120831 Quiz 1 Polymer Properties

1) Paul Flory stated that the properties we associate with polymers and the definition of polymers involves chain-like molecules that display many conformations associated with thermal fluctuations. Thermal fluctuations are said to "probe conformational space".
   a) What is are thermal fluctuations?
   b) Explain how spring constant of a polymer chain is associated with the conformations of the chain.
   c) What happens to the chain spring constant at absolute zero?
   d) Explain the phrase "probe conformational space" in the context of thermal fluctuations (as best you can).
   e) Polymers are described by statistical parameters such as the root-mean-square (RMS) end to end distance, $\langle R^2 \rangle^{1/2}$. Is there a relationship between thermal fluctuations and the need to use statistics to describe polymers? Explain your answer.

2) In *PRL* **66** 2758-61 (1991) Hu, Carson and Granick found that the viscosity of low molecular weight linear (dodecane) and cyclic (octamethylcyclotetrasiloxane) fluids display shear thinning behavior in extremely thin films with film thicknesses on the order of 3-4 times the molecular thickness. The following two graphs show their results.

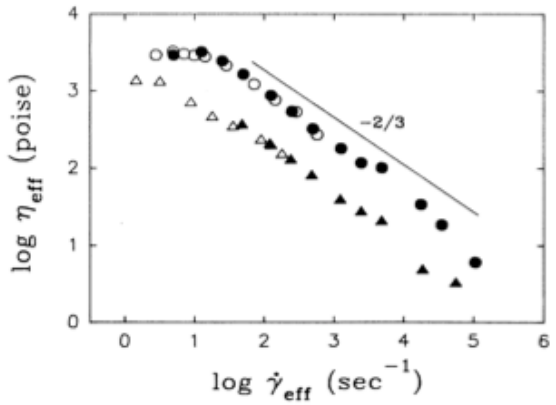

FIG. 2. Log-log representation of changes in the effective viscosity as a function of strain rate. Circles: dodecane film specified in Fig. 1. Triangles: OMCTS film of thickness 2.7 nm and net normal pressure 0.14 MPa. Open symbols: amplitude varied at constant frequency. Solid symbols: frequency varied at constant amplitude.

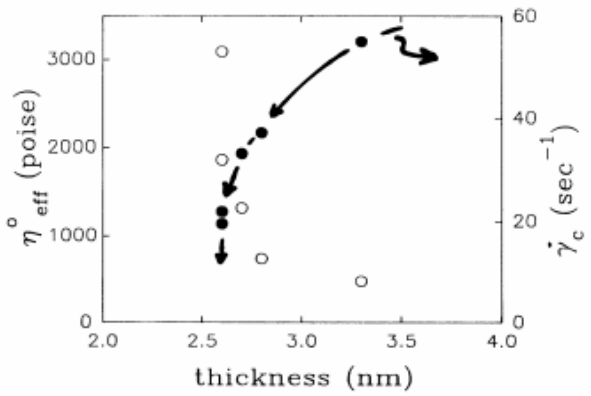

FIG. 3. Effective limiting viscosity at low shear rate (open circles), and critical effective strain rate at onset of nonlinear behavior (solid circles), plotted against film thickness for confined dodecane films. Arrows indicate direction of increasing net normal pressure.

   a) How does the behavior, shown in Fig. 2 compare with the viscosity of long-chain polymers? Explain the relationship between these low molecular weight molecules in confined geometries and long-chain polymers in this context.
   b) What do you think $\dot{\gamma}_c$ is in Fig. 3 and how would it relate to a time constant for this system? Explain the behavior seen in Fig. 3 for $\dot{\gamma}_c$.
   c) What could the time constant reflect in this system and how would that compare with the time constant for a long-chain polymer?
   d) What do you think η^{0}_{eff} is in Fig. 3 (explain with a graph) and what kind of plot would you rather see for this parameter (Granick has use a linear-linear plot in Fig. 3).
   e) How do thermal fluctuations relate to the time constant?

ANSWERS: 120831 Quiz 1 Polymer Properties

1) a) The thermodynamic features of a system deviate from their equilibrium values. In this way systems can explore differences in free energy between different states and find points of lowest free energy. For example, atoms in a crystal are constantly vibrating due to thermal energy leading to fluctuations in density as a function of position in space and in time for a give position. Thermal fluctuations are the basis for thermodynamics and especially for statistical thermodynamics.

b) The conformation of a polymer chain is subject to thermal fluctuations which means that the chain is constantly changing its conformation and weighing the change in free energy versus this change to determine the conformation of lowest free energy. This motion of a chain means that there is a net retractive force that opposes stretching of the chain out of the most random state (state of highest entropy). This entropic force is the basis of a chain spring constant.

c) At absolute zero the entropy of the chain is zero and the spring constant would theoretically go to zero. Similarly an ideal gas has no pressure at absolute zero.

d) Thermal fluctuations cause the chain to vary its conformation, this leads to a chain of different free energy. The system will favor a lower free energy. Conformational space is space made up of the various chain conformations and measuring the free energy of the chain. Conformational space would have various peaks and local minima as well as a global minimum in free energy. The chain explores this space through thermal fluctuations in the chain conformation.

e) There is a direct link between the presence of thermal fluctuations that cause the chain to display a myriad of conformations and the stastical distribution in these conformations that require a stasticial description.

2) a) The behavior is reminiscent of shear thinning in polymers in that it displays a low-shear rate Newtonian plateau and a power-law decay at high shear rate. The power law decay is weaker than in polymers. This may be associated with the 2d nature of the constraints put on the system, in polymers the entanglement constraints are 3d for instance. For both systems some type of molecular orientation may occur that leads to shear thinning. The constraint of a 2d system restricts molecular rotation in the low molecular weight systems preventing thermal relaxation of molecular orientation in the shear flow. For polymers chains entanglements constrain the molecular relaxation.

b) $\dot{\gamma}_c$ is the shear rate at the transition from the Newtonian plateau to the power-law decay. This is the inverse of the time constant for the molecules. The shear rate at this transition decreases with decreasing film thickness as the constraint on the molecules increases, at about 2.5 nm the molecules can not relax and the shear rate extrapolates to 0 with an infinite time constant for a glassy system (glass transition). Thicker films have a smaller time constant and a larger critical shear rate.

c) The time constant reflects the time needed for the molecules to relax to an unperturbed or unoriented state. The time constant for a polymer is the time for the polymer chains to relax to the unperturbed state. The difference lies in the specifics of the constraints that prevent relaxation. For polymers the constrains are entanglements and for the low molecular weight molecules it is the confinement of the thin film that leads to a constraint on relaxation through thermal fluctuations.

d) η_{eff}^{0} is the viscosity in the Newtonian plateau regime at low rate of strain. We expect a power-law dependence of the zero shear rate viscosity similar to that seen for polymers in molecular weight so a log-log plot would be more appropriate. The slope of a log-log plot could give information of the mechanism of constraint relaxation in these systems.

e) The process by which constraints are released is through thermal fluctuations of molecular conformations or orientations.