ICFP M2 – SOFT MATTER PHYSICS
Tutorial 9. Introduction to the glass transition

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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 triggered an important research activity. Here, we wish to revisit the two classical 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 : $\log(\eta/\eta_\infty) \propto 1/(T - T_\mathrm{V})$ 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 $\eta \propto \exp(V/V_\mathrm{f})$ 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 ($\sim$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 $\sim \exp[-C/(TS_\mathrm{c})]$, where C is a constant.

5 On 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 $S_\mathrm{c}(T)$.

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.