In class it was mentioned that polymers can be defined in different ways from the perspective of chemists, rheologists (engineers), and physicists. Additionally, different aspects of polymers are observed in different arenas of application, chain folded crystals, shear thinning and normal force in flow, a large number of random conformations in simulations and modeling. Flory considered that all of these aspects relate back to a polymer’s “ability to assume an enormous array of configurations” (Flory PJ *Polymer Chemistry* Cornell University Press (1955)). This was demonstrated in class by running simulations of random walks.

a) Consider a program that generates random walks by taking random steps of equal length on a Cartesian lattice. Plot the probability of an end-to-end distance, R, as a function of R. What are the largest and smallest values of R? What function describes this 2d curve to a fair degree accuracy? What part of the actual curve does this function not describe? What is the value for $<R>$? What would be a reasonable measure of the average size of a polymer?

b) 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 that determines the thickness of polymer crystals based on their crystallization temperature. Hoffman and Lauritzen used an expression for the Gibbs free energy that included a surface term for the two 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 tension and the first term is for the bulk enthalpy of crystallization. At equilibrium for an infinite thickness crystal 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).

c) Sketch the log of viscosity versus log of rate of strain for a polymer melt and explain the behavior based on Flory’s statement concerning an enormous array of configurations. How can the viscoelastic relaxation time be determined from this plot?

d) Polymers form the basis of all known forms of life. Dimarzio (in *Structure and Dynamics of Confined Polymers* Eds. Kasianowicz JJ, Kellermayer MSZ, Deamer DW NATO Science Series Series 3 Vol 87 (2002) *Profound implications for biophysics of the polymer threading a membrane transition*) mentions that chemists consider that this is the case because, using the example of proteins, 20 amino acids arranged in a polymer of N units can display $20^N$ arrangements, and “the complexity of life lies in this arrangement”. Dimarzio points out that,

This argument is part of the answer, but the chemist is speaking of the variety contained in a homogeneous, isotropic bag of stuff. To get the variety of the spatial and temporal structures that one sees in life-forms one has to do some physics. We shall see that what is special about polymers are the 5 classes of phase transitions that occur only in polymers. They are the:

1) polymer threading a membrane transition,
2) helix to random-coil transition,
3) isolated polymer molecule attracted to a surface transition,
4) polymer collapse transition, and the
5) equilibrium polymerization transition.

These 5 transitions, unique only to polymers, along with the 5 other classes of transitions common to all materials (both polymeric and non-polymeric) provide a basis for understanding the self-assembled structures of biology.

Consider DNA which is a polymer in the famous double helix conformation which folds into a chromosome with the assistance of various cellular apparatuses. DNA is read in the process of transcription where it is unfolded by enzymes in a transcription bubble of about 14 unzipped base pairs to produce messenger RNA which travels through the nuclear membrane to the ribosome to form proteins (very roughly). Try to mesh Dimarzio's paragraph with the statement of "chemists" concerning $20^N$ to explain the importance of a physical view of polymers.

e) Dimarzio goes through a complicated discussion of the importance of connectedness to the physical properties of polymers in the context of a polymer (such as a messenger RNA strand) transporting through the nuclear membrane compared to gas atoms leaking through a hole in the membrane. This is shown in Figures 1 to 3. For the polymer, transport across the membrane is a first order transition, that is the chain instantly ports through the membrane once two parts of the chain on either side can be identified, while the gas slowly leaks. Discuss why this might be important to transport of messenger RNA from the nucleus, where DNA resides, to the cytoplasm where ribosomes exist to manufacture proteins.
ANSWERS: Polymer Physics
Quiz 1
January 15, 2021

a) Consider a program that generates random walks by taking random steps of equal length on a Cartesian lattice. Plot the probability of an end-to-end distance, $R$, as a function of $R$.


What are the largest and smallest values of $R$? 
Largest is $N$, smallest and most probable is 0.

What function describes this 2d curve to a fair degree accuracy?
$P(R) = K \exp(-3R^2/(2\sigma^2))$  Gaussian function (Bell-shaped curve)

What part of the actual curve does this function not describe?
It describes between $-N$ and $N$. The Gaussian has a finite probability at $R = \infty$

What is the value for $<R>$?
$<R> = 0$

What would be a reasonable measure of the average size of a polymer?
$<R^2>$ which is $\sigma^2$ in the Gaussian function. $\text{RMS} = <R^2>^{1/2}$

b) 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 that determines the thickness of polymer crystals based on their crystallization temperature. Hoffman and Lauritzen used an expression for the Gibbs free energy that included a surface term for the two 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 tension and the first term is for the bulk enthalpy of crystallization. At equilibrium for an infinite thickness crystal 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).

$\Delta G = V(\Delta H - T\Delta S) + A(2\sigma)$
\[ \Delta G = V \Delta H \left( 1 - \frac{T}{T_\infty} \right) + A(2\sigma) = 0 \]
\[ \frac{V}{A} = t \]
\[ t = \frac{2\sigma}{\Delta H \left( 1 - \frac{T}{T_\infty} \right)} = \frac{2\sigma T_\infty}{\Delta H(T_\infty - T)} \]

c) Sketch the log of viscosity versus log of rate of strain for a polymer melt and explain the behavior based on Flory’s statement concerning an enormous array of configurations. How can the viscoelastic relaxation time be determined from this plot?

![Viscosity vs. Shear Rate](https://en.wikipedia.org/wiki/Shear_thinning#/media/File:Shear_thinning_2.png)

The polymer chain deforms in a shear field, it relaxes to the most random state driven by thermal fluctuations. When it is random the coil can be visualized as a symmetric object on average. The orientation of any asymmetry is in a random direction. Under shear any asymmetric polymers align with the shear field and symmetric chains deform. This reduces the number of entanglements in the melt and reduces the viscosity. The deformation and orientation of the chains that impacts the viscosity takes an average time, the viscoelastic relaxation time. This corresponds with the inverse of the rate of strain where the viscosity deviates from the Newtonian plateau at low strain rates.

d) This argument is part of the answer, but the chemist is speaking of the variety contained in a homogeneous, isotropic bag of stuff. To get the variety of the spatial and temporal structures that one sees in life-forms one has to do some physics. We shall see that what is special about polymers are the 5 classes of phase transitions that occur only in polymers. They are the:

1) polymer threading a membrane transition,
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From the example of DNA during transcription and the process of protein synthesis it is clear that the machinery of life relies heavily on the five polymeric transitions listed by Dimarzio. The coding of 20 amino acids or four nucleic acids in codons of 3 \(4^3 = 64\) codes for amino acids) could be retained in a 3d or 2d structure. For example, in all microelectronics information is stored in a 2D format which is a convenient form for the
mechanics of reading using a 2d reading head of some type. The limitation of this technology is associated with molecular thermal vibrations that interfere with read/write/storage. It is possible to imagine a life form based on 2d storage. 2d objects can be subject to a collapse transition, such as crumpling a sheet of paper, which would increase the information density. However, imagine reading a molecular size square at the center of a crumpled sheet of paper without unfolding the entire sheet. For the process of DNA transcription, a 14nm section is read from a linear structure that is three meters long, an expansion of five million times. This is done without perturbing the folded structure of the remainder of the chromosome. This is like reading a few cellulose units of a sheet of paper that is crumpled into less than one micron without uncrumpling the remainder of the paper. Dimarzio proposes that this is not possible unless a linear chain is the basis for the operation.

It should be kept in mind that Dimarzio’s theories are generally based on dilute conditions since he is a theorist/physicist. A biopolymer exists, at best, in a semidilute condition and at times in a concentrated condition in a mixture of an array of different polymer chains and low molecular weight organics and ions. None-the-less his argument is impressive.

e) Dimarzio goes through a complicated discussion of the importance of connectedness to the physical properties of polymers in the context of a polymer (such as a messenger RNA strand) transporting through the nuclear membrane compared to gas atoms leaking through a hole in the membrane. This is shown in Figures 1 to 3. For the polymer, transport across the membrane is a first order transition, that is the chain instantly ports through the membrane once two parts of the chain on either side can be identified, while the gas slowly leaks. Discuss why this might be important to transport of messenger RNA from the nucleus, where DNA resides, to the cytoplasm where ribosomes exist to manufacture proteins.

If the transport of mRNA through the nuclear membrane were subject to diffusion we could expect the need to produce an order of magnitude more mRNA in transcription, the vast majority of which would be wasted. mRNA for a protein that is needed immediately, such as insulin, would be gradually diffusing through the nuclear membrane from a large oversupply making blood sugar regulation impossible. The process relies on instant transmission of mRNA and chaperoning of the mRNA to the ribosome where the protein can be produced in short order. Further, the protein synthesized in the cytoplasm must be transported through the cell membrane to the blood stream in a rapid manner. Again, the absence of a first order transition would lead to the need of a large concentration of insulin which would slowly diffuse across the cell membrane making regulation of blood sugar impossible. These type problems are obvious in current insulin therapy that is based on a slow release of an insulin hexamer using zinc 4+ ions that slowly release insulin over an hour or so. Such a process is extremely clumsy and leads to many of the medical implications of the disease. Further, a 2d or 3d structure in this process and in many other biological processes is not plausible.
Possibly the main question that comes up in Dimarzio’s polymeric argument is why haven’t we taken advantage of these 1d mechanisms in digital storage/processing/computation.