

ICFP M2 – SOFT MATTER PHYSICS

Tutorial 9. Glass transition in thin polymer films

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According to Anderson, the deepest and most interesting unsolved problem in solid-state physics is probably the glass transition. Fundamental to glass formation are the suggestions that particles are increasingly crowded, and relaxation requires the cooperative participation of a growing number of particles. The associated existence of a length scale for cooperative rearrangement has led to tremendous interest in confined glass formers. Perhaps, the most active example is the study of glassy polymer films where fascinating observations have been made – such as the sharp reductions of the glass-transition temperature for free-standing polystyrene films with large molecular weights. One tentative mechanism based on a reptation-like sliding motion has been sketched by de Gennes. Here, we present the latter after having revisited the two classical bulk concepts of free volume and cooperativity.

I Free volume

One experimental fact associated with the glass transition of polymer melts is that their viscosity η increases tremendously with respect to the high-temperature reference η_∞ , over a narrow temperature region. Typically, it follows the empirical Vogel-Fulcher-Tammann (VFT) form : $\log(\eta/\eta_\infty) \propto 1/(T - T_V)$ for a temperature T near T_V – the so-called Vogel temperature where the extrapolated viscosity would diverge.

- 1 We recall that the temperature dependence of the viscosity for a pure liquid far from its glass transition is of Arrhenius type. Explain the molecular origin of such a behaviour.
- 2 The volume V of a liquid typically depends linearly on temperature, in some temperature range. Express the relation $V(T)$ using the expansion coefficient α .
- 3 The concept of free volume was introduced as the volume V_f left for molecular rearrangements, once the actual molecular volume is removed. Assuming the free volume to vanish at a finite temperature T_0 due to molecular crowding, express the free-volume fraction as a function of temperature, near T_0 .
- 4 In the fifties, the Doolittle Ansatz $\eta \propto \exp(V/V_f)$ was proposed. Deduce $\eta(T)$ and comment.
- 5 Microscopically, give the typical free volume v_f per monomer of size a , and propose a free-volume probability for a molecular motion requiring a volume w . The molecular time scale being τ_0 (~ 10 ps), express the time scale τ for a typical relaxation to occur.

- 6 The glass transition being empirically associated to a given (large) time scale (\sim few hours), define the glass-transition temperature T_g .
- 7 What are the limitations of such a description?

II Cooperativity

In 1965, a seminal article published by Adam and Gibbs introduced the concept of cooperativity. Let us divide a mole of supercooled liquid into an ensemble of N independent, identical, and distinct subsystems, each containing z monomers. A given subsystem is characterized by a volume V and an energy E , and is connected to the ambient reservoir at temperature T and pressure P .

- 1 Write the partition function for one subsystem and define the chemical potential μ .
- 2 The cooperative rearrangement of a given subsystem is only possible for certain E and V values. Define the associated reduced partition function, and the corresponding new chemical potential $\mu' = \mu + \Delta\mu$, and express the probability of cooperative relaxation of a subsystem containing z monomers.
- 3 Relaxation of a subsystem is only possible if there are at least two available configurations. Express the minimal configurational entropy of a subsystem and, by extensivity, deduce the minimal value of z as a function of the (molar) configurational entropy S_c of the complete system.
- 4 Due to molecular crowding, we expect the chemical-potential barriers to be much higher than thermal energy. By summing on the possible values of z , show that the total probability of rearrangement behaves as $\sim \exp[-C/(TS_c)]$, where C is a constant.
- 5 One can define S_c as the difference of molar entropy between the supercooled liquid and the crystalline state. We assume the (molar) heat capacity difference ΔC_p (at constant pressure) between the two states to be independent of temperature in the range of interest; obtain $S_c(T)$.
- 6 Kauzmann postulated the existence of a finite temperature T_K at which the configurational entropy vanishes. Describe the total probability of rearrangement in the vicinity of T_K . Comment.

III Sliding model

When the glass-forming liquid is made of polymer chains of N monomers ($N \gg 1$), one can imagine a secondary, reptation-like, relaxation mechanism along one chain : if a given monomer happens to move, the monomer i next to it along the chain can follow through an easier jump (*i.e.* involving a smaller volume w_i).

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- 1** Assuming all the successive jumps along the chain to be independent, and w_i to be Gaussian-tail-distributed with a standard deviation $w_0 \ll a^3$, calculate the average relaxation time along one chain.
- 2** What about the chain ends? Conclude on the efficiency of this mechanism in the bulk.
- 3** Considering now a freestanding film of thickness h , explain when and how the interfaces can modify notably the previous conclusion through bridges.
- 4** What is the typical size g of relevant bridges? Express the relaxation time for such objects.
- 5** Define and calculate the associated effective glass-transition temperature.
- 6** Estimate the critical film thickness h^* below which the sliding mechanism reduces the glass-transition temperature with respect to the bulk value.
- 7** Discuss the different regimes induced by the combination of all the sizes involved; and conclude.