Phys150 Term Paper
A Brief Review of Polymer Extension

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In my experiences of learning Physics, statistic mechanics, one of the four core subjects, leaves me a clear impression of "Fly by Night" Physics. It is barely possible to calculate the precise state or evolution of system with number of atoms comparable to Avogadro's Number. In the experimental application of statistic mechanics, namely condensed matter Physics, it is of great significance to learn about Fly-by-Night ideas like dimensional analysis, characteristic scales, and opposition and compromise.

In this paper, I will briefly review the basic methods to calculate the extension for both ideal and real polymers with Fly-by-Night style and introduce some applications related to the thermodynamics of polymer extension.

1   What is Polymer?

Polymers are abundant in our daily life. They take a critical role in our body, as proteins and DNA are all polymers and their properties and behaviors dominate our biological activities.

By definition, polymer is a chain of repeating units known as monomer. In this paper, I will focus only on the linear polymer, which has no branches or tree-like structure.

As Fly-by-Night physicists, we can ignore the chemical properties like polarity or electronegativity of monomers and build a simple model. We can consider polymer as $N + 1$ little spheres connected one-by-one with N rigid rods each with length l, with $N >> 1$. The covalent bonds between monomers are so strong compared to thermo-fluctuation around room temperature that we can treat them like rigid rods instead of springs. The
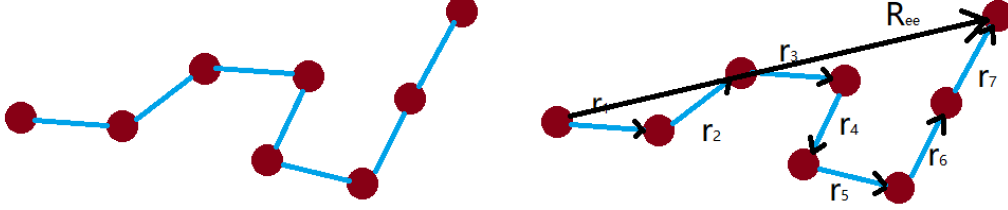
Figure 1: Left: the sphere-rod model of a polymer ignores the chemical properties of monomers and simplify the freedom of bonds. Right: the end-to-end displacement is the summation of all bond vectors.

degree of freedom of a polymer is mainly provided by the rotational freedom of bonds, forming kinks in the chain (Fig. 1 Left).

Talking about extension, there is a trivial and boring answer: the contour length of the polymer $R_c = Nl$. However, the contour length gives us no information about behaviors of the polymer, because it is the intrinsic property of the given polymer. A natural and better measurement of extension might be the end-to-end length, which is defined as the average spacial distance between two ends of a polymer. Mathematically, we can calculate the end-to-end extension by summation of bond vectors, as shown in Fig. 1 Right.

$$\langle R_e^2 \rangle = \langle \mathbf{R}_e \cdot \mathbf{R}_e \rangle = \langle \left(\sum_{i=1}^{N} \mathbf{r}_i \right) \cdot \left(\sum_{j=0}^{N} \mathbf{r}_j \right) \rangle \tag{1}$$

2 Ideal Polymer and Random Walk

We can simplify the model even more by ignore the volume taken up by the little spheres and rods, which gives us the ideal polymer, also known as "phantom chain": the polymer can overlap with itself. Assume each monomer is completely independent from others, and bonds have uniform probability in all directions, we get the simplest freely joint chain(FJC) model. It is equivalent to making N random steps with length l from a

given starting point in the space, known as a random walk. In this case,

$$\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = l^2 \delta_{ij} \tag{2}$$

since two different bonds are completely independent. Note that this result holds in any spacial dimension. Take this result into Eq. 1, we have

$$\langle R_e^2 \rangle = Nl^2 \implies R_e = lN^{\frac{1}{2}} \tag{3}$$

It turns out that for arbitrary ideal polymer, even if we fixed the polar angle θ in each bond(freely rotating chain, FRC), the relationship $R_e \sim \sqrt{N}$ is untouched. Other measurements of extension, radius of gyration R_g for example, also follow the same scaling power[4]. The Physics is indeed lying in this $1/2$.

We can interpret the end-to-end extension statistically. Consider a polymer in 1D starting from origin and ending at position x. It can only move left or right in each step. By symmetry, $\langle x \rangle = 0$. By definition, $X_e = \sqrt{\langle x^2 \rangle} = \sqrt{\langle (x - \langle x \rangle)^2 \rangle}$. We can recognize that it is the standard deviation of the x distribution.

When N is large, we can use binomial approximation and write the distribution of x as a normal distribution. The probability density is

$$f_{1D}(x) \sim e^{-\frac{x^2}{2X_e^2}} \implies f_{3D}(\mathbf{R}) \sim e^{-\frac{x^2+y^2+z^2}{2X_e^2}} = e^{-\frac{3R^2}{2R_e^2}} \tag{4}$$

where symmetry tells us that the variance should be equally divided into three dimensions: $X_e = R_e/3$. The probability density is directly related to number of configurations and therefore the entropy. Surprisingly, we can get an expression for free energy for a given end-to-end distance,

$$F(R) \sim -TS(R) \sim -T \ln[f(R)] \sim \frac{3TR^2}{2R_e^2} \tag{5}$$

ignoring all irrelevant constants. This calculation is by no means to be accurate, but it can give us a relationship between free energy and other quantities and thus offer us a chance to go beyond ideal polymer.

3 Real Polymer and Flory Exponent

It is much more exciting to estimate the extension of real polymer. Real polymer in this case means that we restore the volume of monomers so that
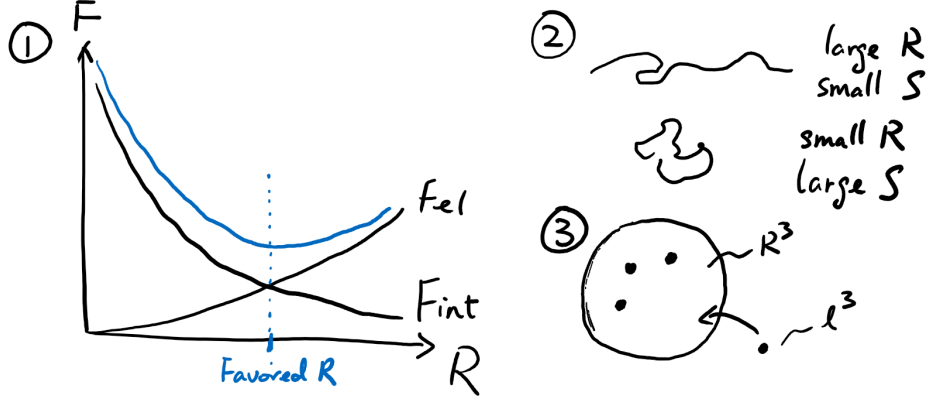
Figure 2: (1): Opposition-compromise between entropy elasticity and repulsive interaction. (2): Entropy elasticity favors small extension. (3): Estimate the repulsive interaction free energy from throwing N spheres with volume l^3 into a pool with volume R^3.

the polymer cannot overlap with itself. Obviously the the extension of real polymer tends to be larger than that of an ideal polymer. The reason behind can be summarized as a repulsive interaction between monomers. Clearly, it is an opposition-compromise between two major free energy contributed by entropy elasticity F_{el} and repulsive interaction F_{int} (Fig. 2). Entropy wants the extension to be as small as possible so that the whole chain can take more configurations, while the repulsive interaction between monomers wants to push nearby monomers as far as possible.

Paul John Flory (Nobel Prize of Chemistry, 1974) made the famous Flory Argument about this compromise[1]. The model he proposed is in some sense too simple to be right. On one hand, assume that the entropy elasticity is the same as ideal polymer, $F_{el} \sim TR^2/R_e^2$ from Eq. 5. On the other hand, estimate the repulsion as if there are N spheres with volume l^3 without any connection between them.

Imagine randomly throwing a sphere with volume l^3 into a big pool with volume R^3 (Fig. 2 (3)). If there is another sphere already in the pool, the probability of hitting is roughly the volume fraction l^3/R^3. Now you throw N spheres into the pool one-by-one, the total number of "hit" is estimated

as $N^2l^3/2R^3$. For each "hit", assign an free energy penalty T, since the temperature is the only energy around this model. Therefore, $F_{int} \sim TN^2l^3/R^3$

With the trick of "driving calculus teacher mad", we calculate the extension R with minimum free energy by $F_{int} = F_{el}$, with $R_e^2 = Nl^2$. Finally, we have

$$\frac{TR^2}{Nl^2} = \frac{TN^2l^3}{R^3} \implies R \sim N^{3/5} \tag{6}$$

Although this estimation is very sloppy, it is very close to experimental measurement[5]. The reason is that Flory Argument is another example of double-mistake. The real polymer should have a smaller entropy due to restriction on configurations, which leads to an overestimation on F_{el}. Simultaneously, the connection between monomers can drive the whole chain away from itself easier than N independent spheres, leading to an overestimation on F_{int} as well. Hence, both free energy are overestimated, and the compromise is not affected significantly!

In contrast to various modified ideal model like FRC, the real polymer has a fundamental difference: the scaling relationship between R and N is no longer $1/2$, but $3/5$. For Fly-by-Night physicists, this scaling power is much more important than the bond length determined by Chemistry. Flory define the scaling exponent between length measurement and number measurement as Flory Exponent ν.

$$R \sim N^\nu \implies N \sim R^D \quad \text{where} \quad D = \frac{1}{\nu} \tag{7}$$

It is interesting that the reciprocal of Flory exponent $D = 1/\nu$ can be interpreted as the equivalent dimension[3]. The number of atoms in a solid with side length R goes like $R^3 \implies D = 3$, which implies it is 3D-like, while for a large piece of paper with side length R, $D = 2$ indicating it is 2D. For Koch curve (Fig. 3), $D = \ln(4/3) \approx 1.3 > 1$, it goes between a 1D line and a 2D area. It is worth noticing that ideal polymer is a fractal if we only consider sufficiently large subsets. Its dimension is exactly 2, which is equivalent to a 2D sheet.
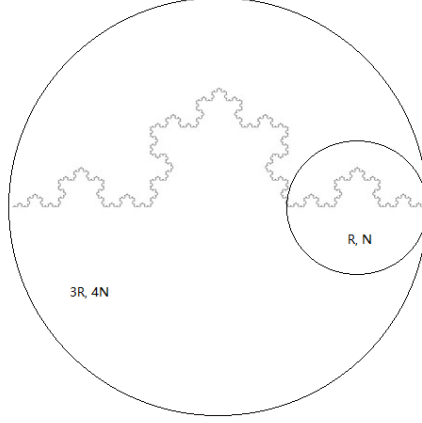
Figure 3: Koch curve has a dimension $D \approx 1.3$. It goes between a 1D line and a 2D area.

4 Confined Polymer and Colloid Separation

Now we impose another constraint on the polymer, which is the geometrical confinement. We want to estimate the free energy cost for a confinement with characteristic length h, for example, polymers in tube with diameter h, or polymers within a gap of width h. In either case, the random walk process is interrupted each time the local polymer size reaches h. Thus, we can treat the confined polymer as a series of unconfined blobs with extension h. Each blob has $\tilde{N} \sim h^{1/\nu}$ monomers. The free energy cost is related to the loss of freedom between blobs, which should be proportional to the number of blobs $\sim N/h^{1/\nu} \sim h^{-1/\nu}$. With a dimensional analysis ($[F] = [T]$, $[R_e] = [h]$), we have

$$F = T \left(\frac{R_e}{h} \right)^{1/\nu} \tag{8}$$

With the free energy cost of confinement, polymers tend to spontaneously free themselves. This property is used for keeping colloid particles separated.

As we would expect, colloid particles in a liquid solvent like water tend to aggregate due to Van der Waals attraction, as the colloid size is far beyond micro-molecular level. However, in particular applications we need to keep them apart from each other. An effective method is to chemically attach

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polymers to the surface of colloids. When two colloids are getting too close to each other, some poor polymers between them are confined to a small gap, increasing free energy cost. This opposition-compromise between Van der Waals attraction and confinement cost forms a more complex free energy dependent on the geometry and density of colloids and polymers, making this application more delicate.
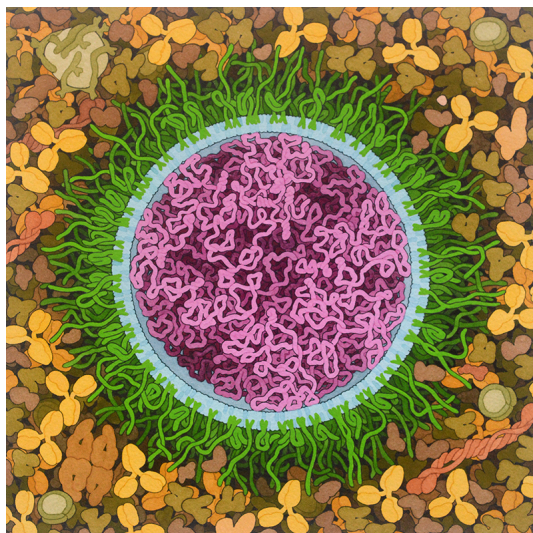

Figure 4: Vaccine particles of mRNA Covid 19 vaccine[2]. The polymers attached to the surface prevent them from aggregating.

A famous example of such application is the virus and vaccine particles (Fig. 4). They are kept apart from each other partly by the brush-like polymers attached to their surfaces. These polymers fighting for freedom should take the credit for preventing our vaccine particles collapsing into a pile of useless bio-materials.

Acknowledge

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