Introduction to Polymer Physics. [1]

Pankaj Mehta

March 8, 2021

In these notes, we will introduce the basic ideas of polymer physics – with an emphasis on scaling theories and perhaps some hints at RG.

Introduction

Polymers are just long floppy organic molecules. They are the basic building block of biological organisms and also have important industrial applications. They occur in many forms and are an intense field of study, not only in physics but also in chemistry and chemical lectures. In these lectures, we will just touch on these ideas with an aim of understanding the basics of protein folding. A distinguishing feature of polymers is that because they are long and floppy, that *entropic effects* play a central role in the physics of polymers.

A polymer molecule is a chain consisting of many elementary units called monomers. These monomers are attached to each other by covalent bonds. Generally, there are N monomers in a polymer, with $N \gg 1$. This means that polymers behave like thermodynamic objects (see Figure 1). It will be helpful to understand some basic scales for the problem of polymers.

- First, entropic effects will be important and we will often ask about exerting forces on the polymers. For this reason it is helpful to keep in mind that at room temperature $1pNnm \approx 4.1k_BT$.

- To break covalent bonds between monomers, we need 1000K. So they are essentially never broken by thermal fluctuations

- However, "bending" and non-covalent interactions (electrostatics) compete with k_BT.

- Monomers are typically of order 1 Angstrom or 1nm.

- Polymers are typically composed of $N \sim 10 - 10^9$ monomers with lengths of $10nm - 1m$.

It's also helpful to look at some examples. Fig. 2 shows polymers of various kinds that occur in biological systems.

We see that there is a lot of diversity in polymers. What are the key things we have to pay attention to. Well there are number of things that will be important. In particular, the things that we will care about are:

Figure 1: A polymer is composed of many monomers. Figure from Grossberg Polymer lectures in Boulder Summer School 2012.

Polymer molecule is a chain:

Examples: polyethylene (a), polysterene (b), polyvinyl chloride (c)...
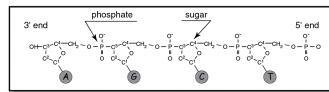
- Polymeric from Greek *poly-merēs* having many parts; First Known Use: 1866 (Merriam-Webster);
- Polymer molecule consists of many elementary units, called monomers;
- Monomers – structural units connected by covalent bonds to form polymer;
- N number of monomers in a polymer, degree of polymerization;
- M=N*m$_{monomer}$ molecular mass.
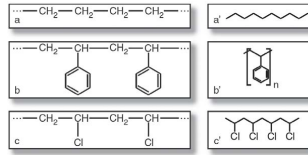
... and DNA
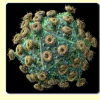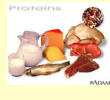
- The first important property is whether the polymer is a *homopolymer* – composed of a single kind of monomer – or a *hetropolymer* – composed of many kind of monomers. Most of the interesting biological polymers are hetropolymers (DNA with 4 bases, proteins with 20 amino acids, etc.)

- The second major thing that will be important is how flexible the polymer is. The more flexible, the more entropic configurations that are available. All polymer bend but the question is how much?

- Another thing that will be important is if the polymer is charged. This is because electrostatic interaction compete with entropic interactions.

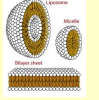- Finally, the basic topology is important. We can have a single chain, or branching chains, or complicated topologies. We are focusing almost entirely on single chains here.

The final important thing about physics is that the properties of polymers are often strongly effected by the solvent in which they are dissolved. The reason for this is again because the solvent changes the free energy of the polymers by changing the balance between entropic and energetic effects. In fact, we can characterize a polymer by its radius of gyration R defined the typical distance between the two

Polymers in living nature

	DNA	RNA	Proteins	Lipids	Polysaccharides
N	Up to 10^{10}	10 to 1000	20 to 1000	5 to 100	gigantic
Nice physics models	Bioinformatics, elastic rod, charged rod, helix-coil	Secondary structure, annealed branched, folding	Proteomics, random/designed heteropolymer, HP, funnels, ratchets, active brushes	Bilayers, liposomes, membranes	??? Someone has to start
Uses					
Molecule					

ends. In general, this is much smaller than a fully stretched polymer since polymers like to bend. In fact, we will see that typically this radius goes like the number of polymers to some power

$$R \sim N^{\nu} \tag{1}$$

The solvent, elasticity, and electrostatic interactions can change this power dramatically from $\nu = 1$ for repulsive polymers to $\nu = 1/3$ in poor solvents. This is summarized in Fig. 3.

We can also directly measure this in experiment using X-ray crystallography in the small k limit.

Neutral Flexible Polymers

We will start with "ideal" polymers. These are neural, flexible polymers that serve as an important starting point for understanding polymer physics. Ideal polymers ignore all interactions between monomers, except between neighboring monomers. Conceptually, they play the same role as an ideal gas for understanding the statistical mechanics of gases.

Polymer Size

Monomer size b~0.1nm; Number of monomers N~10^2-10^{10};
Contour length L~10nm – 1m;
Depending on how much polymer is bent,
its overall size R varies widely and depends on solvent quality

Long-range repulsion $R \simeq bN$	Good solvent $R \simeq bN^{3/5}$	θ-solvent $R \simeq bN^{1/2}$	Poor solvent $R \simeq bN^{1/3}$

Environment change

R~1m   R~100mm   R~10mm   R~100nm
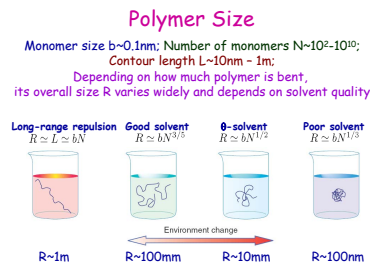
Astronomical Variations of Polymer Size

Increase monomer size by a factor of 10^8: b ~ 1cm; let N=10^{10}.

Poor solvent
$R \simeq bN^{1/3} \approx 20$m

θ-solvent
$R \simeq bN^{1/2} \approx 1$km

Good solvent
$R \simeq bN^{3/5} \approx 10$km

Long-range repulsion
$R \simeq L \simeq bN \approx 10^5$ km

Figure 3: (Top) Polymer sizes in different solvents. (Bottom) Analogy to understand dramatic change in sizes. Figure from Grossberg Polymer lectures in Boulder Summer School 2012.

$\vec{r_i}$

$\vec{R}$

Figure 4: In Freely-Jointed Chain, a polymer can be viewed as a random walk where monomers are connected by bonds whose orientation is uncorrelated with the orientation of other bonds. Notice that we have assumed that there are no other interactions (electrostatic, excluded volume, etc). Picture from Wikipedia.

Freely Jointed Chain

We can start by considering polymers as composed of monomers joined by "bonds" between monomers. As a first approximation, we assume that the bonds are of a fixed length b but the *orientation* of every bond can vary and is uncorrelated with all other bonds (see Figure 4). We will see that this very simplistic picture captures many of the essential features of polymers— especially entropic effects.
In fact, we will be mostly concerned with long polymers where the length L is much larger than b so that the total number of monomers $N = L/b \gg 1$. In this case we expect entropy to dominate energetic effects. The FJC model model does this by treating polymers as random walks. In this way, we can assign a probability to each allowed configuration. In doing this, we have neglected things like energetic interactions and excluded volume.

Let us now analyze the FJC in greater detail. Let us call the posi-

tion of the j-th monomer $\vec{r}_j$. Let us also define the bond vector for the j-th bond by

$$\vec{\tau}_j = \vec{r}_j - \vec{r}_{j-1} \tag{2}$$

By definition, we know that the bond vectors satisfy the relationships

$$|\vec{\tau}_j| = b \tag{3}$$
$$\langle \vec{\tau}_j \rangle = 0 \tag{4}$$
$$\langle \vec{\tau}_i \vec{\tau}_j \rangle = b^2 \delta_{ij}. \tag{5}$$

The first of these just fixes the length of the bond, the second that the bond is equally likely to be oriented in all directions, while the final equation is simply the statement that the bonds are uncorrelated.

Let us start with first calculating the mean end-to-end displacement of the polymer $\vec{R}$. We know that

$$\langle \vec{R} \rangle = \langle \sum_j \vec{\tau}_j \rangle = \sum_j \langle \vec{\tau}_j \rangle = 0. \tag{6}$$

This is simply the statement that polymer is equally likely to be pointed in all directions just like a random walk. However, we can also look at the root-mean square displacement R defined by

$$R^2 = \langle \vec{R} \cdot \vec{R} \rangle = \langle \sum_{j,k} \vec{\tau}_j \vec{\tau}_k \rangle = \sum_{j,k} \langle \vec{\tau}_j \vec{\tau}_k \rangle = b^2 N. \tag{7}$$

This is the more accurate measure of the size of the polymer that we discussed earlier. We see that this argument gives us a simple scaling relation

$$R \sim bN^{0.5}, \tag{8}$$

and a scaling exponent $\nu = 0.5$ (defined in Eq. 1).

At this point, it is worth better understanding what this exponent ν means. Notice that if we have

$$R \sim bN^{\nu}, \tag{9}$$

then we can invert this relationship to get

$$N \sim \left(\frac{R}{b}\right)^{\frac{1}{\nu}} \tag{10}$$

This implies that the fraction of the polymer contained in a radius R_0 is just $R_0^{1/\nu} \equiv R_0^{d_f}$, where this equation defines the fractal dimension $d_f = \frac{1}{\nu}$. This is the usual way we define dimension since for $d = 1, 2, 3$ we would expect number of things contained to go like R_0, R_0^2, and R_0^3 respectively. This is an interesting line of reasoning that tells us something about the geometry of polymers.

From FJC to Gaussian Chain

It will also be helpful to derive a general probability distribution for
this chain. To do so, we will make use of the general relationship
between random walks and the diffusion equation (Fokker-Planck)
equation. It will be helpful now to consider a more concrete setting
of a polymer in d-dimensions. Let us label the three components of $\vec{\tau}$
by τ_α with $\alpha = 1, \dots, d$ labels the different directions. We known that

$$\langle \vec{\tau} \rangle = \sum_\alpha \langle \tau_\alpha \rangle = 0. \tag{11}$$

From symmetry, we conclude that in fact we must have that each
of these individual directions is zero. More tricky, is to consider the
correlation function

$$\langle \tau_{i\alpha} \tau_{j\beta} \rangle. \tag{12}$$

To calculate this, we rewrite

$$\langle \vec{\tau}_i \vec{\tau}_i \rangle = b^2 \delta_{ij} \tag{13}$$

in component form to get

$$\sum_\alpha \langle \tau_{i\alpha} \tau_{j\alpha} \rangle = b^2 \delta_{ij}. \tag{14}$$

Once again, by symmetry we know that all directions are equivalent
so that we conclude

$$\langle \tau_{i\alpha} \tau_{j\alpha} \rangle = \frac{b^2}{d} \delta_{ij} \tag{15}$$

Finally, since different components are uncorrelated, we can write

$$\langle \tau_{i\alpha} \tau_{j\beta} \rangle = \frac{b^2}{d} \delta_{ij} \delta_{\alpha\beta} \tag{16}$$

To proceed, we will write a recursive equation for the probability
$P(\vec{R}, N)$ that a polymer with N monomers has end-to-end displace-
ment $\vec{R}$. In particular, using Bayes theorem we can write

$$P(\vec{R}, N) = \int d\vec{\tau} p(\vec{\tau}) P(\vec{R} - \vec{\tau}, N - 1), \tag{17}$$

where $p(\vec{\tau})$ is just the probability of having an orientation $\vec{\tau}$ for the
last bond. In the limit where $N \gg 1$ and $\vec{R} \gg b$, we can perform a
Taylor expansion of the right hand side. This yields (in component
notation)

$$P(\vec{R}, N) = \int d\vec{\tau} p(\vec{\tau}) \left(P(\vec{R}, N) - \frac{\partial P(\vec{R}, N)}{\partial N} - \vec{\tau} \frac{\partial P(\vec{R}, N)}{\partial \vec{R}} + \frac{1}{2} \sum_{\alpha\beta} \tau_\alpha \tau_\beta \frac{\partial^2 P(\vec{R}, N)}{\partial R_\alpha \partial R_\beta} \right) \tag{18}$$

This yields using expectation values above the d-dimensional effective diffusion equation

$$\frac{\partial P(\vec{R}, N)}{\partial N} = \frac{b^2}{2d} \frac{\partial^2 P(\vec{R}, N)}{\partial \vec{R}^2}, \tag{19}$$

with N playing the role of time and effective diffusion constant $D_{eff} = b^2/2d$. We already know the solution to this equation is a Gaussian distribution of the form

$$P(\vec{R}, N) = \left(\frac{d}{2\pi Nb^2}\right)^{\frac{d}{2}} e^{-\left(\frac{d\vec{R}^2}{2Nb^2}\right)} \tag{20}$$

In other words, the polymer behaves like a Gaussian chain. This suggests that we should be able to replace the more complicated FJC by a Gaussian model and still capture the long-distance physics of the problem. In fact, the reason for this is that the chain is essentially composed on N random steps each with variance b^2/d. Since variances of independent processes add, this tells us that We will return to this universality in a little bit.

This same argument also essentially tells us about the probability distribution describing the difference between $\vec{R}_n - \vec{R}_m$. In particular, we know that this will be a sum of $n - m$ terms each with variance b^2/d. For this reason, we know that

$$P(\vec{R}_n, \vec{R}_m) = \left(\frac{d}{2\pi |n - m|b^2}\right)^{\frac{d}{2}} e^{-\left(\frac{d(\vec{R}_n - \vec{R}_m)^2}{2|n-m|b^2}\right)} \tag{21}$$

Polymers as springs

Before proceeding, this also gives us some idea about how entropic forces work. In the absence of external forces, polymers of course like to contract. We can ask, how much force f is needed to fully extend the polymer to distance R_f. We will now treat this as a one-dimensional problem in the direction of the force. In other other words, how much do you have to pull the polymer in order to . Well we know that we can also thing of this as a partition function

$$P(\vec{R}, N) \propto e^{\frac{-F(R,N)}{k_B T}}, \tag{22}$$

where $F(R, N)$ is the effective free energy which we can identify as

$$F(R, N) \sim \frac{k_B T R^2}{2Nb^2}. \tag{23}$$

Notice this means that a polymer essentially behaves like a spring with effective spring constant that is proportional to the temperature:

$$k_{eff} \sim \frac{k_B T}{2Nb^2}, \tag{24}$$

since partition function for spring is just

$$P_{spring}(x) \sim e^{\frac{-k_{eff}x^2}{k_BT}} \tag{25}$$

Now, we know if we exert a force f that the free-energy will be modified to yield

$$P(\vec{R},N) \propto e^{-\frac{F(R_f,N)-fR_f}{k_BT}}, \tag{26}$$

This combined free energy must be minimized at the force needed to stretch polymer implying

$$\frac{\partial F(R_eff,N)}{\partial R} = \frac{k_BTR_f}{Nb^2} \sim f \tag{27}$$

This basic idea that entropy can give rise to forces is an interesting one – and one that periodically gets revived in fundamental physics as a possible origin of quantum gravity (most recently by Verlinde https://en.wikipedia.org/wiki/Entropic_gravity).

Beyond Gaussian Chains

So far we have ignored everything except for Gaussian effects. How can we incorporate these non-thermodynamic interactions. In general, this will be really hard. However, surprisingly mean-field theory does an incredibly good job of capturing the essential physics.

Accounting for excluded volume/short range repulsive interactions

Let us start with the simplest version of mean-field theory. Let us try to take into account excluded volume. In particular, let us write the volume of one segment as v_c. Then the probability that a given monomers does not overlap a second monomer is just 1 minus the fraction of volume occupied by the second segment in d-dimensions is just

$$q \sim (1 - v_c/R^d). \tag{28}$$

In general, for a polymer composed on N monomers, there are N^2 such potential overlaps. The probability that none of the segments overlap is given by

$$w(R) = q^{(N(N-1)/2)} \approx (1 - v_c/R^d)^{N^2} \approx_{R^3 >> v_c} e^{\frac{-N^2v_c}{R^d}} \tag{29}$$

where in writing this, like in all mean-field models we have ignored the correlations between monomers.

Now we make the further assumption, that the we can write the probability of having a polymer of length R with excluded volume

interactions, $p_{flory}(R)$ is just the probability of having a Gaussian chain of length R given by Eq. 20 times the probability that no monomers occupy the same volume

$$p_{flory}(R) = p(R)w(R)$$

$$\propto e^{-\left(\frac{d\vec{R}^2}{2Nb^2}\right)} e^{\frac{-N^2 v_c}{R^d}} \tag{30}$$

$$\propto e^{-\frac{N^2 v_c}{R^d} - \frac{d\vec{R}^2}{2Nb^2}} \tag{31}$$

This allows us to identify an effective scaling free energy

$$F \sim \frac{N^2 v_c}{R^d} + \frac{d\vec{R}^2}{2Nb^2}. \tag{32}$$

The equilibrium R_* will minimize this energy. Let us now differentiate this equation to get

$$-\frac{dN^2 v_c}{R_*^{d+1}} + \frac{dR_*}{Nb^2} = 0 \tag{33}$$

which yields the scaling relation

$$R_* \sim N^\nu = N^{\frac{3}{d+2}}. \tag{34}$$

Thus, we see that the repulsive interaction have modified our exponent ν from the ideal model where $\nu = 1/2$ to $\nu = 3/5$ in $d = 3$ dimensions and $\nu = 3/4$ in two dimensions. Surprisingly, this is in good agreement with experiments!

Basic Phase Diagram of Polymers

We thus far considered only repulsive interactions. One can also think about attractive interactions. Obviously, attractive interactions will make the polymer more compact. With attractive interactions and hard core repulsion due to steric occlusion, the polymer monomer would like to stay as close as possible. In particular, we expect the density of monomer to be $\mathcal{O}(1)$. Thus, we expect that $N/R^d \sim 1$, so that we have

$$R \sim N^{1/d}. \tag{35}$$

These basic considerations allow us to think of a stylized phase diagram for polymers. Since the temperature controls the relative effects of entropic versus energetics. Thus, at low temperatures we would expect that attractive interactions dominate and the polymer is "collapsed" with $R \sim N^{1/d}$. At some transition temperature often called $T = T_\theta$, we expect a phase transition to an extended phase

where $R \sim N^v$. These two regions are separated by a critical regions around $T = T_\theta$ where $R \sim N^{1/2}$. This is summarized in Figure 5. We will not have time to work through this in detail. However, rest assured this can be made more precise using field theoretic methods and methods from RG. These are quite interesting and involved calculations.

Figure 5: Phase diagram of polymers from "Flory Theory of Polymers" (arxiv:1308:2414).
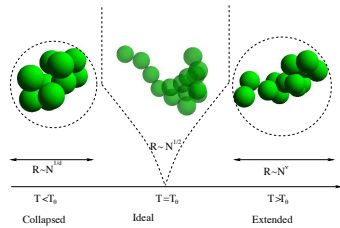
FIG. 2: Schematic phase diagram of an isolated homopolymer. At high temperature $T > T_\theta$, the polymer is in a swollen phase (right), whereas one expects a compact globule at sufficiently low temperatures $T < T_\theta$ (left). These two regimes are separated by a transition regime at $T = T_\theta$ (center) where the polymer behaves more or less as a Gaussian chain, at least in $d > 3$.

Understanding Universality and Self-Similarity: From WLC back to FJC

One of the most powerful and interesting ideas to come out of polymer physics is the idea of scaling [2]. These ideas have their origin in the work of Michael Fisher and collaborators on phase transitions, but polymers are arguably the place where they were most widely and successfully used outside this original setting. The basic idea of the scaling theory is that at long distances, the physics should be independent of the scale at which I view the problem at short distances.

One of the defining properties of random walks is that they are self-similar. This essentially means that as I view a random walk at different scales, it essentially looks the same [3]. The under lying reason for this is that we we ask how the radius of the random walk scales with the number of steps, this takes the form of a *powerlaw*:

$$R \sim N^\nu. \tag{36}$$

To see why power laws are special, let us consider two kinds of functions

$$f_l(x) = \frac{A}{x^\alpha} \tag{37}$$

[2] Here we will follow the discussion of Doi as wall as Bhattacharjee et al in arxiv:1308:2414

[3] A great demonstration of this can be found from Wolfram applet found `https://demonstrations.wolfram.com/ SelfSimilarityInRandomWalk/`

and

$$f_s(x) = \frac{Be^{-\frac{x}{\xi}}}{x^\alpha}. \tag{38}$$

Notice that the second of these has a natural length scale associated with it ξ whereas there is no length scale with the first function. Imagine now, we measured x on a different length scale $x' = \lambda x$, the we we that by setting $A' = A\lambda^{-\alpha}$ the functional form of $f_l(x)$ remains invariant. Thus, no matter the scale λ at which one looks the basic power law behavior remains the same. This is the idea of *scale invariance*. We can contrast this with the function f_s. If $\lambda x \gg \xi$ we cannot simply rescale the parameter B and then obtain the same functional form.

In fact, one can go a little further. We have shown that any power law function is scale invariant. In fact, one can also show the opposite must also hold: a scale invariant function (defined below) must take the form a power law. Assume we have a scale-invariant function so that:

$$f(\lambda x) \sim \lambda^{-p} f(x) \tag{39}$$

for *all choices of* λ (this is known as *continuous scale invariance*). In this case, we see that by setting $\lambda = 1/x$, we get that

$$f(1/x) \sim f(1)x^p. \tag{40}$$

Substituting, $y = 1/x$ we come to the conclusion

$$f(y) \sim y^{-p}. \tag{41}$$

Thus, we see that continuous scale invariance implies power law scalings and vice versa.

In the context of polymers, let us revisit the FJC model, and in particular Fig. 4. Notice that the scale b_0 we chose for the length of the links and the number of corresponding monomers $N = L/b$ was somewhat arbitrary. We could have just as easily chosen a different scale b' and different number of monomers N'. However, we expect that the long distance physics should be independent of these choices. In particular, for long polymers $L \gg 1$, we expect the physics to be independent of all these choices.

Consider the probability $P(\vec{R}, L)$ that a polymer of length L has end to end displacement $\vec{R}$. In principle, this probability depends on all the exact details of our microscopic model. However, we know that for long distances this should only depend on L. Let us now imagine changing the macroscopic scale of the problem so that

$$L \to \lambda L, \tag{42}$$

while keeping the microscopic scale b fixed. This is called a scale transformation. Notice in Flory theory, we will be keeping the microscopic scale fixed. In particular, since we have

$$R \sim b^{1-\nu}(Nb)^{\nu} \sim L^{\nu} \tag{43}$$

Thus, under a scale transformation $L \to \lambda L$ and $R \to \lambda^{\nu} R$. The probability will show *scaling* if

$$P(\vec{R}, L) = \lambda^x P(\lambda^{\nu} \vec{R}, \lambda L), \tag{44}$$

for all λ. Let us now choose a $\lambda = 1/L$. This yields

$$P(\vec{R}, L) = \frac{1}{L^x} P(\frac{\vec{R}}{L^{\nu}}, 1) \equiv \frac{1}{L^x} \mathcal{P}(\frac{\vec{R}}{L^{\nu}}), \tag{45}$$

where in the last line we have defined the scaling function $\mathcal{P}$.

Now, we know that

$$\int dr^d P(\vec{R}, L) = 1. \tag{46}$$

This implies that

$$1 \sim \int dr^d \frac{1}{L^x} \mathcal{P}(\frac{\vec{R}}{L^x})$$

$$L^x \sim \int dr^d \mathcal{P}(\frac{\vec{R}}{L^x})$$

Substituting $r = \tilde{r}L^{\nu}$ gives

$$L^x \sim L^{d\nu} \int d\tilde{r}^d \mathcal{P}(\vec{\tilde{R}}) \tag{47}$$

This implies that $x = d\nu$ and our scaling function takes the form

$$\frac{1}{L^{d\nu}} \mathcal{P}(\frac{\vec{R}}{L^{\nu}}) \tag{48}$$

We can compare this with our expression in Eq. 20 using $L = Nb$ and $\nu = 1/2$. In particular, we have that

$$P(\vec{R}, L) = \left(\frac{d}{2\pi Lb}\right)^{\frac{d}{2}} e^{-\left(\frac{d\vec{R}^2}{2bL}\right)} \tag{49}$$

and indeed this scales as $\sim L^{-d\nu}$.

More scaling analysis of polymers in solutions

Thus far we have basically considered an isolated polymer. However, polymers often occurs in solution. We are interested in understanding polymers in a solution. After all the cell, is a very crowded place as this famous picture from David Goodsell shows (see Fig. **??**. We will largely confine ourselves to some simple scaling arguments.
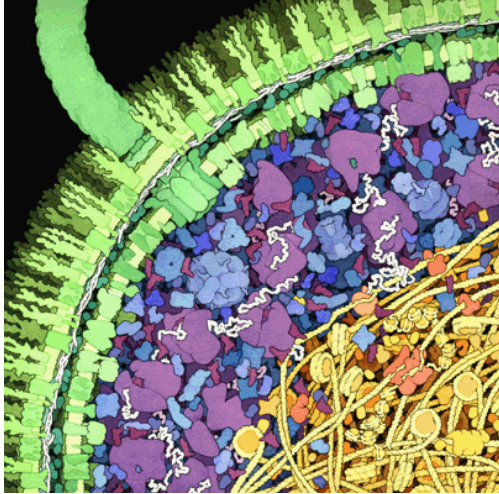
Critical Concentrations

Consider polymers in solution at some concentration c of monomers in solution. We know that if this concentration is very small, we can think about the polymers as isolated and non-interacting. However, at large concentrations where the distance between polymers approaches the radius of the polymers themselves R_g, the properties of the polymer solution will differ from the isolated polymers. This is depicted in Fig. **??** from Doi's book.

Let us denote the concentration that separates these regimes by c_*. We can actually recover this from simple scaling arguments. We know that

$$c^* \sim N/R_g^3 \tag{50}$$

However, we know that $R_g \sim N^\nu$ so that we have

$$c^* \sim N^{1-3\nu} \tag{51}$$

Recalling that $\nu = 3/(d+2)$, we see that for $d = 3$ that we have that $c_* \sim N^{-0.8}$ so that if N is very large that there is strong interactions even at very small concentrations. For example, polyesterene with molecular weight $\sim 10^6$ starts to interact at 0.5% weight concentrations.

Correlations length of polymers

Since the polymers are interacting in solution, the polymer solution is no longer scale free but instead defined by a correlation length ξ. Let us now try to use dimensional analysis and scaling arguments to try to figure out the scaling properties of the correlation length. By

(a) $c < c^{\bullet}$ (b) $c \cong c^{\bullet}$ (c) $c > c^{\bullet}$
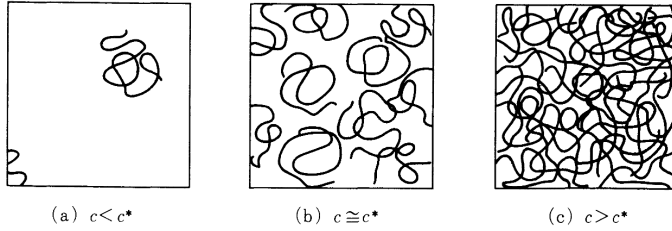
Fig. 2.1 (a) A dilute solution; (b) a solution at the overlap concentration c^{*}; (c) a concentrated solution.

dimensional analysis, we know that we we expect that the properties of the polymer will take the form

$$\xi \sim R_g f(cb^3, N), \tag{52}$$

where f is some arbitrary function of the dimensionless numbers cb^3 and N.

We will ask what happens as we "coarse-grain" the chain so that we group together some segments into a smaller number of segments: $N \to \lambda^{-1}N$ where $\lambda > 1$. In particular, we expect that for large N the fundamental physics should not change under such a coarse graining. Under such a transformation, we have that the concentration will decrease like N but the length scales will scale as λ^ν:

$$N \to \lambda^{-1}N, \, b \to \lambda^\nu b, \, c \to \lambda^{-1}c \tag{53}$$

Since the correlation lengths and the radius of gyrations are *physical quantities*, they must be invariant under such a transformation so that

$$\xi \to R_g f(\lambda^{3\nu-1}cb^3, \lambda^{-1}N) \tag{54}$$

Let us choose $\lambda = N$, to get that

$$\xi = R_g f(\frac{cb^3}{N^{1-3\nu}}, 1)$$

$$= R_g f(cb^3 \left(\frac{N^{1-3\nu}}{b^3}\right)^{-1}, 1)$$

$$= R_g f(\frac{c}{c_*}, 1)$$

$$\equiv R_g \mathcal{F}(\frac{c}{c_*}) \tag{55}$$

This shows us the correlation function is a scaling function of c/c^*.

To proceed, we will make some more scaling assumptions. In particular, for $c > c_*$, we know the correlations do not depend of the details of the polymer involved. In fact, the correlation length must be *independent of N*. Since we know that the powers of N come from $R_g \sim N^\nu$ and $c_* \sim N^{1-3\nu}$. This means that

$$\mathcal{F}(\frac{c}{c_*}) \sim \left(\frac{c}{c_*}\right)^x \sim N^{-x(1-3\nu)}. \tag{56}$$

This implies that since ξ is independent of N that

$$x = \nu/(1 - 3\nu) \tag{57}$$

so that we get

$$\xi = R_g \left(\frac{c}{c_*}\right)^{\nu/(1-3\nu)}, \tag{58}$$

which for $d = 3$ implies $\xi \propto c^{-3/4}$ which has been confirmed experimentally.