Polymer Physics
Quiz 1
January 14, 2021 (Due January 16)

Kos PI, Ivanov VA, Chertovich AV *Crystallization of semiflexible polymers in melts and solutions* Soft Mat. **17** 2392-2403 (2021) used dissipative particle dynamics (DPD) coarse grain simulations to describe the impact of entanglements on the crystallization process and the lamellar thickness which Kos calls "crystallite size". Luo C, Kröger M, Sommer J-U *Entanglements and Crystallization of Concentrated Polymer Solutions: Molecular Dynamics Simulations* Macromolecules **49** 9017-9025 (2016) used molecular dynamics (MD) simulations to study the relationship between entanglement length (molar mass between entanglements, N_e) and features of the chains and crystals, particularly the crystalline stem length or thickness.

a) Polymer crystals differ from oligomers (intermediate molecular weight chains) due to chain folding. Lauritzen JI and Hoffman JD J. Res. Nat. Bur. Std. 64A 73 (1960) *Theory of Formation of Polymer Crystals with Folded Chains in Dilute Solution* derived a function, eq. 104 on page 93, that determines the thickness of polymer crystals based on their crystallization temperature. Hoffman and Lauritzen equation can be obtained from an expression for the Gibbs free energy that includes a surface term for the two lamellar fold surfaces of a lamellar crystal, $\Delta G = V(\Delta H - T\Delta S) + A(2\sigma)$ where the last term is for the surface area and surface fold energy and the first term is for the bulk enthalpy of crystallization. At equilibrium for a crystal of infinite thickness there is no surface and $\Delta G = 0$ so $\Delta S = \Delta H/T_\infty$. Derive the Hoffman-Lauritzen equation for polymer crystal thickness by setting $\Delta G = 0$ at the quasi-equilibrium point for a crystal crystallized at a temperature T (assume lateral size L (and A) is constant).

b) The entanglement molecular weight, N_e, is determined from a log-log plot of the zero-shear viscosity, η_0, versus the polymer molecular weight, N. Explain how η_0 is obtained and how N_e is determined. Explain why shear thinning occurs for polymers.

c) DPD simulations of Kos contain only repulsive interactions between chains (Eq. (1) and the discussion following it on page 2394) so the approach must ignore the fundamental feature of phase separation, an attractive interaction between chains. Kos states: "*Connectivity of monomer beads in chains, intrachain stiffness and topological restrictions (entanglements of non-phantom chains) are the three ''whales'' on whom the crystallization behavior in our model ''rests''.*" (sentence bridging 2393 and 2394). Despite this limitation, Kos is able to generate polymer "crystals" as seen in figure 3 page 2396 by manipulating the repulsive force term in Eq. (1) for the polymer beads and the solvent beads to lead to polymer phase separation. In the Kos crystallization, chains straighten out due to the terms in Eq. (1), they align with each other in a liquid crystalline transition (nematic transition) and form domains that resemble a polymer crystal. There is no inherent enthalpy of crystallization or surface-fold energy such as in the Hoffman/Lauritzen model since there is no attractive enthalpy whatsoever.
Figure 7a on page 2399 indicates the conformation of the chains in the Kos simulation for the initial and final situation and for chains in crystals and in the amorphous parts of the semi-crystalline structure. There are three power-law regimes that are indicated by the lines in the log-log plot. Explain to what these three lines refer (use the words random, and ballistic if you can). Do you believe that the ½ slope exists? (Explain)

d) On page 9017 Luo describes the possible impact of chain entanglements on lamellar thickness in polymer crystals. He proposes to use increasing concentration to vary the number of entanglements. Make a log-log plot of the specific viscosity $\eta_{sp} = (\eta_{solution} - \eta_{solvent})/\eta_{solvent}$ versus concentration indicating the entanglement concentration. Why is the specific viscosity used rather than the solution viscosity?

e) Luo uses a coarse-grain MD simulation where beads represent groupings of polymer monomers and attractive and repulsive potentials are used such as the Leonard-Jones 6-12 potential based on experimentally determined interaction energies between real chemical groups. The chains have an initial "random" conformation, are subject to random thermal motion with dissipation related to drag coefficients on the beads and are allowed to "equilibrate" until features (such as the density) reach a plateau, figure 1. Figure 3d shows that the equilibrated lamellar thickness decreases with concentration of the solution and figure 4a shows that there is a linear relationship between the lamellar thickness and the molecular weight between entanglements. This contradicts the Hoffman/Lauritzen theory which has no dependence on entanglement density. Make an argument either in favor or opposed to the proposition made by Luo. Can you think of alternative explanations for the observations? For instance, does the simulation "equilibration time" differ for different concentration solutions? Has this been accounted for?

f) The pseudo-equilibrium Hoffman/Lauritzen model explains how the crystal thickness can be calculated once chain folds exist, but it doesn't make an argument for why chain folds occur. The simulation results of Lou and Kos demonstrate that a relationship might exist between the kinetic phenomena of entanglement and the crystal thickness. For instance, in the conclusion on page 9024 Lou indicates that the stem length (eventually the crystal thickness) and the entanglement length are proportional.

Comment on the distinction between equilibrium thermodynamics and kinetics and the difficulty of understanding polymeric systems which might be governed by both equilibrium thermodynamics and kinetics.

ANSWERS: Polymer Physics
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