Thermally Activated Processes in Polymer Glasses

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A derivation is given for the Vogel-Fulcher-Tammann thermal activation law for the glassy state of a bulk polymer. Our microscopic considerations involve the entropy of closed polymer molecular chains (i.e. polymer closed strings). For thin film polymer glasses, one obtains open polymer strings in that the boundary surfaces serve as possible string endpoint locations. The Vogel-Fulcher-Tammann thermal activation law thereby holds true for a bulk polymer glass but is modified in the neighborhood of the boundaries of thin film polymers.

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INTRODUCTION

There has been considerable recent interest on the general dynamics of the glass transitions in bulk polymer systems[1, 2, 3, 4, 5, 6, 7]. A central experimental law which controls the rate of transition was long ago formulated by Vogel, Fulcher and Tammann[8]; The empirical VFT law of transition rates reads

$$\Gamma = \nu \exp \left\{ -\Phi / k_B(T - T_0) \right\}, \quad (1)$$

wherein $\Phi$ is the free energy of thermal activation. The VFT thermal activation law is quite similar to the well known Arrhenius[9] thermal activation law except for the temperature singularity in the denominator on the right hand side of Eq.(1). The singularity occurs at a dynamical temperature $T_0$ which is somewhat lower than the thermodynamic glass transition temperature $T_g$. The singularity is thereby never quite attained. Nevertheless, the critical slowing down of the VFT Eq.(1) is experimentally well obeyed in bulk polymer glasses. There exist somewhat different physical views[10, 11, 12] as to why the VFT law might theoretically be true. Nevertheless there is presently no agreed upon theory of Eq.(1).

Our purpose is to derive the VFT thermal law through the following quite simple quantum mechanical considerations. The transition rate per unit time for an activated process involves an absolute squared transition amplitude (matrix element) times a density of final states. The logarithm of the density of final states represents the final entropy. Thus, the quantum mechanical rule for computing transition rates is that

$$\Gamma = \nu_\infty \exp[S(E)/k_B], \quad (2)$$

wherein $S(E)$ is the entropy of activation to a state with energy $E$. The theoretical problem is to deduce the nature of the excitations[13, 14, 15] and compute the entropy of activation from the the logarithm of the final state phase space magnitude

$$S(E) = k_B \ln \Omega(E). \quad (3)$$

FIG. 1: Schematically shown are two closed mobile chains of polymers which occur as “bulk closed strings”. Also schematically shown are three polymer chains which begin and end on the surface boundaries of the bulk polymer and constitute “open strings”.

The polymer glass excitation configurations pictured in FIG.1 are of two types: (i) There are - in the bulk of the polymer - closed chains of atoms referred to as closed strings. (ii) Also, there are open polymer chains which begin and end on the boundary surfaces of the bulk polymer and are referred to as open strings. It will be shown below that the closed strings have an entropy obeying the VFT thermal activation Eq.(1). On the other hand, the open string configurations with end points in the neighbourhood of surface boundaries obey shifted thermal activation laws.

The distinction between the thermal activation properties of open and closed strings is crucial for an understanding of surface effects which are of importance for thin films[19, 20, 21]. The VFT thermal activation law holds only for the bulk polymer. By contrast, the dynamical singularity temperature $T_0$ decreases as the ratio of boundary surface area to the bulk volume, $L^{-1}$, increases. Consequently, the singularity temperature is
sharply lowered when $L$ is decreased to a few nanometers.

**ENTROPY OF CLOSED MOBILE CHAINS**

Closed polymer chains in the form of “polygons” are treated as a self avoiding random polygons. The number of closed self avoiding polygon polymer chains containing $n$ links is thought to obey

$$\Omega_n = \tilde{\Omega} n^{(3-\alpha)} \mu^n. \quad (4)$$

Wherein $\mu$ denotes the connectivity. The de Gennes scaling law in $d$ dimensions for the exponent $\alpha$ is given by

$$3-\alpha = \left\{ 1 + \frac{d}{D} \right\} \quad (5)$$

wherein $D$ is the fractal dimension of the complete closed chain configuration. In mean field theory we have

$$d = 3 \Rightarrow D \approx \frac{5}{3} \Rightarrow \alpha \approx \frac{1}{5}. \quad (6)$$

If $\varepsilon$ denotes the activation energy per link for a mobile closed chain (closed string), then the energy

$$E = \varepsilon n \quad (7)$$
determines the entropy via Eqs. (3), (4) and (7) according to

$$S(E) = \tilde{S} + \frac{E}{T_0} - (3-\alpha) k_B \ln \left( \frac{E}{\varepsilon} \right) \quad (8)$$

wherein

$$\tilde{S} = k_B \ln \tilde{\Omega}, \quad k_B T_0 = \frac{\varepsilon}{\ln \mu}. \quad (9)$$

The activation entropy as a function of energy exhibits a minimum as shown in FIG. 2. For stable entropy functions, the maximum entropy principle dictates upward convexity while metastable entropy functions exhibit downward convexity. Since the density of final states $\propto e^{S/k_B}$, rates become slower as the minimum activation entropy is approached.

In terms of the temperature $T$,

$$\frac{1}{T} = \frac{dS(E)}{dE} = \frac{1}{T_0} - \frac{(3-\alpha) k_B}{E}, \quad (10)$$

we have at $T_0$ the activated energy singularity

$$E = \left( \frac{(3-\alpha) k_B T T_0}{T - T_0} \right). \quad (11)$$

**Activated Entropy**

FIG. 2: The activation entropy of mobile closed strings, $\Delta S(E) = S(E) - \tilde{S} - (3-\alpha) k_B \ln(\ln \mu)$, is plotted as a function of energy. The entropy function is convex downward indicating a metastable entropy activation. There is a slower rate as the entropy is pushed toward a minimum value.

Eqs. (6), (8) and (11) imply

$$S = S_\infty + k_B \left[ \frac{(3-\alpha) T_0}{T - T_0} \right] - (3-\alpha) k_B \ln \left[ \frac{T}{(T - T_0)} \right]. \quad (12)$$

Using Eqs. (2), (6) and (12), we may now complete the proof that the closed chain activation law has the VFT form given by Eq. (1). Explicitly, we have

$$\Gamma = \nu e^{-\Phi/k_B(T - T_0)}, \quad \Phi = (3-\alpha) k_B T_0 \approx 2.8 k_B T_0,$$

$$S_\infty \approx \tilde{S} + 2.8 k_B$$

$$\nu \approx \left[ \frac{(T - T_0)}{T} \right]^{2.8} \nu_\infty e^{S_\infty/k_B}. \quad (13)$$

In practice, the VFT activation process is often observed by measuring viscosity,

$$\eta \approx \rho b^2 T \approx \rho b^2 \nu e^{-\Phi/k_B(T - T_0)}, \quad (14)$$

wherein $\rho$ is the mass density and $b$ is the length scale of the polymer links. In this regard, the prediction for the activation free energy $\Phi \approx 2.8 k_B T_0$ is subject to an experimental test of the scaling critical index in Eq. (6).

**SURFACE EFFECTS**

Consider the problem of how much activation energy would be required to remove a given section of chain from the condensed matter piece of polymer. If the given section of chain were deep within the polymer, the removal
would be quite difficult. For example, if one exerted a force on the given chain section, then it would become knotted with other polymer chain sections and would be rendered immobile. On the other hand, if the given section of chain was entirely located in the neighborhood of the surface boundary of the polymer, then it would be relatively easier to peel the chain off the surface.

Let us consider, in more detail, the activation energy to slide a section of polymer chain along a given path. Such an activation energy has been denoted above as $\varepsilon$ per link of the chain section. Furthermore, let $z$ denote the distance from a chain link to the boundary surface. By the above physical arguments we expect $\varepsilon(z)$ to sharply decrease as $z \to 0$. From Eq. (14) we expect, for uniform connectivity ($ln \mu \approx $ const.), the dynamical singularity temperature to be a decreasing function of $z$ varying as

$$\frac{T_0(z)}{T_0} \approx \frac{\varepsilon(z)}{\varepsilon} \quad \text{and} \quad \frac{dT_0(z)}{dz} < 0 \quad \text{as} \quad z \to 0^+. \quad (15)$$

In a local density theory, $\varepsilon(z)$ may be parameterized by

$$T_0(z) \approx T_0 \tanh^2(z/\xi), \quad (16)$$

in which the coherence length is related to the density

$$\xi \sim \rho^{-\nu(3\nu-1)} \quad \text{wherein} \quad \nu = D^{-1} \approx \frac{3}{5}. \quad (17)$$

The $\lim_{z \to 0^+} T_0(z) = 0$ relation invalidates the VFT Eq. (11) for the case of very thin polymer films.

**CONCLUSION**

A derivation has been provided for VFT activated transition rates in bulk polymer glasses. Our derivation depends on the micro-canonical counting of the number of closed polymer chain configurations within the bulk glassy system. The configuration counting is mapped into the self avoiding polygon problem. The activation energy $\varepsilon$ per link determining the chain mobility also determines the dynamical glass transition temperature in the empirical VFT law. The critical indices employed are calculated as in Flory’s theory. The chain movements also lend strong support to “co-operative” motion inside the bulk.

It is also to be stressed that the dynamical glass transition temperature, $T_0$, varies with the distance from the surface boundary through that a coherence length scale of about a few nanometers. This surface effect is due to the fact polymer strings localized near the surface boundary are more mobile than the polymer chains embedded in the bulk. For sufficiently thin films, the VFT activation law thereby becomes modified as in Eqs. (15) - (17).