, t) + (t' - t)\frac{\partial \mu}{\partial t} + \ldots \right)$$

$$\approx \phi(k, \mu(x, t)) + \frac{\partial \phi}{\partial \mu}(x' - x)\frac{\partial \mu}{\partial x} + (t' - t)\frac{\partial \mu}{\partial t} + \ldots + \ldots$$

$$\approx \phi(k, \mu(x, t)) + \frac{\partial \phi(k, \mu(x, t))}{\partial \mu}\Delta \mu + \frac{1}{2}\frac{\partial^2 \phi}{\partial \mu^2}\Delta \mu^2 + \ldots$$

where $\Delta \mu \equiv \mu(x', t') - \mu(x, t) = (x' - x)\nabla \mu + (t' - t)\frac{\partial \mu}{\partial t} + \mathcal{O}(\nabla^2 \mu, \frac{\partial^2 \mu}{\partial t^2})$.

Now we can expand $\phi(x, \mu(t))$ and keep the lowest terms in the gradients. The
gradient expansion of $\mu_{\text{mct}}$ thus has the form:

$$\mu_{\text{mct}}(x, t) = \bar{\mu}_{\text{mct}}(x, t) + w_0 \frac{\partial \mu_{\text{mct}}}{\partial t} + w_1 (\nabla^2 \mu_{\text{mct}}) + w_2 (\nabla \mu_{\text{mct}})^2$$

(2.4)

where $\bar{\mu}_{\text{mct}} = \bar{\mu} - \mu_{\text{hop}} = (1 - \lambda) \bar{\mu}$. $\bar{\mu}$ is a locally equilibrated mobility field which we will discuss later. The parameter $\lambda$ is the ratio of the part of the mobility field coming from the activated events alone to the total mobility. This quantity depends on the local structure factors and has been computed for Salol by BBW [32]. For salol they find $\mu_{\text{hop}} = \lambda \bar{\mu} \approx 0.25 \bar{\mu}$. For convenience we will assume in our numerics that this factor $\lambda = 0.25$ is the same for all glasses. The coefficients $w_0, w_1$ and $w_2$ are also given by integrals over the MCT kernel. For example the coefficient $w_0$ can be written explicitly as

$$w_0 = \int_{-\infty}^{0} V(\delta R = 0, t, t') \left[ \phi_k \frac{\partial \phi_p}{\partial \mu} + \phi_p \frac{\partial \phi_k}{\partial \mu} \right] (t - t') dt(t - t'),$$

where $V(\delta R = 0, t, t')$ is the vertex function of standard mode-coupling theory [21].

Notice if we approximate each term of $\phi$ by its long time behavior we can write $\phi \approx \phi_0 e^{-\int_{-\infty}^{t'} \mu d\tau} \approx \phi_0 e^{-\mu(t - t')}$, so then we obtain

$$\frac{\partial \phi}{\partial \mu} = -(t - t') \phi(t - t')$$

Carrying out the integral, we then get a simple form for the coefficient $w_0 = -\frac{1}{2\mu} \bar{\mu}_{\text{mct}}$.

In the absence of spatial inhomogeneity, the equation of motion for $\mu_{\text{mct}}$ is

$$\mu_{\text{mct}} - \bar{\mu}_{\text{mct}} = -\frac{\bar{\mu}_{\text{mct}}}{2\mu^2} \frac{\partial \mu_{\text{mct}}}{\partial t}$$

(2.5)

Now we examine the other gradient terms, within each term of the Taylor series, a term of the type $\partial \phi / \partial \mu$ or $(\partial \phi / \partial \mu)^2$ is generated. In each term again using the
exponential approximation for the local decay gives for the derivative \((t - t')\phi(t - t')\).

Thus within this approximation one generates terms of the same form as in the MCT kernel but now with extra powers of \((t - t')\). Upon integrating then one finds extra factors \(\frac{1}{\mu K} \cdot K!\) for a term containing \((t - t')^K\). Except for powers of \(\delta R^N\) one again gets the mode coupling kernel. Thus a typical term will be \(\frac{K!}{\mu K} \int d\delta R \int \delta R^N M (x - \delta \frac{R}{2}; x + \delta \frac{R}{2}, t - t') d(t - t').\) With the spatial variation, the equation of motion for \(\mu_{mct}\) also has spatial gradient terms:

\[
\mu_{mct} - \bar{\mu}_{mct} = -\frac{\bar{\mu}_{mct}}{\mu_{mct}^2} \frac{\partial \mu_{mct}}{\partial t}
\]

\[
+ \kappa (\nabla \nabla \mu_{mct}) \cdot \frac{1}{\mu_{mct}} \int d\delta R \, dt \, \delta R^2 M \left(x + \frac{\delta R}{2}, x - \frac{\delta R}{2}\right)
\]

\[
+ (\nabla \mu_{mct})^2 \cdot \frac{1}{\mu_{mct}^2} \text{(similar integral)}
\]

Notice that a characteristic length \(\xi\) naturally emerges from the ratio of the two integrations in the gradient term versus uniform MCT:

\[
\frac{\int \delta R^2 \, M dt \, d\delta R}{\int M dt \, d\delta R} \sim \xi^2
\]  

(2.6)

So the coefficient of the \(\nabla \nabla \mu_{mct}\) can be written as \(\xi^2 \bar{\mu}_{mct}\). Thus we see that \(\xi^2 \bar{\mu}_{mct}\) can be thought of as the mobility diffusion coefficient. Since activated events are included in the kernels the \(\xi\) obtained in this way will not precisely be equal to the correlation length of the pure mode coupling theory \(\Xi_{MCT}\) which was determined by Reichman et al. [25], but it will be related to it sufficiently far from \(T_d\) itself.

By taking the static limit we can see that the coefficient of the linear Laplacian term contains a length \(\xi\) which would be the correlation length of the four-point correlation function consistent with an analysis by Biroli et al. [63]. The gradient squared term arises because of the nonlinear relation of the MCT closure between the memory kernel and the correlation functions. The coefficients \(\xi^2\) and \(w_2\) depend
on the details of the microscopic mode coupling closures employed. For simplicity we will choose the value of \( w_2 \) so that the locally linearized equation can be written as a mobility flow equation with a source term

\[
\frac{\partial \mu_{mct}}{\partial t} = \frac{\partial}{\partial x} \left( \frac{2\mu^2 \xi^2}{\bar{\mu}_{mct}} \frac{\partial \mu_{mct}}{\partial x} \right) - \frac{2\mu^2}{\bar{\mu}_{mct}} \left( \mu_{mct} - \bar{\mu}_{mct} \right) \quad (2.7)
\]

where \( \mu_{mct} = \bar{\mu} - \mu_{hop} \). We believe that apart from this bulk source term any violation of the local “conservation” laws for mobility will be small and in any case one can see they would only modify the results in a modest quantitative fashion.

The uniform solution of the extended mode coupling theory with activated events \( \bar{\mu}_{mct} \) which is used for input can be approximated by using the ultralocal theoretical analysis of aging glasses by Lubchenko and Wolynes [18]. They suggest activation will still be the dominant effect below \( T_d \) so that the rates depend on the local fictive temperature \( T_f \) and ambient temperature \( T \)

\[
\bar{\mu} = \mu_0 \exp \left\{ -\frac{\gamma^2}{4k_B T \Delta c_p T g \left( \frac{T_f - T}{T_f - T_f} \right)} \right\} \quad (2.8)
\]

where \( \gamma(T) = \frac{3\sqrt{3\pi}}{2} k_B T \ln \left[ \frac{(a/d_L)^2}{\pi e} \right] \), \( d_L \) is the Lindemann length and \( a \) is the interparticle spacing. The details of their derivation can be found in Appendix A.

The fictive temperature approximately obeys an ultralocal relaxation law with the local decay rate \( \mu(r, t) \).

\[
\frac{\partial T_f}{\partial t} = -\mu (T_f - T) \quad (2.9)
\]

In the bulk itself there are dynamic inhomogeneities from fluctuations in the local fictive temperature and from the happenstance nature of the activated events.
which generate and transport the mobility field. We treat the corresponding random force terms in the equation as coarse-grained white noises with strengths and correlation lengths that reflect the length scale of the activated events. The intensities of the noises may be found by requiring the linearized equations to satisfy locally fluctuation-dissipation relations. The local fictive temperature fluctuation $\delta T_f$ is taken to be $\langle \delta T_f(x,t)\delta T_f(x',t') \rangle = 2\mu T^2 \frac{k_B}{\Delta c_p N^\dagger} \delta(x - x')\delta(t - t')$, where $N^\dagger$ is the number of molecular units in a cooperatively rearranging region. The fluctuations in mobility generation $\delta g$ and transport $\delta j$ arise due to fluctuations in free energy barrier heights which are the primary cause of the stretched exponential relaxation with a bare stretching parameter $\beta_0 = 1/\sqrt{1 + (\delta F^\dagger/k_B T)^2}$. Linearizing the mobility equation and treating $\bar{\mu}$ as constant, the local fluctuation-dissipation relation yields a mobility generating noise with correlations $\langle \delta g(x,t)\delta g(x',t') \rangle = 2\bar{\mu}\mu^2(1/\beta_0^2 - 1)(T_g/T)^2 \delta(x - x')\delta(t - t')$ and a mobility random flux with correlations $\langle \delta j(x,t)\delta j(x',t') \rangle = 2\bar{\mu}\xi^2\mu^2(1/\beta_0^2 - 1)(T_g/T)^2 \delta(x - x')\delta(t - t')$ [49].

### 2.3 Inhomogeneous Dynamical Susceptibilities

Both the equilibrated liquid and the nonequilibrium glass have intrinsically disordered structures. Even if all particles are identical, in each system, individual particles experience different local environments at any given time. In the high temperature liquid, the disorder may be averaged over and the system described via uniform equilibrium. But, as the glass transition is approached, the structural relaxation time increases dramatically and the system takes a long time to relax and may find itself out-of-equilibrium [64, 18]. Disorder in the glass seems to be static yet molecules are in motion and change their locations through activated dynamics [65]. Some particles may move large distances, while others remain localized near their original
position. We may refer these behaviors as particles being “mobile” or “immobile”, and any given sites may be characterized by quantity describing themselves the so-called “mobility” [66]. Experiments show that the mobility of particles in adjacent regions can vary by several orders of magnitude [51].

Over the last decade, direct molecular dynamics simulations of supercooled liquids have given some insight into the nature of dynamic heterogeneity [67] but it has been a challenge to go further into deeply low temperature region characteristic of laboratory experiments because of diverging relaxation time. Here we can study realistic levels of supercooling by using the methods described in the previous section to simulate the heterogeneity of the glass starting from the mesoscopic equations for the mobility field. A snapshot of the mobility and the fictive temperature field of 1,3,5-Tris(naphthyl)benzene (TNB) glass which has been equilibrated at $T = T_g = 347$ K by solving the fluctuating field equations in two dimensions is shown in figure 2.1. The highly mobile regions of particles are colored in red and the low mobility regions are colored in blue. As seen in the figure, the mobility field varies throughout the space in a way that correlates with the local values of the fictive temperature. The high mobility regions (low relaxation time) are generally less stable than the regions with low mobility and are ready to reconfigure to lower energy state. The fictive temperature and the mobility are coupled in a non-linear fashion; however, their values are consistent with each other in general. The low mobility regions generally map on to the low fictive temperature and vice versa. In equilibrium both fields fluctuate around their equilibrium values.
2.3.1 Activation Free Energy Barrier Distribution

It is an important point to mention that the domains surrounding any region may reconfigure before that central region can move. When this happens local constraints on the slow region will be removed. This change of environment effect can be called "facilitation." As Xia and Wolynes argued this effect means the static barrier height distribution coming from fictive temperature fluctuating will be cut off on the high barrier side. A simple cutoff distribution follows from the idea that it is primarily those domains slower than the most probable rate that would actually reconfigure only when their environmental neighbors have changed; thus they actually will reconfigure at something close to the most probable rate, which has already been predicted by the RFOT theory. The resulting cutoff distribution for activation barrier, as discussed by Xia and Wolynes [15], has a form

\[
P(\Delta F^\dagger) = \begin{cases} 
P_f(\Delta F^\dagger), & \text{for } \Delta F^\dagger < \Delta F_0^\dagger \\ 
C\delta(\Delta F^\dagger - \Delta F_0^\dagger). & 
\end{cases}
\]

The delta function is an exaggeration of the effect as pointed out by Lubchenko who has provide a more elegant distribution [68]. The free energy barrier found from the simulation does not contain a sharp delta function in Eq. (2.10). Figure 2.2 illustrates the free energy distribution from the simulation. Like the Xia-Wolynes distribution
Figure 2.2: (Color online) Probability distribution of activation free energy from the numerical simulation of the mobility field and the fictive temperature. Notice that the distribution has a long tail on the low energy barrier side and its shape is not Gaussian distribution.

[15] and Lubchenko’s [68], the shape of the distribution is not symmetric and has a long tail to the low energy barrier side. This result reflects that the mobility can be transported from higher region to lower region through the facilitation effect.

It should be noted that because of the Arrhenius law the free energy barriers being even modestly distributed in space leads to the wide variation of the relaxation times. Each domain relaxes independently with something close to a simple exponential decay function. By virtue of the ensemble average done in most bulk experiments, however, the resulting bulk relaxation exhibits a highly non-exponential distribution of times for the whole sample $\phi(t) \sim e^{-(t/\tau)^\beta}$. That this is the primary origin of dynamical heterogeneity in glasses and other disordered material has been emphasized by several studies [69, 70, 71]. Defect diffusion in three dimensional systems is a secondary effect.
2.3.2 Nonexponentiality of relaxation below $T_g$

As the supercooled liquid falls out of equilibrium, particles can be considered to form groups of cooperatively rearranging regions. This mosaic structure of the liquid gives rise to dynamical heterogeneity and the overall non-exponential relaxation. The driving force for reequilibration varies from mosaic cell to cell. This leads to a wide range of activation barriers $\Delta F^\dagger$. Computing these fluctuations allowed Xia and Wolynes to predict $\beta$ for a range of substances in the equilibrated liquid [15]. Their approach was extended to the aging regime by Lubchenko and Wolynes [18].

Below the glass transition temperature $T_g$, the local structure of the liquid is initially frozen at $T_g$. The ratio of the size of the $\Delta F^\dagger$ fluctuations in the frozen, cooled state, $\delta\Delta F^\dagger_{n.e.}$ to that found at $T_g$, $\delta\Delta F^\dagger_g$ is predicted by Lubchenko and Wolynes to be:

$$\frac{\delta\Delta F^\dagger_{n.e.}}{\delta\Delta F^\dagger_g} = \frac{\Delta F^\dagger_{n.e.}}{\Delta F^\dagger_g} \frac{T_g s_e(T_g)}{\phi_{in} - \phi_{eq} + T s_e(T)} .$$

(2.11)

For a strong liquid, $\Delta c_p$ is small so that there are small energy fluctuations leading to small $\delta\Delta F^\dagger$. Thus $\beta$ remains near to one until very low temperature for strong liquids. For the fragile liquid, however the fluctuations are very large, so we would find

$$\beta \approx \frac{k_B T}{\delta \Delta F^\dagger} .$$

(2.12)

Lubchenko and Wolynes thus predicted the change of the stretching exponent in the non-equilibrium regime immediately after a quench to temperature $T$ from a equilibrated sample at $T_g$. They found:

$$\frac{\beta_{n.e.}(T)}{\beta(T_g)} = \frac{T}{T_g} \left[ \frac{\Delta F^\dagger_{n.e.}(T)}{\Delta F^\dagger_g} \right]^{-2} \left[ \frac{\gamma(T)}{\gamma(T_g)} \right]^2 .$$

(2.13)
This ratio predicted by Lubchenko and Wolynes is plotted as a solid line in figure 2.3 along with the ratio obtained from the present numerical simulation of the TNB glass and that for the TNB equilibrium liquid. The immediately quenched results shown in red are obtained by computing the correlation function for a series of instantaneous quenches to $T$ and averaging over many such runs. As we can see, both simulations and the earlier RFOT estimations for the ratio agree quite well. The equilibrium $\beta$ decreases faster than the non-equilibrium $\beta$ as the temperature is lowered and vanishes at $T_K$. This is in accord with Lubchenko-Wolynes’s prediction. This suggests time-temperature superposition is a better approximate in the glass than for liquids. Unfortunately carrying out simulations further below $T_g$ where a change in slope of the $\beta$ versus $T$ relation is predicted to be more apparent takes a very long time, so we do not have a comparison for the slope change at the present.

2.3.3 Length Scales of Dynamical Heterogeneity from Four-Point Correlation Functions

In this section, by using simulations based on the equations developed in section 2.2, we can study the evolution of the spatial character of the fluctuations below $T_g$. For our results, samples were first equilibrated at $T_g$. Then the temperature is quenched immediately to a new temperature $T$ lower than $T_g$ before data collection. Data after several typical relaxation time is excluded since the system will have equilibrated by then. We focus, in particular, on the four-point correlation function used to probe dynamical heterogeneity and show that the four-point susceptibility $\chi_4(t)$ increases as the temperature decreased.

The four-point correlation function was first studied in molecular dynamic simulations of a Lennard-Jones mixture by Dasgupta et al. [75] The motivation of their
Figure 2.3: (Color online) The variation with temperature of the stretch exponent $\beta$ for TNB glass (red squares) and TNB equilibrium liquid (blue circles) in comparison with $\beta(T_g)$. The predicted values for the non-equilibrium and equilibrium stretch exponents from the static RFOT are respectively shown as a solid line and a dashed line. The numerical results are in agreement with the RFOT prediction. Unfortunately experimental data for this difference between the equilibrated $\beta$ and the quenched one is not yet available for TNB. We note that there has been some discrepancy about the temperature dependence of $\beta$ in the equilibrated phase for ortho-Terphenyl [72, 73]. The origin of this issue has been resolved recently by Eastwood et al. [74]
work was to demonstrate the presence of a growing length scale associated with fluctuations of the Edwards-Anderson order parameter. We show in this section that the growth of the four-point susceptibility follows naturally from mobility fluctuations with kinetic inputs from material specific thermodynamic properties.

The mobility \( \mu \) indicates how long a particle \( i \) takes to reconfigure since its last reconfiguration event. Thus a local two-point correlation function can be defined as

\[
C(r; t_0, t) \equiv \exp \left( \int_{t_0}^{t} dt' \mu(r, t') \right).
\]  

(2.14)

The spatial fluctuation of this local two-point correlation function then naturally leads to the four-point correlation function

\[
G_4(r; t) \equiv \left\langle \int dr' C(r'; t_0, t) C(r' + r; t_0, t) \right\rangle - \left\langle \int dr' C(r'; t_0, t) \right\rangle^2.
\]  

(2.15)

We can define a susceptibility associated with this correlation function

\[
\chi_4(t) \equiv \int dr G_4(r; t).
\]  

(2.16)

The function \( \chi_4(t) \) has been computed from our numerical field theoretic simulations of TNB in both the equilibrated liquid and the glassy state found immediately upon quenching to \( T \). These results are shown in figure 2.4a for the system as equilibrated and in 2.4b for the system below its glass transition. The qualitative course of the temporal behavior is the same at all the different temperatures: as a function of time \( \chi_4(t) \) first increases, then has a peak on a time scale that tracks the structural relaxation time scale and then finally decreases.

The peak value of \( \chi_4(t) \) measures the volume over which the structural relaxation processes are correlated. From figure 2.4, the temperature evolution of the peak
Figure 2.4: (Color online) The time and temperature dependence of $\chi_4(t)$ for the TNB liquid (left) the TNB glass (right) from the simulation. For each temperature, $\chi_4(t)$ has a maximum, which shifts to larger times and has a larger value when $T$ is decreased, revealing the increasing length scale of dynamic heterogeneity.

height, which is found to increase when the temperature decreases and the dynamics slows down. One sees directly that increasingly long-ranged spatial correlations emerge as the temperature is lowered. This conclusion supports the idea that at low temperatures the growing length scale calculated from RFOT theory is what should actually appear in the dynamical four point function. The detailed calculation of the length scale at temperature below $T_g$ is shown in Appendix B. It is clear also that the quenched correlation length grows more slowly than the equilibrated one. This is consistent with recent experiments on glycerol [76].

Figure 2.5 shows the time corresponding to the maximum value of $\chi_4(t)$ obtained from the TNB samples in the equilibrated liquid and the quenched glassy states. The behavior of $\tau^*$ is similar to the structural relaxation time below the glass transition which increases as the temperature is decreased. However the $\tau^*$ in the glassy regime is shorter than the relaxation time in the equilibrated state, as expected.
2.4 Calorimetry

2.4.1 Introduction

As the glass transition is approached by cooling, the relaxation time of the supercooled liquid increases significantly. At the glass transition temperature itself, the inverse of the normalized cooling rate $d \log T/dt$ is approximately equal to the relaxation time. As the cooling process continues, the structural relaxation of the liquid cannot catch up with the changing ambient temperature so the system remains out-of-equilibrium and becomes a glass. Just below the glass transition temperature, the system freezes into the amorphous state with the structure of supercooled liquid at $T_g$. But small changes continue to occur as the system continues to cool and these changes can be monitored by calorimetry. These changes can then be undone by heating the sample.

We now study with our numerical solution an idealized calorimetric experiment based on simple cooling and heating protocols. Usually calorimetry experiments measure
the (vibrational) temperature $T$ as a function of time. The temperature is lowered with the cooling rate $\nu_c \equiv \Delta T/\Delta t < 0$. Then the temperature is raised with the heating rate $\nu_h \equiv \Delta T/\Delta t > 0$. Conventionally the glass transition temperature is the mid-point temperature on the cooling scan where the heat capacity changes from that of the liquid state to that characteristic of the amorphous state. This kind of experiment is often called differential scanning calorimetry (DSC). DSC is a standard technique for determining the glass transition temperature $T_g$ of noncrystalline materials such as supercooled organic liquids, metallic glasses [77]. This technique measures the difference in the amount of heat required to increase or decrease the apparent temperature of a sample as a function of temperature. In an equilibrium liquid or solid, both the sample and the reference thermometer are maintained at nearly the same vibrational temperature.

The DSC experiment thus determines a nonequilibrium heat capacity, or more precisely said, the rate of change of enthalpy as a function of time. To a good approximation, the equilibrium density of configurational enthalpy is a linear function of temperature over the relevant range of temperatures. With this approximation, the non-equilibrium configurational heat capacity is $C_p = C_p^{\text{glass}} + \Delta C_p \nu^{-1} dT_f/dt$, that is,

$$\tilde{C}_p(T) \equiv [C_p(T) - C_p^{\text{glass}}]/\Delta C_p = dT_f/dT,$$

(2.17)

where $\Delta C_p$ is the difference between liquid and glass heat capacities outside the glass-transition region and $T$ refers to the ambient temperature at the time when the non-equilibrium heat capacity is measured. The (global) fictive temperature, has been defined as the temperature at which the properties of a vitreous system in a given state are equal to those of the equilibrium liquid. Locally fictive temperature is not uniform but varies following the ultra local relaxation law with the rate depending
on the local mobility field $\mu(x, t)$,

$$\frac{dT_f}{dt} = -\mu(T_f - T) + \delta \eta. \quad (2.18)$$

The local mobility field is explicitly determined by the continuum equation that we derived earlier and supplemented by fluctuating mobility generation and transport

$$\mu = \mu_{\text{hop}} + \mu_{\text{mct}}$$

$$\frac{\partial \mu_{\text{mct}}}{\partial t} = \frac{\partial}{\partial x} \left( \frac{2\mu^2 \xi^2}{\bar{\mu}} \frac{\partial \mu_{\text{mct}}}{\partial x} \right) - \frac{2\mu^2}{\bar{\mu}_{\text{mct}}} \left( \mu_{\text{mct}} - \bar{\mu}_{\text{mct}} \right) + \delta g + \frac{\partial \delta j}{\partial x} \quad (2.19)$$

where $\bar{\mu}_{\text{mct}} = \bar{\mu} - \mu_{\text{hop}}$.

Below the glass transition temperature $T_g$ the structural relaxation time $1/\mu$ is longer than time required to lower the ambient temperature so that the fictive temperature $T_f$ is approximately fixed at $T_g$. In contrast, above $T_g$, $T_f$ is close to the actual ambient temperature.

2.4.2 Results: Calorimetry at Constant Heating and Cooling Rate

Figure 2.6 presents the both heating and cooling $\tilde{C}_p$ curves for GeO$_2$, Glycerol, O-terphenyl (OTP), and propylene carbonate (PC) and those found by solving the numerical equation of MCT/RFOT theory. These substances were chosen because they cover a wide range of fragility, ranging from strong to fragile glasses. The standard scans are considered with the cooling and heating rates equal to 20 K/min as in experiment. The graphs include both the experimental data [78, 79, 80, 81] (circles) and the simulation results (solid lines). The corresponding cooling and heating curves obtained from our model are depicted by blue and red lines, respectively. The solid lines in these plots are the results of numerically solving the coupled equations of the
mobility field and the fictive temperature following Eq. (2.19) and Eq. (2.18). Overall our simulation results show excellent quantitative agreement with the experiments; however, some small deviations between our simulations and the experiments might be seen. Whether these errors are systematic or statistical on our part or on the experimentalists’ parts remains to be seen. All of the input parameters are obtained from other kinetic and thermodynamic experiments and are based on the framework of RFOT theory. There are no adjustable parameters in these comparisons.

2.4.3 Results: Calorimetry at Different Cooling Rates

Figure 2.7 illustrates DSC measurements recorded with various cooling rates, for a single material that is reheated from several lower temperature states and compare them with numerical results simulated using the experimental cooling and heating rates. The experimental results on glycerol were obtained by Wang et al.[79] The
four scans differ in the cooling rate (-20, -5, -2.5, -0.5 K/min) and only the up-scans at a common heating rate of +20 K/min are reported. As can be seen, a slower cooling rate yields a more prominent peak in the heat capacity on heating scan and the glass transition temperature \( T_g \) shifts toward lower temperature. Clearly our continuum equations also produce correct quantitative behavior for nonstandard cooling and heating protocols. Again no parameters are available for adjustment in the RFOT predictions.

We note that recently Keys et al.\cite{82} have simulated similar calorimetric data using a specific facilitated model based on the East model for localized “excitations.” In their model excitations are treated as being on discrete lattice sites. An excitation is allowed to move if the adjacent region to the east is also excited. This model gives a structural relaxation time that is non-Arrhenius and that can be fitted to a parabolic law.\cite{83} In contrast in our model the mobility field is derived from the expansion of the extended MCT along with activated processes computed using RFOT theory. The relaxation time in our theory depends on the activation free energy barrier through the expansion given in Eq. (2.7). We see that RFOT theory is in very good agreement with these history dependent experiments despite using only equilibrium input data.

### 2.5 Aging and Two Equilibration Mechanisms in Glasses

Within the RFOT theory the mosaic structures which correspond to local free energy minima give rise to dynamical heterogeneity both in the supercooled liquid and the glass. In an equilibrium system, the statistics of the energies in the local energy-landscape libraries of the sample shows the resulting cutoff Gaussian distribution for activated barrier. However, in an aged sample where the system has already fallen out-of-equilibrium, this statistics have to be determined self-consistently by the dy-
Figure 2.7: (Color online) Comparison with heat capacity data obtained through DSC. Experimental data are depicted by red circles for heating scan. Red and blue lines represent heating and cooling curves obtained from our calculation.

Dynamics of the system and by its detailed past thermal history [18]. If the spatial structure is neglected, Lubchenko and Wolynes suggest this can be approximated by the NMT phenomenology. They also predicted deviations from that phenomenology for certain temperature histories.

As we have seen in the RFOT treatment complex spatiotemporal structures develop during the process of aging glasses and rejuvenating glasses. When the system is cooling, the least stable local regions become replaced by regions equilibrated to the ambient temperature $T$. Thus the mosaic now contain patches of distinct well equilibrated cells and poorly equilibrated cells in terms of fictive temperature. In this way, the aging glass becomes more stable and is more inhomogeneous in its energy distribution than it was initially when it first fell out of equilibrium [36]. Lubchenko and Wolynes thus argued that RFOT theory implies there would be additional heterogeneity to be found at intermediate times which would lead to additional ultraslow
relaxations. Such extra relaxations have sometimes been reported in aging studies [55, 84, 56]. The statistics in this case of very deep quenched system are distinguished by the fast patches and the slow patches that have reconfigured first. Lubchenko and Wolynes pointed out that a clearly two-peaked distribution of local energy will arise in such a situation.

To test these ideas quantitatively we performed numerical simulations of the coupled field equations to investigate the statistics of local energy of a polystyrene glass ($M_n = 85 \text{ kg/mol}, T_g = 375 \text{ K}$) aged at temperatures significantly below the glass transition temperature. This system has recently been studied experimentally [56]. The samples were first simulated at high temperature ($T_g + 10$) for long time. Then the samples were cooled down at a cooling rate of 20 K/min to reach 350 K, followed by stabilization at the aging temperature $T_a$.

Figure 2.8 shows the distribution of the logarithm of the relaxation times (the inverse of the mobility field roughly equivalent to the local energy) after the samples were stabilized at low temperature $T_a$. The fast peak of the relaxation times corresponds to the regions which have not yet been equilibrated to the new ambient temperature. These fast regions are relatively unstable regions. The slow peak appears due to the regions that originally were less stable and that now have already reconfigured themselves to the new ambient temperature and are now much more stable than those left unequilibrated. The ultraslow peak time is seen to be consistent with the equilibrium relaxation time, i.e. it follows the Vogel-Fulcher-Tammann equation. Obviously the bimodal statistics of the aged glass is different from the mostly single peaked distributions found in equilibrium supercooled liquids. Our simulation results agree quite well with recent experimental and detailed observations by Cangialosi et. al. [56] on the polystyrene glass. The separation of the two peaks
Figure 2.8: (Color online) Bimodal distribution of logarithm of relaxation times which represents local energy. The samples were equilibrated at high temperature, then cooled down to a significantly low temperature and aged at the aging temperature $T_a = 365 \, K$ (left) and $T_a = 363 \, K$ (right).

will become even more pronounced at lower temperatures. Numerical calculations for samples stabilized at still lower temperature would require considerably longer computational times than we had available. While the dichotomic nature of the aged glass structure shows up sharply in relaxation experiments it may also show up as mild density fluctuations that might be detected by scattering or scanning probes.
Figure 2.9: (Color online) Logarithm of relaxation times corresponding to the first (circle) and the second (triangle) peaks of the distribution of the relaxation times. Blue markers denote experimental data [56] and black markers are simulation results.
Chapter 3

Fluctuating Mobility Generation and Transport in Glasses

3.1 Introduction

On human length and time scales glasses seem static, yet glasses constantly move at molecular scales. These molecules change their locations through rare, activated events at a rate which varies throughout the glass owing to its aperiodic structure. Motions in one location cause or relieve constraints thereby changing the rate of transitions in neighboring regions. From these considerations it follows that the apparent mobility of regions fluctuates both in space and time and appears to be locally transported. In this paper, we explore, using numerical methods, fluctuating mobility generation and transport in glasses focussing on rejuvenation after heating. The framework used is based on the random first order transition (RFOT) theory of glasses [37, 38, 12, 39, 15, 18, 2].

The static appearance of glasses has been formally addressed by mean field theories such as the explicitly dynamical mode coupling theory (MCT) [12, 21] as well as by outwardly static approaches [37, 38]. The similarities between these different approaches lead to the suggestion that they are approximately equivalent [12]. These disparate analogous approaches indeed do provide exactly equivalent results for a

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Chapter 3, in full, is a reprint of the material as it appears in Physical Review E 88 022308 (2013), A. Wisitsorasak and P. G. Wolynes.
large class of spin glass models with infinite range interactions [39, 13, 85]. In mean field models, a dynamic transition to immobility occurs discontinuously at a high dynamic transition temperature, $T_d$, below which an exponentially large number of frozen states emerges. At a lower temperature, $T_K$, the configurational entropy of these states vanishes and a true thermodynamic transition ensues [39]. For systems with finite range interactions, the transition at $T_d$ is wiped out by local activated transitions between the frozen states [39]. RFOT theory argues that activated transitions resembling nucleation events become the source of mobility in deeply supercooled liquids. These thermally activated motions would cease at the thermodynamic transition if the entropy crisis occurs or otherwise cease only at absolute zero.

While the activated mechanism of mobility generation is a key aspect of RFOT theory, owing to its connection with the mode coupling theory, RFOT theory shares with kinetically constrained models [43, 86, 87] the idea that mobility can be transported i.e. the notion of facilitation. Mobility transport effect is an essential feature of RFOT theory, diminishing the effects of the instantaneous heterogeneity in activation barriers which otherwise would lead to a broader distribution of relaxation times than observed [15].

The idea that the mobility of a region of the fluid depends on the mobility of its neighbors provides the historic basis for MCT. Bhattacharyya, Bagchi and Wolynes (BBW) suggested a way to bridge the gap between MCT which is adequate above the dynamical transition and mobility generation through activated transitions which occurs below the mean field dynamic transition by including an activated event vertex in the self-consistent MCT [30, 32]. BBW’s treatment did not make explicit the spatiotemporal nature of the dynamical heterogeneity. To make clearer the connection we can allow the mobility to be an explicitly varying dynamical variable in
the BBW analysis. The resulting coupled inhomogeneous nonlinear self-consistent differential-integral equations are cumbersome to study but assuming slow variations in time and space in the mobility allows a continuum approximation to be made [63, 36, 57]. This gives a simple description of a rich set of phenomena especially in the case of “rejuvenating” glasses that are heated after falling out of equilibrium. Wolynes argued on the basis of the continuum theory that mobility transport and generation conspire to set up moving fronts in heated glasses that resemble flames [36]. Ignition by mobility generation occurs at points within the bulk but cooperative rearrangements occur with especially large rapidity at a free interface which acts as an external source for a rejuvenation front [57]. The theory thus predicts then there are both heterogeneous and homogeneous mechanisms by which glass “melts” into an equilibrated fluid. These two mechanisms have been observed by Ediger in his studies of ultrastable glasses prepared by vapor deposition [34]. The approximate continuum treatment of rejuvenation agrees qualitatively with the more precise later measurements [34, 35, 33] but according to Ref. [35] the simple analytical result for the front speed is quantitatively off by about two orders of magnitude. In the first set of measurements [34] there was also evidence for a modest overshoot phenomenon in which, just after a front passes, the mobility seems to be higher than it will eventually become in the fully equilibrated liquid. This overshoot, not anticipated by Wolynes’s calculation, is, however, not apparent in later experimental studies [35]. The possibility of a large deviation from the simple approximation inspired us to explore more completely the continuum equations for mobility generation and transport in glasses. Here we show that a more accurate numerical treatment of the fluctuating continuum equations gives better quantitative agreement with observed front propagation speed but no sign of the overshoot occurs in the average behavior.
3.2 Mobility and Fictive Temperature Equations

We first recount the continuum equations emphasizing the role of fluctuations. Starting from the spatially inhomogeneous MCT with activated events we approximate the memory kernel as being explicitly time and space dependent but treat it as locally frequency independent thus representing a mobility field \( \mu(x, t) \). Expanding the inhomogeneous MCT equation in Taylor series in the derivatives of the mobility yields a continuum equation which we can supplement with local random terms [36]

\[
\frac{\partial \mu}{\partial t} = \frac{\partial}{\partial x} \left( \bar{\mu} \xi^2 \frac{\partial \mu}{\partial x} \right) - \bar{\mu} (\mu - \bar{\mu}) + \delta g + \frac{\partial \delta j}{\partial x} \quad (3.1)
\]

where \( \bar{\mu} \) is the uniform solution of the homogeneous MCT equation and \( \xi \) is the size of a cooperatively rearranging region (CRR). We will refer to Eq. (3.1) as linearized inhomogeneous mode coupling theory (Li-IMCT). In deeply glassy systems \( \bar{\mu} \) the mobility from the uniform solution of the BBW equations can be reasonably approximated by the traditional aging formulation of Narayanaswamy-Moynihan and Toolin term of a fictive temperature \( T_F \), which measures the local energy, as in RFOT theory by Lubchenko and Wolynes [18] \( \bar{\mu}(T_F, T) = \mu_0 \exp \left\{ -\frac{cE^1}{k_B T} - \frac{(1-c)E^4}{k_B T_F} \right\} \). The parameter \( c \) is predicted by RFOT theory to be inversely proportional to the heat capacity discontinuity \( \Delta c_p \). We use this RFOT prediction later. To complete the description we take the local fictive temperature to approach the ambient temperature through an ultralocal relaxation law

\[
\frac{\partial T_F}{\partial t} = -\mu (T_F - T) + \delta \eta. \quad (3.2)
\]

Since activated motions occurring right at the surface of the glass feel no mismatch energy penalty on the interface along the free surface they have to overcome only the mismatch energy on the hemisphere facing the bulk [57]. Free surfaces thus represent
a source of inhomogeneous mobility. In the bulk itself there are dynamic inhomogeneities from fluctuations in the local fictive temperature and from the activated events which transport the mobility field. Equations in which density fluctuation can be thought of as having a mobility that fluctuates and nonlinearly affects transport have been discussed before [88, 89]. In contrast, in our work the coupling between mobility and fictive temperature is a key feature which has been left out of those descriptions. We treat the random force terms as coarse-grained white noises with correlation lengths reflecting the length scale of the activated events. The intensities of the noises may be found by requiring the linearized equations to satisfy locally the fluctuation-dissipation relations. The local fictive temperature fluctuation $\delta \eta$ is taken to be $\langle \eta(x, t)\eta(x', t') \rangle = 2\mu T^2 \frac{k_B}{\Delta c_p N^\dagger} \delta(x-x')\delta(t-t')$, where $N^\dagger$ is the number of molecular units in a CRR. The fluctuations in mobility generation $\delta g$ and transport $\delta j$ arise due to fluctuations in free energy barrier heights which are the cause of stretched exponential relaxation with a bare stretching parameter $\beta_0 = 1/\sqrt{1 + (\delta F^\dagger/k_B T)^2}$. Again $\beta_0$ is predicted by RFOT theory to depend on $\Delta c_p$ [15]. Linearizing the equations and treating $\bar{\mu}$ as constant, the fluctuation-dissipation relation yields a mobility generating noise $\langle \delta g(x, t)\delta g(x', t') \rangle = 2\bar{\mu} \xi^2 \mu^2 \left( \frac{1}{\beta_0^2} - 1 \right) \left( \frac{T_g}{T} \right)^2 \delta(x-x')\delta(t-t')$ and a mobility random flux $\langle \delta j(x, t)\delta j(x', t') \rangle = 2\bar{\mu} \xi^2 \mu^2 \left( \frac{1}{\beta_0^2} - 1 \right) \left( \frac{T_g}{T} \right)^2 \delta(x-x')\delta(t-t')$ [90].

While Li-IMCT is a natural perturbation result, it is worth noting that to the same order of perturbation the rate of relaxation of $\mu$ to its local value could be taken as $\mu$ itself rather than $\bar{\mu}$. This leads to a nonlinear transport equation $\frac{\partial u}{\partial t} = \frac{\partial}{\partial x} \left( \mu \xi^2 \frac{\partial u}{\partial x} \right) - \mu (\mu - \bar{\mu}) + \delta g + \frac{\partial \delta j}{\partial x}$. This equation has the structure of the Fisher-Kolmogorov-Petrovsky-Piskounov equation [91, 92] so we call this set of coupled equations the FKPP inhomogeneous mode coupling theory (FKPP-IMCT). This equation turns
out to do a somewhat better job of describing the experiments than the Li-IMCT does.

Eq. (3.1) resembles the diffusion equation for some kind of excitation. Of course, such “excitations” are quite fictional – there is no regular structure in a glass that can be used to a priori define a defect. The formal analogy between inhomogeneous mode coupling and excitation models explains why such defect or excitation models while being microscopically unrealistic do manifest phenomena reminiscent of molecular glasses.

Exact analytical treatment of the equations for mobility generation and transport is difficult. It has been argued, however, that for aging glasses i.e. systems that have been quickly quenched to low temperatures, the aging dynamics that can be easily studied in the laboratory will not be very different from what occurs initially and so involves primarily the mobility generation events themselves [36]. When a glass is heated however the autocatalytic interplay between mobility generation and transport qualitatively changes the picture completely. Recognizing the analogy to combustion, Wolynes invoked some of the simpler approximations used in the analysis of flames [93] which then predict the front propagates at a speed $\sqrt{2/3} \xi \mu_{\text{high}}$. This upper bound to the speed depends only on the mobility in the high $T$ equilibrated material, $\mu_{\text{high}}$, but is independent of the mobility of the initially prepared low mobility material. Here we test that idea by complete numerical solution of the complete nonlinear equations.

The numerical calculations were carried out using parameters referenced to tris(naphthyl)benzene or TNB [34] whose glass transition temperature for $\tau = 100 \text{ s}$, $T_g$ is 347 $K$, with $\xi = 2.5 \text{ nm}$. Fluctuations follow using RFOT theory from the measured $\Delta c_p = 2.94 \; k_B$ per bead. In 1D, the calculations use a lattice of 200 cells with a spacing $\Delta x = 1 \text{ nm}$. For the 2D case, a square two-dimensional lattice of $20 \times 100$ cells with
mesh size $\Delta x = 1$ nm was employed. Periodic boundary condition are assumed for all cases but the surface is represented by a region with intrinsically high mobility given by the Stevenson-Wolynes formula $\tau_s = \sqrt{\tau_0 \tau_\alpha}$ [57]. Owing to the stiffness of the equations we cannot study them at as low a fictive temperature as the experiment.

### 3.3 Numerical Results

We first report numerical results obtained from 1D deterministic theory. Due to the symmetry of the deterministic problem, these results would also apply in two dimensions. In the Li-IMCT case, the interface width as measured by full-width-at-half-maximum of the source term $-\bar{\mu}(\mu - \bar{\mu})$ is about 5 nm. This scale is only a bit larger than the size of the entropic droplets that generate mobility [15]. The width of the interface from the FKPP-IMCT is as wide as 10 nm, more consistent with the experimental measurement which are however somewhat uncertain [34].

The speeds of front propagation at various temperatures predicted from the 1D deterministic Li-IMCT and FKPP-IMCT are shown in Fig. 3.1. Increasing the ambient temperature increases the speed. The predicted linear trend of $\log(v_{gr})$ with temperature $T$ agrees with observations. No calculated point differs from the experimental line [35] by more than a factor of 2. The predicted speed from the deterministic Li-IMCT however does vary somewhat more with the initial fictive temperature in the simulation than it does in experiment. Wolynes’s approximate solution on the other hand showed independence of the speed on the initial fictive temperature in agreement with observation. The discrepancy in the numerical study contrasting with the correct prediction from the approximation may arise because the initial fictive temperature in the study is not low enough thus leading to a “cold boundary difficulty”, a problem extensively discussed in combustion theory using intermediate asymptotics.
Figure 3.1: (Color online) The speed of the mobility front from the dynamics of the 1D deterministic Li-IMCT (solid red markers), the 1D deterministic FKPP-IMCT (opened red markers), the 1D stochastic Li-IMCT (solid green markers), the 1D stochastic FKPP-IMCT (opened green markers), the 2D stochastic Li-IMCT (solid blue markers), and the 2D stochastic FKPP-IMCT (opened blue markers). Different kinds of symbols indicate different initial fictive temperatures, the triangles are for $T_{\text{initial}} = 310\,K$, circles for $T_{\text{initial}} = 315\,K$, and squares for $T_{\text{initial}} = 320\,K$. The experimental measurements as reported in Ref. [34] are shown as magenta stars and the black stars represent the more recent results from Ref. [35]. All lines are drawn as guides for the eye. Inset: The front speed versus relaxation time. The continuum approximation of the front speed $\sqrt{2/3}\xi\mu^{\text{high}}$ is drawn as the black solid line. Notice the front speed does not scale quite as strongly as $\tau^{-1}$.

We now consider the stochastic models in one and two dimensions. While the three-dimensional situation is numerically too demanding for us to treat presently the lower dimensional cases already allow a good comparison with experiment. Realizations of the front evolution from the 2D stochastic version of the Li-IMCT are shown in Fig. 3.2 through the mobility field $\mu$. Initially the sample is prepared in an ultrastable phase by simulating the stochastic equations for a uniform system at a low temperature,
\(T_{\text{initial}} = 310 \, K\). The system is then instantaneously heated to a higher ambient temperature, \(T = 342 \, K\), making the former low mobility state unstable. As the fictive temperature increases, the front propagates into the bulk leaving the stable state behind. Due to the periodic boundary conditions fronts initiate at both ends and travel towards the “inner” bulk.

In addition to the fronts emanating from the surfaces at high mobility reconfiguration events take place at some bulk locations faster than they do at others. Once these initially nucleated regions reconfigure, they catalyze rearrangement of their low mobility neighbors and lead to fronts emanating radially from the rejuvenated centers - as described earlier [36]. Fast regions cannot as easily jump over slow regions which are more stable, so they often detour to avoid an immobile region or become jammed up at the interface between the two regions. This latter effect in a specific realization can give the appearance of the overshoot of the mobility behind the propagating front as shown in Fig. 3.2. Both stochastic Li-IMCT and FKPP-IMCT equations give similar fluctuating overshoot phenomena.

To assign a typical speed to the stochastic front, the front position may be defined using a one dimensional integral of a threshold function \(z(t) = \frac{1}{2} \int_L dx \Theta[\mu(x, t) - \mu^{\text{threshold}}]\), where \(\Theta[f(x)]\) is Heaviside step function, \(\mu^{\text{threshold}}\) is a constant threshold [94]. The integration measures the amount of sample which has not yet been transformed much as in calorimetry [33]. Physically \(z(t)\) gives the depth of the front from each surface. The growth front speed is determined by \(v = \Delta z/\Delta t\), where \(\Delta t\) is somewhat larger than a typical relaxation time \(\mu^{-1}\). Averaging this quantity over initial times and initial ensemble yields the average front speed \(v_{gr}\).

The front speeds for ultrastable TNB glasses prepared at various initial temperatures from both 1D and 2D of stochastic Li-IMCT and FKPP-IMCT are displayed
Figure 3.2: (Color online) Snapshots of mobility fields from 2D stochastic Li-IMCT at $t = 1.5 \times 10^4 s$ (top panels), $t = 3.8 \times 10^4 s$ (middle panels), $t = 4.7 \times 10^4 s$ (bottom panels). The figures in the left column show average values of the mobility fields along the $y$-axis. The color schemes on the right column show the mobility on a log-scale with the corresponding color bars on the right.

in Fig. 3.1. The resulting speeds do slightly depend on the initial temperatures, but more strongly exponentially depend on the ambient temperature rapidly rising as the ambient temperature increases. The front speeds for all stochastic cases are larger than for the deterministic cases by a factor of two. These speeds from the stochastic simulations for both dynamics now deviate by less than 50% from the front speeds reported in the experiments of Ref. [35]. The growth front velocities reported in Ref. [34] are about three times greater than those found in Ref. [35] in which it was suggested the samples prepared earlier may contain impurities such as the vacuum pump oil which increase the mobility.

In the present paper we have numerically solved fluctuating continuum equations coming from inhomogeneous MCT that were previously introduced to account for
spatiotemporal structures in aging and rejuvenating glasses. Numerically accounting for fluctuations in mobility field and fictive temperature gives closer quantitative agreement with experimental measurements than does the previous approximate treatment.

The front propagation phenomena discussed here are of a very general nature. Any external influence that can increase mobility, if it is inhomogeneous in space can lead to such fronts. For example plasticizer diluents which lower $T_g$ will give fronts which will propagate into the bulk. The coupled diffusion may give an overshoot phenomenon like that seen in some of the experiments perhaps explaining the sensitivity to impurities [95]. Stress also acts to increase mobility by lowering activation barriers [96]. Shear banding may arise from the coupling of stress to inhomogeneously propagating internal mobility fronts [97].
Chapter 4

On the Strength of Glasses

A fundamental question about solid matter is what ultimately determines its mechanical strength. Glasses, in the popular mind, are easy to break but in fact, if surface cracks are carefully avoided, glasses turn out to be intrinsically quite strong. Nearly a century ago, Frenkel provided an elegant argument for the maximum stress that a solid could withstand [98]. Crystalline metals were found to be hundreds to thousands of times weaker than the Frenkel estimate [99]. This observation inspired the extremely fruitful ideas of dislocations and grain boundaries that provide easy ways for polycrystalline metals to rearrange and plastically deform [100, 101, 102, 103]. Glasses come much closer to the Frenkel limit but still fall short in strength [104]. In this paper we explore quantitatively the notion that the mechanical failure of glassy materials ultimately arises from strain catalyzed rearrangements of the same kind as those responsible for the high supercooled liquid viscosity. The idea that there is a relation of yield strength to the glass transition itself is not new and has been examined in various ways [105, 106, 107, 103, 108, 109]. Here we go further by exploiting the current quantitative understanding of cooperatively rearranging regions that has emerged from the random first order transition (RFOT) theory of glasses [41, 39, 12, 14, 2, 15, 110] in order to make some specific predictions. RFOT theory describes the microscopic origin of cooperatively rearranging regions and predicts

Chapter 4, in full, is a reprint of the material as it appears in Proceedings of the National Academy of Sciences 109(40) 16068 - 16072 (2012), A. Wisitsorasak and P. G. Wolynes.
they are compact containing a few hundred molecular units near the laboratory glass transition temperature $T_g$. These regions become more fractal, resembling strings or percolation clusters [111] at higher temperatures where flow is no longer thermally activated [112] but rather dominantly collisional. The quantitative predictions of RFOT theory concerning the well-established thermodynamic/kinetic correlations in the viscous liquid state, dynamical heterogeneity in supercooled liquids [15] and the aging [18] and rejuvenating [110] properties of the glassy state proper agree quite well with observations [47]. It is thus natural to enquire as to what the theory predicts for the material strength of glasses.

We begin by reviewing how activated events occur in liquids and glasses in the absence of stress. The easiest way to conceptualize activated events in the RFOT theory is through what is called the landscape library construction by Lubchenko and Wolynes [18]. This construction has also been used to define point-to-set correlation lengths [28, 113] allowing many key points of RFOT theory to be confirmed via computer simulations [114, 115, 116, 117]. This construction is schematically pictured in Figure 4.1 and 4.2. In mean field RFOT theory, below a dynamical transition temperature $T_A$, the system becomes trapped in one of an exponentially large number of possible metastable states which are minima of a free energy functional [39]. For molecular fluids these states can be taken as nearly structurally synonymous with the inherent structures which precisely correspond to minima of the potential energy [14], but the individual stability of these states at finite temperature depends not only on their energy but also on their vibrational entropy. Irreversible reconfiguration events eventually take place by rearranging molecules in ever larger regions of size $N$ until a critical size is reached. Above the Kauzmann temperature, $T_K$, the configurational entropy is extensive and so as the size of a reconfiguring region increases the number
of possible local rearrangements grows as well. Generally moving to any one of these rearranged structures costs free energy because the environment of the rearranging region does not fit the new locally accessible alternative structures as well as it fits the original free energy minimum from which rearrangement starts. The typical mismatch energy $\Delta E(N)$ near the Kauzmann transition scales as $\gamma N^x$. The power law in mean field theory represents a surface energy [39] so the exponent $x = 2/3$ but scaling arguments [41] suggest there should be a somewhat weaker scaling with $x = 1/2$ near an ideal glass transition at $T_K$ due to wetting from the numerous alternative states that can be interpolated between the fixed environment and the core of the rearranging region.

Xia and Wolynes showed the coefficient in the mismatch energy can be computed near $T_K$ by assuming a locally sharp interface and by making a microscopic estimate using density functional theory of the localization free energy which is entropic:

$$\gamma = \frac{3\sqrt{3}\pi}{2} k_B T_K \ln \left( \frac{\alpha_L a^2}{\pi e} \right).$$

(4.1)

Here $\alpha_L$ determines the size of the vibrational fluctuations in a minimum and is roughly 100, reflecting displacements following Lindemann’s stability criterion allowing localized motion of about one tenth of the interparticle spacing, $a$.

Above $T_K$ any mismatch energy can however be overcome by the entropic driving force favoring reconfiguration to one of the many alternate structures, $F_{\text{bulk}}(N) = -T s_c N$ where $s_c$ is the configurational entropy per particle. Balancing $F_{\text{bulk}}(N)$ and $\Delta E(N)$ gives an activation free energy to be overcome for irreversible rearrangement, $\Delta F^\dagger$, which is a function of $s_c$. $\Delta F^\dagger$ diverges near $T_K$ as $s_c$ vanishes. This prediction then connects the kinetics of rearrangements with thermodynamics, a hallmark of the RFOT theory. Using the approximate coefficient $\gamma$ obtained by Xia and Wolynes the absolute magnitude of barriers is also predicted to follow an Adam-Gibbs-like relation.
Figure 4.1: We show in the upper part of the figure schematic snapshots of local rearrangement starting from an initial frozen configuration in an imposed stress field $\sigma$. Following Lubchenko and Wolynes [18] the lower left panel shows the spectrum of possible free energy minima for a large sample of glass. Levels are listed in order of the internal free energy $\phi$, comprising the potential energy along with a vibrational entropic contribution. When the glass is trapped in a single such state, local regions of size $N$ can rearrange to new minima while only weakly disturbing their environment elastically. Connected energy levels are shown in the next two panels. When an imposed stress $\sigma$ is imposed the energy levels are shifted and the energy cost of moving $N$ particles is reduced by an amount $(\kappa\sigma^2/2G)NV_{\text{bead}}$ where $G$ is the elastic modulus and $\kappa$ is a factor that includes the elastic response of the environment which does not shift to a new minimum. $V_{\text{bead}}$ is the volume of a molecular unit. Eventually for sufficiently large $N$ a distinct structure is formed coincident in free energy with the initial state, allowing irreversible motions to occur.
\[ \Delta F^\ddagger = A/s_c \] but with a specific numerical value for \( A = (27\pi/16)k_B(\ln(\alpha_L a^2/\pi e))^2 \).

Because the Lindemann parameter \( \alpha_L \) depends only weakly on the potential, in RFOT theory then \( \Delta F^\ddagger/k_B T \) is again dominantly a function of the configurational entropy, across a range of substances.

The landscape library argument can also be used in the so-called “aging” regime to describe motion in the glass [18]. In the aging regime, the initial configuration is not one chosen from the thermal equilibrium ensemble at the ambient temperature but instead structurally resembles a system that was equilibrated at a higher so-called “fictive” temperature. In a simple quench to low temperature the fictive temperature initially is the laboratory glass transition temperature \( T_g \). For this nonequilibrium situation the initial configuration then will not only gain entropy by reconfiguring locally but also will release an additional energy per particle \( \Delta \Phi \) which represents the energy frozen in at the glass transition [18]. If we assume the configurational heat capacity has the empirical form \( \Delta c_p(T_g) \cdot (T_g/T) \) this excess energy is \( \Delta \Phi = \Delta c_p(T_g) T_g \ln(T_g/T) \).

Owing to this excess driving force, reconfiguration events occur sooner in a glass than they would in a liquid structurally equilibrated to the same ambient temperature. The nonequilibrium activation free energy can be written in terms of the activation free energy for an equilibrium liquid at a higher specific configurational entropy:

\[ \Delta F^\ddagger_{n.e.} = \Delta F^\ddagger_{eq}(T s_c + \Delta \Phi) \] (4.2)

\( \Delta F^\ddagger_{eq}(T s_c) \) is the function giving the activation barrier in the equilibrium liquid, written in terms of its configurational entropy at temperature \( T \). In the glass below its \( T_g \) this formula implies the rates follow something close to an Arrhenius law but with an activation enthalpy diminished from what it was at the higher temperature at which it fell out of equilibrium. In this way, this RFOT argument accurately predicts
the so-called nonlinearity parameter \( x \) describing the ratio of activation enthalpy for motion in an equilibrated liquid to that for glasses that have fallen out of equilibrium [18].

The Volger-Fulcher law, while describing the deep glassy behavior, breaks down at higher temperatures in supercooled liquids. In mean field theory this breakdown occurs because the mismatch coefficient \( \gamma \) itself vanishes at the mean field spinodal temperature \( T_A \) [39, 116, 20]. Schmalian, Stevenson and Wolynes have argued that the Volger-Fulcher relation will actually break down at a somewhat lower temperature \( T_c \) because the shape of correlated activated regions changes at higher temperatures in such a way that the mismatch energy now scales linearly in \( N \) [111]. The high temperature, entropically favored shapes are lattice animals whose exposed surface scales directly with their number of constituents as does their shape entropy. In this regime the scaling of mismatch energy can be written as \( v_{int} b \) where \( b \) is the number of equivalent broken bonds at the surface of the rearranging region. Schmalian, Stevenson and Wolynes showed that near \( T_K \), \( b \) is approximately \( 3.2N \) and the coefficient of \( v_{int} \) can (like the surface mismatch energy \( \gamma \)) be obtained from density functional reasoning \( v_{int} = (1/z)(3/2)k_B T \ln(\alpha_L a^2/\pi e) \).

The free energy profile for such fractal rearranging regions either monotonically increases with \( N \) or decreases monotonically with \( N \). This means that there will be a change in the rearrangement mechanism from activated dynamics to one dominated by collisions at high temperature. The crossover to barrierless reconfiguration is thus determined by the condition \( s_c(T_c) = s_c^{perc} - \Delta \Phi/T_c = \Delta c_p(T_g)T_g/T_K(1-T_K/T_c). \) The critical crossover parameter under the assumption the clusters are percolation-like is \( s_c^{perc} = 1.28k_B \). For equilibrated liquids this relation predicts crossover temperatures agreeing with those found using Stickel plots [118]. The RFOT argument then also
predicts barrierless reconfiguration will occur for nonequilibrium glasses if heated when

\[ \frac{k_B T_c}{\Delta c_p(T_g) T_g - \Delta \Phi} = \frac{k_B}{\Delta c_p(T_g) T_g} \left( 1 - \frac{s_c \text{perc} T_K}{\Delta c_p T_g} \right)^{-1}. \]  

This specific prediction for crossover to collisional dynamics in superheated glasses has not yet been tested in the laboratory although it would be interesting to check it experimentally by using lasers to rapidly heat glasses. Below the crossover temperature, fractal rearranging regions also provide the low barrier tail to the barrier distribution since fluctuations can allow the nonuniformly linear increasing free energy profile to cross zero. This tail, for large fluctuations, manifests itself as a separate relaxation peak, the so-called secondary or $\beta$ relaxation [119].

What does RFOT theory then suggest about how reconfiguration events occur under stress? If a sample of glass is put under a uniform shear stress, $\sigma$, the energy per unit volume is immediately raised by an amount $\sigma^2/2G$ where $G$ is the elastic shear modulus [120]. It has long been known this energy can be explosively released by cracking the glass. This effect is demonstrated by the famous Prince Rupert’s drops [121]. The stress need not always lead to cracking directly. It is reasonable to expect that, of the myriad of possible states envisioned in RFOT theory, a significant fraction will also allow this stress energy to be released without cracking or forming voids. Indeed a vanishing stress energy of the rearranged state is expected since the most stable mean field free energy minimum corresponding to delocalized molecules can be thought of as being a typical disordered liquid ensemble and is thus completely incapable of sustaining static shear. Since the imposed stress energy can be removed by appropriately rearranging a region, imposed strains will lower the activation barrier and will catalyze the rearrangement. If the stress is sufficiently large the rearrangement may even occur without any significant barrier at all, just as takes place at the
thermal crossover at $T_c$. This crossover to barrierless reconfiguration would thus give the limiting strength of the glass if we assume there are no easier routes for the glass to rearrange (like cracking). Strain catalysis means that a stressed glass will always flow at some finite rate even for the smallest stresses [103, 120, 122] and thus a glass will deform, given time, at somewhat lower stresses than this limit. This gentler flowing situation is probably quite relevant in many practical situations. Flow itself can act to further catalyze rearrangements. The resulting additional enhancement of reconfiguration speed is a facilitation or mode coupling effect. Lubchenko has shown that this effect (that would be contained in a more complete RFOT theory including mode coupling effects [32]) does a good job describing the crossover to steady state nonlinear rheology [123]. Similar effects have been studied in mode coupling treatments of dense colloid rheology [124, 125]. We will, in this paper, however, concentrate on the immediate effect of stress on the activated events that occur before flow starts and leave the physics of developed plastic flows for future work. The limiting strengths we calculate in this paper then should be upper bounds representing extremely rapid failure of the glass.

Naively speaking, in order to compute the effect of stress catalysis on the activation barrier one merely needs to account for the strain energy lost in the fluidized region and thus must add to the bulk thermodynamic driving force term $(-T_s - \Delta \Phi)N$ an additional contribution $\sigma^2NV_{\text{bead}}/2G$ to compute the lowering of the thermal barrier for compact clusters or to find the limiting stress where barrierless rearrangement may occur. Here $V_{\text{bead}}$ is the volume of a “bead” i.e. movable unit of the glass, which can be inferred from the molar fusion entropy [20, 47]. There is a subtlety, however; as pictured in Figure 4.3 fluidizing a region of the glass also allows Hookean elastic rearrangements of the surrounding matrix to occur without it being necessary for the
Figure 4.2: The local level libraries in Figure 4.1 when thermally averaged yield a free energy profile for rearranging a specific region as a function of the number of displaced particles $N$. The average mismatch energy is balanced against a term containing the configurational entropy (from averaging over all the states), any initially excess energy frozen into the glass along with a contribution from relaxing strains via reconfiguration in an imposed stress field. The activation barrier is lowered by the imposed stress, eventually vanishing when the stress is sufficiently large, leading to rapid failure of the glass’s structural integrity.

outside region to move to any alternate free energy minima. This outer region while elastically responding thus does not elicit any mismatch energy. The strain energy relieved by rearrangement of a region of size $N$ [126] nevertheless becomes larger than $\sigma^2N\nu_{\text{head}}/2G$.

For an arbitrarily shaped rearranging region the exact calculation of the additional strain energy relieved by harmonically distorting the outer region would seem to be a complex problem in elastic theory. The result for spherical regions, however, has been known for some time where it has been used to develop the theory of the elastic modulus of composite media containing holes [127]. The calculation is mathematically quite analogous to the calculation of intrinsic viscosity made first by Einstein [128] for the effect on viscosity of suspending solid colloidal particles in a fluid and still more closely follows Taylor’s analysis of the viscosity changes due to suspending liquid drops or bubbles in a fluid [129]. For spheres the additional energy
Figure 4.3: The upper panel shows a uniform strain field acting on the glass sample in its original state. A fluidized region allows the surrounding material to elastically deform in a nonuniform way in the imposed stress field shown schematically in the lower panel. This allows additional strain energy to be released without costing any additional mismatch energy.

released (analogous to the excess viscous dissipation in the hydrodynamic problems) is still proportional to the sphere’s size and according to MacKenzie depends on the Poisson’s ratio characterizing bulk versus pure shear deformations. Taking over MacKenzie’s correction gives then an energy increment for rearranging a region of size $N$, $\Delta E_{\text{elastic}} = \kappa \frac{\pi}{6} NV_{\text{bead}}$ where $\kappa = 3 - 6/(7 - 5\nu)$ in terms of the Poisson’s ratio $\nu$. For the typical Poisson’s ratio of metallic glasses $\kappa \approx 1.8$.

Directly calculating the correction for non-spherical shapes is indeed complex. In addition, considerable distortions from spherical geometry are energetically still more favorable in relieving stress than for the region to remain compact and thus at high stress such distortion should again lead to barrierless breakup, just as critical flow rates lead to dissolution of drops in emulsions [130, 131, 132]. The latter problem has led to an extensive literature [133, 126]. We will use, nevertheless, the spherical value
of the correction $\kappa$ for all shapes of cooperatively rearranging regions. We suspect this simplification is probably not too bad for small stresses and not too far from $T_K$. This surmise is buttressed by the experience for the corresponding hydrodynamic problem of computing the intrinsic viscosity of complex shapes, a problem that has been extensively studied in polymer chemistry [126]. In that problem the shape effects are quite modest. By adding the increased relieved strain energy to the reconfiguration driving force, in analogy with equation [4.2], the activation barrier for flow in a strained glass can again be written in terms of the function giving the barrier for equilibrated liquids $\Delta F^\parallel = \Delta F^\parallel (Ts_c + \Delta \Phi + \kappa \sigma^2 V_{\text{bead}}/2G)$. With this simplification then barrierless reconfiguration should finally occur when $s_c(T_c) = s^\text{perc}_c - \frac{\Delta \Phi}{T} - \kappa \frac{\sigma^2}{2GT} V_{\text{bead}}$. As in the popular J-point scenario [134] an apparent spinodal to reconfiguration apparently can be approached by tuning either the temperature $T$ or the stress $\sigma$. Again fluctuations in local stability should favor the same fractal rearrangements that are eventually responsible for barrierless reconfiguration before this point is actually reached. Following Stevenson and Wolynes's arguments for the secondary relaxations without stress, the weight for such rare fluctuations is still exponentially suppressed when the increment $s^\text{perc}_c - \frac{\Delta \Phi}{T} - \kappa \frac{\sigma^2}{2GT} V_{\text{bead}} - s_c(T)$ is positive.

The argument, just given, relating barriers in the glass under stress to those for thermal motions in the equilibrated liquid should hold for temperatures not too far from $T_K$ since the shapes of rearranging regions are then determined entropically. There are corrections, however, away from $T_K$. At very high temperatures near to the mean field spinodal $T_A$ the mismatch energy cost goes down, leading to an additional weakening of the glass. Conversely at low temperatures, much below $T_K$, we also must account for both the fact that the mismatch energy becomes pinned at its $T_K$ value and that at the same time the importance of shape entropy is lessened by
the diminished temperature. A detailed account of the latter effects is contained in the Supplementary Information. When the latter effects are included along with the calculation of the excess energy we find an explicit equation for the limiting strength $\sigma^*$:

$$\sigma^\ast_{\text{pred}} = \sqrt{\frac{2Gk_BT}{\kappa V_{\text{bead}}}} \left( \frac{3.20}{T} T_K \frac{T}{T} - 1.91 \right) - \frac{\Delta c_p(T_g) T_g}{k_B} \frac{T_g}{T_K} \ln \frac{T_g}{T_K} \right)$$ (4.4)

The contribution in this expression involving $\Delta c_p$ represents the weakening caused by the excess energy which has been frozen in at the glass transition. If we could be cosmologically patient this excess energy would disappear by annealing to $T_g = T_K$ giving then the ultimate achievable strength of a glass. At very low temperatures the strength of this most stable glass will be then $\sigma^\ast_{\text{ideal}} = \sqrt{3.6Gk_BT_K/V_{\text{bead}}}$. We can write the shear modulus in terms of the spinodal temperature $T_A$ and the bead size, following Rabochiy and Lubchenko by estimating vibrational displacements from Debye continuum theory and assuming a limiting Lindemann ratio for the maximal thermal excursions [135, 102]. Using this relation gives $G = 24.9k_BT_A/V_{\text{bead}}$. If we now take $T_A \approx T_m$ the melting point and use the typical ratio of $T_K/T_m$ of between 0.4 and 0.7 we find the ultimate limiting $\sigma^*$ is proportional to the elastic modulus. Such a linear correlation between strength and modulus, resembles Frenkel’s estimate, and indeed has been examined experimentally. We find the ideal limit strength from RFOT theory to be uniformly about 30% higher than Frenkel’s. The weakening of the glass due to energy frozen in at the glass transition is however substantial. This excess energy lowers the strength quite a bit below the RFOT ideal value and below the Frenkel value but still gives strengths greatly exceeding the measured strength of polycrystalline metals. We have gathered from the literature data for the input thermodynamics. We then compared the RFOT theory predictions to measured strengths for some metallic glasses, silica and a polymer glass, PMMA. Details of the input data
and measured strength data can be found in the Supplementary Information.

In Figure 4.4 we display results for the strength versus shear modulus. The predicted strengths generally exceed but are close to the measured yield strengths. On this plot we also show both the Frenkel estimate and our $T_g = T_K$ ideal value. A typical polycrystalline material value of one-hundredth of the Frenkel value is also plotted. Clearly the present RFOT predictions account very well not only for the trends but even the actual magnitude of the strength. In Figure 4.5 we show the comparison of measured strengths against the complete predictions. Not only the glassy metals but also silica and the plastic PMMA have strengths not terribly far off the RFOT predictions. Although the main dependence on elastic modulus is clear, the RFOT theory results also depend on other quantities, such as $\Delta c_p$ and the ratio of the ambient temperature to glass transition temperature. However, as we can see, both the predicted ratios of strength to modulus for the measured systems and the measured ratios show no overall trend with liquid fragility or glass transition temperature, see Figure S1 in the Supplementary Information. Of course since modulus and $T_g$ are well correlated the absolute strengths themselves do correlate with $T_g$. It may be possible to test the theory further. Again, rapid heating should lower the yield strength in a predictable way. In addition, superstable glasses can be made via vapor deposition [136]. Their effective temperature corresponds to being roughly half way to the Kauzmann temperature. We see their strength should thus be proportionately closer to the Frenkel limit.

RFOT theory accounts well for the measured strength of laboratory glasses of various composition. The good agreement between theory and experiment suggests that the correlated rearranging regions responsible for high temperature viscosity in supercooled liquids also limit the strength of nonequilibrium glasses. There seems
Figure 4.4: Strength as a function of shear moduli. The experimental strength (red triangle) and the predicted strength (black circle) have nearly the same slope and are quite different from Frenkel strength (blue solid line). Typical value of crystal strength (violet solid line) and strength in the limit $T \to 0, T_g \to T_K$ (black solid line) are also shown in comparison.

to be no necessity to invoke then any additional defects of a point-like or line-like character to play a prominent role in weakening glasses that are prepared in an ordinary fashion by cooling a melt.
Figure 4.5: A plot of the strength, $\sigma^*$, measured from the experiments versus theoretical estimation derived from the RFOT theory. The dotted line plots the perfect match between the experiments and the predictions, $\sigma_{\text{Expt}}^* = \sigma_{\text{Pred}}^*$. The experimental data used are shown in Table S1 in the Supplementary Information.
Chapter 5

Conclusions

The present study provides a generic framework to understand dynamical heterogeneity of the glassy state. We have derived from an extended mode coupling theory the continuum equations for fluctuating mobility and fictive temperature fields in which the activated dynamics from RFOT theory is included. This derivation forms a bridge between mode-coupling theory and the quasistatic aspects of the random first order transition theory of glasses. This formalism allows us to study dynamical heterogeneity and calorimetric measurements in aging glasses in quantitative detail.

It should be possible to apply the same approach to other phenomena where glassy dynamics couples to other fields in a glass. For example the shear banding observed when a system is under the influence of external stress/strain may be studied by coupling the mobility to the deformation of the system using elastic theory and mechanical flow equations [97]. The coupled diffusion may give overshoot phenomena like those seen in some of the experiments perhaps explaining the sensitivity to impurities [95]. In polymer glasses, adding a field describing the chemical kinetics of forming bonding constraints to the description of mobility field may elucidate a more complete theory of the chemical aging of those polymeric glasses [137].
Appendix A

Derivation of the Relaxation Formula

The free energy profile for conversion from a nonequilibrium initial state to the other usually equilibrium state is [18]

$$F(N) = [f_{eq}(T) - \phi_{in}(T)]N + \gamma N^x.$$  \hspace{1cm} (A.1)

where $f_{eq}(T)$ is the total bulk free energy per particle of the final state at temperature $T$, $\phi_{in}(T)$ is the internal free energy per particle of the initial state, $\gamma = \frac{3\sqrt{3\pi}}{2}k_BT_K \ln \left[ \left( \frac{a/d_L}{\pi e} \right)^2 \right]$ is the surface tension, $a$ is an interparticle spacing, $d_L$ is the mean square fluctuations of a particle in a given basin [138]. Accounting for the wetting effect [139], the mismatch exponent is $x = 1/2$. When this exponent is used in Eq. (A.1), we obtain the most probable rate:

$$\bar{\mu} = \mu_0 \exp \left( -\frac{\gamma^2}{4k_BT[\phi_{in} - f_{eq}]} \right).$$ \hspace{1cm} (A.2)

When the initial state is at equilibrium, the free energy driving force $f_{eq} - \phi_{in}$ equals $-Ts_c$. If the liquid is quenched and aging, the driving force $f_{eq} - \phi_{in}$ is negative. Upon cooling initial glass state is trapped at $T_g$, $\phi_{in}(T) = \phi(T_g) \equiv \phi_g$. The free energy of liquid state at an equilibrium temperature $T$ is:

$$f_{eq}(T) = \phi_K - \int_{T_K}^{T} dT' S_c(T')$$

$$= \phi_K - \Delta c_p(T_g)T_g \left( \frac{T - T_K}{T_K} - \ln \frac{T}{T_K} \right)$$

where we have used Angell’s empirical form for the configurational entropy, $S_c(T) = \Delta c_p(T_g)T_g(1/T_K - 1/T)$ and $\Delta c_p(T) = \Delta c_p(T_g)(T_g/T)$. Noting that, at fictive tem-
perature $T_f$, $f_{eq}(T_f) = \phi_f - T_f s_c(T_f) = \phi_f - \Delta c_p(T_g) T_g \left( \frac{T_f - T_K}{T_K} \right)$ gives the ideal glass state energy $\phi_K = \phi_f - \Delta c_p(T_g) T_g \ln T_f$. The free energy driving force is:

$$
\begin{align*}
  f_{eq}(T) - \phi_{in}(T_f) &= -\Delta c_p(T_g) T_g \ln \frac{T_f}{T_K} \\
  &\quad - \Delta c_p(T_g) T_g \left( \frac{T - T_K}{T_K} - \ln \frac{T}{T_K} \right) \\
  &= -\Delta c_p(T_g) T_g \left( \frac{T - T_K}{T_K} - \ln \frac{T}{T_f} \right).
\end{align*}
$$

Substituting the above equation into Eq. (A.2), the full relaxation formula is given in terms of the ambient temperature $T$ and the fictive temperature $T_f$

$$
\bar{\mu}(T, T_f) = \mu_0 \exp \left( -\frac{\gamma^2}{4 k_B T \Delta c_p T_g \left[ \frac{T - T_K}{T_K} - \ln \frac{T}{T_f} \right]} \right)
$$

where $\gamma(T) = \frac{3 \sqrt{3 \pi}}{2} k_B T \ln \left[ \frac{(a/d_L)^2}{\pi e} \right]$. 

Appendix B

Derivation of the Correlation Length in the Aging Regime

The activation free energy profile is written as

\[ F(N) = [f_{eq}(T) - \phi_{eq}(T)]N + \gamma N^x \]  \hspace{1cm} (B.1)

where the surface energy is equal to \( \gamma = \frac{3\sqrt{3}\pi}{2} k_B T_K \ln \left[ \frac{(a/d_L)^2}{\pi e} \right] \).

Using the mismatch exponent \( x = 1/2 \) in Eq. (B.1) we must solve for the \( N^* \) where \( F(N^*) = 0 \). For \( T < T_g \), the number of particles in the cooperatively rearranging molecular structure is:

\[ N^* = \frac{\gamma_0^2}{[-(f_{eq}(T) - \phi_{in}(T))]^2}. \]  \hspace{1cm} (B.2)

Substituting \( f_{eq}(T) - \phi_{in}(T) \) from Eq. (A.3) into Eq. (B.2), we obtain \( N^* \)

\[ N^* = \frac{\left( \frac{3\sqrt{3}\pi}{2} k_B T_K \ln \left[ \frac{(a/d_L)^2}{\pi e} \right] \right)^2}{\Delta c_p(T_g) T_g \left( \frac{T-T_K}{T_K} - \ln \frac{T}{T_f} \right)^2}. \]

We can write

\[ N^* = \left( \frac{\xi}{\alpha} \right)^3 = \left( \frac{3\sqrt{3}\pi}{2} k_B T_K \ln \left[ \frac{(a/d_L)^2}{\pi e} \right] \right)^2 \frac{1}{\Delta c_p(T_g) T_g^2 \left( \frac{T-T_K}{T_K} - \ln \frac{T}{T_f} \right)^2}. \]

In the equilibrium case \( T_f \to T \), so the \( \ln(T/T_f) \) term vanishes and we recover the correlation length given by Xia and Wolynes [14].
\[
N^* = \left( \frac{\xi}{a} \right)^3 = \frac{\left( \frac{3\sqrt{3} \pi}{2} k_B T_K \ln \left[ \frac{(a/d_L)^2}{\pi e} \right] \right)^2}{[\Delta c_p(T_g) T_g]^2} \cdot \frac{1}{\left( \frac{T - T_K}{T_K} \right)^2}.
\]
## Appendix C

### Material Parameters for Systems Considered in this Work

Table C.1: The material constants employed in this work are obtained from thermodynamics: $\mu_0$ (s$^{-1}$), Kauzmann temperature $T_K$ (K), the glass transition temperature $T_g$ (K), the melting temperature $T_m$ (K), enthalpy of fusion $\Delta H$ (kJ/mol), heat capacity jump $\Delta C_p$ (J/K mol), number of beads $N_{\text{bead}}$ and the stretching exponent $\beta$.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$\mu_0$ (kJ/mol)</th>
<th>$T_K$ (K)</th>
<th>$T_g$ (K)</th>
<th>$T_m$ (K)</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta C_p$ (J/K mol)</th>
<th>$N_{\text{bead}}$</th>
<th>$\beta$</th>
<th>Refs</th>
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<tbody>
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<td>$4.37 \times 10^{14}$</td>
<td>273</td>
<td>347</td>
<td>474</td>
<td>33.3</td>
<td>122</td>
<td>5.0</td>
<td>0.48</td>
<td>[140, 141, 142, 143]</td>
</tr>
<tr>
<td>GeO$_2$</td>
<td>$3.77 \times 10^{16}$</td>
<td>418</td>
<td>810</td>
<td>1388</td>
<td>17.1</td>
<td>6.27</td>
<td>0.9</td>
<td>1.0</td>
<td>[144, 145, 142]</td>
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<tr>
<td>Glycerol</td>
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<td>134</td>
<td>190</td>
<td>291</td>
<td>18.3</td>
<td>90.5</td>
<td>4.5</td>
<td>0.63</td>
<td>[146, 79]</td>
</tr>
<tr>
<td>OTP</td>
<td>$2.37 \times 10^{16}$</td>
<td>204.2</td>
<td>246</td>
<td>329</td>
<td>17.2</td>
<td>111.27</td>
<td>3.7</td>
<td>0.55</td>
<td>[7, 147, 79]</td>
</tr>
<tr>
<td>PC</td>
<td>$1.43 \times 10^{25}$</td>
<td>130</td>
<td>159.54</td>
<td>218.6</td>
<td>7.77</td>
<td>75.4</td>
<td>2.5</td>
<td>0.73</td>
<td>[148, 147, 149]</td>
</tr>
<tr>
<td>PS</td>
<td>$9.48 \times 10^{14}$</td>
<td>325</td>
<td>375</td>
<td>513</td>
<td>6825</td>
<td>2148</td>
<td>953</td>
<td>0.35</td>
<td>[150, 151, 141, 152, 56]</td>
</tr>
</tbody>
</table>
Appendix D

Derivation of the Yield Strength Equation

At low temperature near $T_K$ the RFOT theory of glasses predicts that the cooperatively rearranging regions (CRRs) in glass-forming liquids are compact. Away from $T_K$, CRRs need not be compact and string-like contiguous shapes, called lattice animals, have been observed in computer simulations and experiments. Accounting for the multiplicity of possible shapes of the CRRs [111] and using the landscape library arguments [18], the free energy of a CRR of $N$ sites with $b$ boundary interactions is

$$F(N, b, \sigma) = \left[ f_{eq}(T) - \phi_{in}(T, \sigma) \right] N + v_{int}b - k_B T \ln \Omega(N, b) \quad (D.1)$$

where $f_{eq}(T)$ is the total bulk free energy per particle of an equilibrium state at temperature $T$, $\phi_{in}(T)$ is the internal free energy per particle of an initial glass state, $v_{int} = (1/z)T_K(3/2)k_B \ln(\alpha L a^2/\pi e)$ is a local interaction of pairs with $z$ nearest neighbors, and $\Omega(N, b)$ is the number of lattice animals of given $N$ and $b$. The initial nonequilibrated free energy has an additional contribution due to stress

$$\phi_{in}(T, \sigma) = \phi_{in}^0(T) + \kappa \frac{\sigma^2}{2G} V_{bead} \quad (D.2)$$

where $\phi_{in}^0$ is an internal free energy of the initial state without any stress. The equilibrated bulk free energy at temperature $T$ above $T_K$ is the sum of the internal free energy of a state at the Kauzmann temperature $T_K$ and the configurational
entropy \( s_c \)

\[
f_{eq}(T) = \phi_K - \int_{T_K}^{T} dT' s_c(T')
\]

\[
= \phi_K - \Delta c_p(T_g) T_g \left( \frac{T - T_K}{T_K} - \ln \frac{T}{T_K} \right)
\]

where we have used Angell’s empirical form of the change in heat capacity upon vitrification \( \Delta c_p(T) = \Delta c_p(T_g) (T_g/T) \) and the thermodynamic relation, \( s_c(T) = \int_{T_K}^{T} dT' \Delta c_p(T')/T' = \Delta c_p(T_g) T_g \left( \frac{1}{T_K} - \frac{1}{T} \right) \). Note that \( f_{eq}(T_g) = \phi_g - T_g s_c(T_g) \). The ideal glass state energy is equal to

\[
\phi_K = \phi_g - \Delta c_p(T_g) T_g \ln \frac{T_g}{T_K}.
\]

Consider the first term on the right-hand side of equation (D.1) and let \( \phi^0_{in}(T) \) be the bulk energy at \( T_g \). Then use the relation in equation (D.5) to obtain

\[
f_{eq}(T) - \phi_{in}(T, \sigma) = -\Delta c_p(T_g) T_g \left\{ \frac{T - T_K}{T_K} + \ln \frac{T_g}{T} \right\} - \kappa \frac{\sigma^2}{2G} V_{\text{bead}}.
\]

Substitute this result back into equation (D.1). The free energy becomes

\[
F(N, b, \sigma) = \left[ -\Delta c_p(T_g) T_g \left\{ \frac{T - T_K}{T_K} + \ln \frac{T_g}{T} \right\} - \kappa \frac{\sigma^2}{2G} V_{\text{bead}} \right] N + v_{\text{int}} b - k_B T \ln \Omega(N, b).
\]

If \( T \) is below \( T_K \), the excess energy is frozen at the state \( T = T_K \) and the configurational entropy vanishes

\[
F(N, b, \sigma) = \left[ -\Delta c_p(T_g) T_g \ln \frac{T_g}{T_K} - \kappa \frac{\sigma^2}{2G} V_{\text{bead}} \right] N + v_{\text{int}} b - k_B T \ln \Omega(N, b).
\]

In percolation clusters [153], for large \( N \), the number of lattice animals is approximately

\[
\Omega_{\text{perc}} \equiv \left( \frac{\alpha + 1}{\alpha} \right)^{\alpha+1} N \exp \left( -\frac{N^2 \phi}{2B^2 (\alpha - \alpha_c)^2} \right)
\]
where \( \alpha = t/N \), and \( t \) is the number of unoccupied sites bounding the occupied cluster. Follow the analysis by Stevenson, Schmalian, and Wolynes [111] in which \( v_{\text{int}}b \) and \( k_B T \ln \Omega_{\text{perc}} \) are carried out explicitly, we take the exponent \( \phi \) at mean field value of \( 1/2 \) and a lattice constant \( B = 1.124 \). The number of bonds \( b \) is directly related to \( t \) and should linearly depend on coordination number \( b \approx 1.68 tz/\zeta_{SC} \) [47], where \( \zeta_{SC} \) is the coordination number for the simple cubic lattice. Recall that the interaction energy \( v_{\text{int}} = (1/2)T_K(3/2)k_B \ln(\alpha_La^2/\pi e) = 3.6907k_B T_K/z \). The free energy in equation (D.8) is now a function of \( N \) and \( t \). Minimize this function with respect to \( t \), the most probable value of \( t \) is \( \bar{t} = \bar{\alpha} N \), where \( \bar{\alpha} = 3.10 \) at \( T = T_K \). At this most probable value, \( \Omega_{\text{perc}} \) becomes a simple exponential function, \( \Omega_{\text{perc}} \sim \lambda^N \), where \( \lambda = 6.82 \). Each term in equation (D.8) is now proportional to \( N \) and we can write

\[
F(N, b, \sigma) = \left[-\Delta c_p(T_g)T_g \ln \frac{T_g}{T_K} - \frac{\sigma^2}{2G} V_{\text{bead}} \right] N
\]

\[
+ v_{\text{int}} \frac{1.68 \zeta_{f.c.c.}}{\zeta_{SC}} \bar{\alpha} N - k_B TN \ln \lambda
\]

\[
= k_B TN \left\{ \left[-\Delta c_p(T_g)T_g \ln \frac{T_g}{T_K} \right] - \frac{1}{k_B T} \frac{\kappa \sigma^2}{2G} V_{\text{bead}} \right\}
\]

\[
+ \frac{v_{\text{int}}}{k_B T} \frac{1.68 \zeta_{f.c.c.}}{\zeta_{SC}} \bar{\alpha} - \ln \lambda \right\}. \quad (D.10)
\]

At the thresholding stress \( \sigma^* \) where \( F(N, \sigma^*) = 0 \), one finds

\[
\sigma^* = \sqrt{\frac{2Gk_B T}{\kappa V_{\text{bead}}} \left( \frac{v_{\text{int}}}{k_B T} \frac{1.68 \zeta_{f.c.c.}}{\zeta_{SC}} \bar{\alpha} - \ln \lambda \right) - \frac{\Delta c_p(T_g)T_g}{k_B T} \ln \frac{T_g}{T_K}}. \quad (D.12)
\]

or

\[
\sigma^* = \sqrt{\frac{2Gk_B T}{\kappa V_{\text{bead}}} \frac{v_{\text{int}}}{k_B T} \left( \frac{1.68 \zeta_{f.c.c.}}{\zeta_{SC}} \bar{\alpha} - \ln \lambda + \frac{\Delta c_p(T_g)T_g}{k_B T} \ln \frac{T_g}{T_K} \right)} \frac{k_B T}{v_{\text{int}}}. \quad (D.13)
\]

Substituting the numbers in the previous paragraph, we finally obtain equation (4)

\[
\sigma^* = \sqrt{\frac{2Gk_B T}{\kappa V_{\text{bead}}} \left[ \frac{3.20 T_K}{T} - 1.91 \right] - \frac{\Delta c_p(T_g)T_g}{k_B T} \ln \frac{T_g}{T_K}}. \quad (D.14)
\]
Appendix E

Experimental Data and Numerical Predictions for the Strength of Glasses

In Table S1 we summarize the input thermodynamic data and measured strengths as well as their sources in the literature. The bead count is obtained as described by Lubchenko and Wolynes [20] and Stevenson and Wolynes [47] using the melting entropy. All strength measurements were all made at room temperature 300 K.
Figure E.1: The ratio between strength and shear moduli versus heat capacity change at $T_g$ and the glass transition temperature $T_g$. The black circles are the RFOT theory predictions and the red triangles are the measured values. Typical value of crystal strength (violet solid line), Frenkel strength (blue solid line) and strength in the limit $T \to 0, T_g \to T_K$ (black solid line) are also shown in comparison.

We also show here in Figure E.2 the comparison of measured elastic moduli with those predicted via the relation $G_{cal} = 24.9 k_B T_m / V_{bead}$ from thermodynamic data along with the Lindemann relation and the assignment $T_A \approx T_m$. The predictions for strength use the measured $G$ when available but use the value from Lindemann relation and $T_A \approx T_m$. 
Figure E.2: Comparison between the measured elastic moduli and those calculated using the Lindemann criterion.
<table>
<thead>
<tr>
<th>Glasses</th>
<th>$\rho$</th>
<th>$\Delta H_M$</th>
<th>$N_{\text{bead}}$</th>
<th>$T_K$</th>
<th>$T_g$</th>
<th>$T_M$</th>
<th>$\Delta c_p$</th>
<th>$G_{\text{expt}}$</th>
<th>$\sigma^*_{\text{expt}}$</th>
<th>$\sigma^*_{\text{pred}}$</th>
<th>Refs.</th>
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<tbody>
<tr>
<td>PMMA</td>
<td>1188</td>
<td>4.64</td>
<td>0.84</td>
<td>337</td>
<td>372</td>
<td>397</td>
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<td>3.10</td>
<td>0.07</td>
<td>0.08</td>
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<td>SiO$_2$</td>
<td>2648</td>
<td>9.6</td>
<td>0.78</td>
<td>870</td>
<td>1500</td>
<td>1995</td>
<td>1.67</td>
<td>31.40</td>
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<td>3978</td>
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<td>19.60</td>
<td>0.8</td>
<td>1.29</td>
<td>[165, 166, 167, 168, 169, 170, 171, 172]</td>
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<td>3284</td>
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<td>23.60</td>
<td>0.88</td>
<td>0.92</td>
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<td>-</td>
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<td>746</td>
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<td>-</td>
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<td>0.96</td>
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<td>660</td>
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<td>-</td>
<td>0.6</td>
<td>0.48</td>
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<td>-</td>
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<td>0.60</td>
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<td>570</td>
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<td>497</td>
<td>593</td>
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<td>33.00</td>
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<td>553</td>
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<td>1.5</td>
<td>3.11</td>
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<tr>
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<td>8.2</td>
<td>0.63</td>
<td>553</td>
<td>620</td>
<td>937</td>
<td>4.03</td>
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<td>2.26</td>
<td>[165, 186, 167, 107, 170, 187, 106]</td>
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<td>34.70</td>
<td>1.83</td>
<td>2.68</td>
<td>[165, 166, 182, 107, 168, 188, 189, 183]</td>
</tr>
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<td>8.2</td>
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<td>675</td>
<td>1072</td>
<td>4.35</td>
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<td>33.00</td>
<td>1.7</td>
<td>2.16</td>
<td>[170, 177, 167]</td>
</tr>
</tbody>
</table>

Table E.1: Experimental data and theoretical results of 19 glasses: density $\rho$ (kg/m$^3$), latent heat of fusion $\Delta H_M$ (kJ/mol K), number of bead $N_{\text{bead}}$, Kauzmann temperature $T_K$ (K), glass transition temperature $T_g$ (K), melting temperature $T_M$ (K), heat capacity change at glass transition temperature $\Delta c_p$ (J/mol K), experimental shear modulus $G_{\text{expt}}$ (GPa), measured strength $\sigma^*_{\text{expt}}$ (GPa), and theoretical estimated strength $\sigma^*_{\text{pred}}$ (GPa).
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[186] R. Busch, Y. J. Kim, and W. L. Johnson, “Thermodynamics and kinetics of the undercooled liquid and the glass transition of the Zr$_{41.2}$Ti$_{13.8}$Cu$_{12.5}$Ni$_{10}$Be$_{22.5}$ alloy,” *Journal of applied physics*, vol. 77, no. 8, pp. 4039–4043, 1995.


