Transition zone theory of the glass transition

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ABSTRACT

An energy-based theory of the glass transition is described and validated by evaluation of crystallization and viscosity data of sixteen diverse systems, ranging from the fragile *o*-terphenyl to the strong SiO_2 glass formers, including glass formation in non-crystallizing polymers. Transition zone theory demonstrates an inverse temperature dependence of the entropy of activation for crystallization and viscous relaxation which results in a temperature at which their free energies of activation are equivalent. Below this temperature there is a greater probability of crystallization than of relaxation. Under such conditions, crystal-like organization can propagate only over the internal length scales for which the system has relaxed, i.e. a few nanometers. However, that structural organization makes the barrier to bulk liquid relaxation insurmountable, resulting in glass formation. The temperature of the crystallization-relaxation free energy of activation equivalence point, defines the glass transition temperature. The temperature dependent slope of the free energy of activation for relaxation at the equivalence point reflects the fragility of the system. The time-temperature dependence of viscous relaxation shifts the crystallization-relaxation free energy of activation equivalence point, consistent with the sample history dependence of T_g. Crystal-like formation over nanometer-length scales, which can still occur below T_g, is shown to account for glass aging.

1. Introduction

Glasses, both naturally occurring and synthetic, have captured human imagination for millennia, with artisans and industrialists perfecting strategies to fabricate and manipulate them for diverse purposes. Nevertheless, an understanding of the atomic and molecular processes and structures that create and define the glassy state has been much more difficult to resolve [1–11]. Divergent viewpoints wrestle with the question whether the glass transition is a kinetic or thermodynamic phenomenon. Many presume the definition of the glass transition temperature (T_g) to be arbitrary, occurring when the average relaxation time slows to about $\tau = 10^2$ s or the viscosity (η) increases to 10^{13} Poise. Some authors have also suggested that the glassy slowing down ought to be accompanied by the growth of some internal length scale [5]. Furthermore, while a liquid's internal relaxation rate may be an intrinsic property, the observed relaxation or viscosity is significantly dependent on the frequency of the experimental probe used to measure it. As a result, agreement on standard experimental conditions from which to report T_g is required; typically heat/cool at 10 K/min for DSC, 5 K/min for dilatometry [9]. Nevertheless, most theories seem to recognize some "ideal" glass for which the "ideal" T_g is likely related to the Kauzmann temperature, T_K, where the configurational entropy of the supercooled liquid extrapolates to that corresponding to the crystalline state [12].

A majority of theories used to describe the glass transition are significantly based on the classic Vogel-Fulcher-Tammann (VFT) theory of liquid relaxation and viscosity [13–15]. VFT theory reasonably describes viscous relaxation within 50 to 100 K above T_g, but requires some cross-over between distinct VFT regions, or between VFT and Arrhenius behavior to describe viscous relaxation in higher temperature liquids [1,16]. However, our recently articulated Transition Zone Theory (TZT) [17], which integrates Kauzmann's configurational entropy [12] with Adam and Gibbs conception of cooperativity [18] to establish a condensed matter analog to Eyring's transition state theory [19], more accurately describes viscous relaxation across the liquid temperature range from T_g to the critical temperature T_c. Based on an understanding of the distinct temperature dependence of configurational entropy and cooperativity, TZT also accurately describes the rate of crystal growth across the temperature range from T_g to T_m [17]. Key to TZT is a recognition that because of the temperature dependence of a system's configurational entropy and cooperativity, the enthalpic and entropic activation parameters also are temperature dependent. Interestingly, an inverse temperature dependence is observed for the entropy of activation for crystallization and viscous relaxation, which, as will be demonstrated herein, generally results in a temperature at which the free energies of activation for crystallization and viscous relaxation are

Abbreviations

T_g	glass transition temperature
η	shear viscosity
T_K	Kauzmann temperature
VFT	Volgel-Fulcher-Tamman theory of liquid relaxation and viscosity
TZT	transition zone theory
$()_c$	subscript c refers to crystal growth
$()_{rlx}$	subscript rlx refers to viscous relaxation
APC	aperiodic crystallization
CTON	chemically and topologically ordered network
T_{max}	temperature of maximum rate of crystal growth
$\Delta H^{\ddagger}$	enthalpy of activation
$\Delta S^{\ddagger}$	entropy of activation
$\Delta G^{\ddagger}$	free energy of activation
S_{config}	configurational entropy
W	number of configurations: $W^{\ddagger}$ of the activated state, W_{rct} of the reactant
λ	characteristic wavelength of vibrations that lead to crystal growth, equal to twice the average lattice dimension

v_{pb}	velocity of the phase boundary of a phase transition
ΔH^*	intrinsic (i.e. temperature independent) component of the enthalpy of activation
ΔS^*	intrinsic (i.e. temperature independent) component of the enthalpy of activation
z	a fitting parameter of TZT that modulates the temperature dependence of $\Delta S^{\ddagger}$
OTP	o-terphenyl
ρ	density
v_c	characteristic velocity; the speed of sound for most systems
tTS	time Temperature Superposition
T_{13}	temperature at which the viscosity reaches 10^{13} Poise
T_0	fitting temperature parameter from VFT theory, similar in value to T_K
$f(\Delta v)$	frequency dependent perturbation
$f(\Delta T)$	temperature dependent perturbation
NOC	nano ordered crystal
$T_K{'}$	Kauzamann-type temperature where nonergodic liquid and APC are iso-entropic
GC	glass-to-crystal transition

equivalent. This observation led us to further explore the extent to which TZT for relaxation and crystallization (TZT_{rlx} and TZT_c) can be used to describe both the slowing of viscous relaxation and growth over some internal length scales, which subsequently defines the glass transition. As described below, the free energy equivalence temperature for viscous relaxation and crystal growth is remarkably equivalent to experimentally reported glass transition temperatures.

Specifically in this manuscript, in Section 2 we provide background theory that summarizes the most germane aspects of TZT for Section 2.1 crystal growth rates and Section 2.2 viscous relaxation, exemplified by fitting to experimental data for o-terphenyl. Section 3 describes the TZT approach to the glass transition by fitting our proposed model to fourteen diverse systems, from the fragile o-terphenyl to the strong SiO_2. We begin with, Section 3.1, an articulation of the transition zone theory of glass formation, TZT_{glass}, for which we: Section 3.1.1 demonstrate that the temperature of the equivalence point in the free energy of activation for crystallization and viscous relaxation is equivalent to T_g; Section 3.1.2 demonstrate how this physically defined glass transition relates to the previous arbitrary definition as the temperature at which the viscosity reaches 10^{13} Poise; Section 3.1.3 show the time-temperature superposition of viscous relaxation accounts for the experiment-dependent range of observed T_g; Section 3.1.4 suggest that below the crystallization-viscosity free energy equivalence point where the probability of crystallization is greater than the probability of viscous relaxation, aperiodic crystallization (APC), analogous to that described by random first-order transition theory of glass formation [6,7,10,20,21], or chemically and topologically ordered network formation (CTON) [22], likely occurs, consistent with glass aging. Finally, Section 3.2 the glass transition in non-crystallizing polymer systems is described as the intersection of the free energy of activation for viscous relaxation and APC formation, with atactic polystyrene and poly-propyleneoxide as example systems.

2. Background theory

While transition state theory [23] provides an effective framework with which to understand molecular reactions in dilute media, it does not adequately describe reactivity in the condensed phase. The unique temperature dependence of condensed matter reactions (e.g. the rate of crystallization increases above T_g to a maximum, T_{max}, then slows as T_m is approached) results in descriptions of temperature regimes said to exhibit Arrhenius and non-Arrhenius behavior. Both Arrhenius [23]

and Eyring [19] approaches to transition state theory presume temperature independent activation constants, E_a, or $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively. However, as Kauzmann described, the configurational entropy, S_{config}, of condensed matter systems is temperature dependent, with $\Delta S_{liquid\text{-}solid} \rightarrow 0$ at the Kauzmann temperature, T_K [12]. We noted the further condition that $\Delta S_{liquid\text{-}gas} \rightarrow 0$ at the critical temperature, T_c, the upper limiting temperature at which a liquid can exist [17]. Recognizing that the activation parameters for condensed matter reactions must similarly be temperature dependent led to our development of transition zone theory, TZT. A transition zone being the zone of material involved in the transition configuration of a collective process, such as occurs in condensed matter reactions, as opposed to a transition state which describes discrete transition configurations observed in dilute media. Full details of the transition zone theory for crystal growth, TZT_c, and viscous relaxation, TZT_{rlx}, can be found in our previous manuscript [17]. However, principles of TZT that are essential to understand the glass transition are summarized here.

Like Eyring's molecular based transition state theory [19], TZT is based on the attempt frequency and probability of the transforming events. Instead of events being independent molecular collisions, i.e. a transition state, TZT recognizes that the structural reorganization required for crystallization and viscous relaxation requires Adam-Gibbs-type [18] cooperative interactions of phonons [24,25], i.e. a transition zone. Both theories recognize the probability of the transforming events to be described by $exp\left(\frac{-\Delta G^{\ddagger}}{RT}\right)$. Furthermore, Boltzmann's relation defines $\Delta S^{\ddagger} = R\ln\left(\frac{W^{\ddagger}}{W_{rct}}\right)$, where $W^{\ddagger}$ is the number of configurations in the activated state (zone) and W_{rct} is the number of configurations in the reactant state (zone). In dilute media, the ratio $W^{\ddagger}/W_{rct}$ is essentially temperature independent, leading to the constant $\Delta S^{\ddagger}$ of transition state theory. By contrast, this ratio is significantly temperature dependent for condensed phase reactions, and thus a temperature dependent $\Delta S^{\ddagger}$ becomes a primary unique feature of TZT.

2.1. Transition zone theory of crystallization, TZT_c

The attempt frequency for crystallization is the product of the number of lattice vibrational modes that lead to formation of the transition zone for crystal growth, $\frac{k_B T}{h v}$, and the velocity of the transition zone, λv, where λ is a characteristic wavelength of vibrations that lead to growth, equal to twice the average lattice dimension. Thus, the TZT_c prefactor is $\lambda \frac{k_B T}{h}$.