

## Chapter 2

# Polymers in bulk

### 2.1 Flexible polymer chains

[Reading: Colby Chapter 1, sections 1.1–1.3, 1.5, 1.7 for background; Chapter 2, sections 2.1–2.3]

Polymer molecules are predominately linear structures, in which small chemical units are bonded together. Typically, at least some portion of the repeating interconnections between adjacent monomers are single covalent bonds. We are interested in understanding the origin of flexibility of polymers, their ability to adopt many different conformations at moderate temperature, rather than just one lowest-energy conformation. To understand this, we consider the hierarchy of energy scales related to the deformation of a polymer molecule away from its lowest-energy state.

First, the energy to break covalent bonds is very large, typically a few hundred kJ per mole (100 kJ/mole is  $40kT$  at room temperature); no bonds are broken as the molecule moves. Second, covalent bonds are very particular about their length. The results of quantum mechanical calculations and vibrational spectroscopy may be summarized by describing covalent bonds as harmonic springs with a finite rest length, with a stiffness of order  $xx$  kJ/(mole  $\text{\AA}^2$ ). Thermal energies at room temperature are sufficient to vary the length of such a bond by  $xx$  percent. So we may regard the bond lengths in polymers as fixed.

Third, molecules are also very particular about the angles formed by adjacent atoms, again for quantum mechanical reasons; a typical “angular spring” has some preferred angle and a stiffness of order  $xx$  kJ/(mole  $\text{rad}^2$ ), which means that room-temperature thermal energies are sufficient to vary the angle by  $xx$  percent. Again, we may to good approximation regard bond angles in polymers as fixed.

Finally, the dihedral angle — defined by rotating everything on one side of a covalent bond with respect to everything on the other side, around an axis through the bond itself — also has a potential governing its motion. But this potential, arising only from the residual interactions of the sidegroups of the two bonded atoms, is weak; for example, the difference in energy between the trans and gauche minima in polyethylene is about 3kJ/mole. So some fraction of the bonds in a polymer in solution or melt will typically be found in gauche states. This is the origin of flexibility in polymers.

If we take a long enough subchain of a flexible polymer, we expect that the tangent to the chain at one end will become uncorrelated with the tangent at the other end. Thus, the “step” taken by this subchain will be in a random direction, with some well-behaved distribution of possible lengths (the maximum step length is bounded, so all moments are finite). These are the conditions for applying the central limit theorem; so any sufficiently long polymer should execute a random walk. (We will see later that this argument, which neglects polymer “self-avoidance”, is not quite right.)

So to understand the conformational statistics of the polymer chain on a large scale, we can “coarse-grain” our description on a small scale, from the individual dihedral angles to a sequence of uncorrelated subchain “steps”. (Note that the central limit theorem tells us we can coarse-grain further without changing the large-scale description; a random walk of  $N/2$  steps with variance  $2\sigma^2$  has the same distribution of end-to-end vectors as a random walk of  $N$  steps with variance  $\sigma^2$ .) The question is, how long a subchain do we need before the tangent forgets its direction, and what will be the mean-square end-to-end distance of the whole chain?

### Freely jointed chain and freely rotating chain

The simplest model of a flexible polymer, to which more realistic models are usefully compared, is a freely jointed chain, in which the distance  $a$  between adjacent atoms is fixed but the bond angles are completely free to vary. Then the end-to-end vector  $R(n)$  of a chain of  $n$  segments is the sum of  $n$  random steps of fixed length,

$$R(n) = a \sum_{i=1}^n t_i \quad (2.1.1)$$

Evidently  $R(n)$  has zero average (the steps point in all directions with equal probability); the mean-square end-to-end distance is

$$\langle R(n)^2 \rangle = a \sum_{i,j=1}^n \langle t_i \cdot t_j \rangle = na^2 \quad (2.1.2)$$

Because different  $t_i$  are uncorrelated, and separately average to zero, the only nonzero terms in the double sum are the  $n$  terms with  $i = j$ .

To describe real polymers, at a minimum we need a model for the configurations of a polymer with dihedral angles that vary. There are a lot of possible choices here: Do the dihedral angles take on fixed values (i.e., trans, gauche+, gauche-)? With what probability? Are subsequent dihedral angles influenced by the value of adjacent dihedral angles? Detailed models have been developed for each of these variations.

For our purposes, the simplest model will suffice to illustrate how the tangent correlation decays with increasing arclength distance between monomers; namely, a model in which the bond angle is fixed at some  $\theta$ , but the dihedral angle rotates freely. Then, the direction  $t_i$  of the bond  $i$  can be written in terms of the previous tangent as

$$t_i = t_{i-1} \cos \theta + \delta t_i \sin \theta \quad (2.1.3)$$

in which the  $t_i$  are unit vectors, and  $\delta t_i$  is a random unit vector perpendicular to  $t_{i-1}$ .

Iterating the above equation results in

$$t_n = t_0 (\cos \theta)^n + \sin \theta (\delta t_1 (\cos \theta)^{n-1} + \delta t_2 (\cos \theta)^{n-2} + \dots) \quad (2.1.4)$$

We can now compute the average projection of  $t_n$  onto the original  $t_0$ , as

$$\langle t_n \cdot t_0 \rangle = (\cos \theta)^n = \exp(-n \log(1/\cos \theta)) \quad (2.1.5)$$

which results because the average of all the  $\delta t_i$  are zero (they each spin in a circle, uncorrelated to  $t_0$ ). So the memory of the tangent decays exponentially with the number of monomers.

### Wormlike chain model

Another class of polymers, typified by DNA, are much less flexible than single-bond main-chain polymers, because their structure admits no low-energy deformation like dihedral rotation. Instead, these polymers deform from their lowest-energy straight conformations by small bends all along the contour length. Ultimately, these small bends are the result of either bond angle deformations or bond stretching within the structure of the polymer.

For our purposes, it suffices to describe such deformations in terms of a model in which the angle between successive tangents can be deflected from zero, with an energy cost

$$U(\theta) = K/2\theta^2 \quad (2.1.6)$$

Now a given tangent vector can be chosen to define the  $z$  axis, and we may ask about the probability distribution for the direction of the next tangent vector along the chain. Adopting spherical coordinates to describe its direction, the probability distribution for the next tangent is

$$P(\theta) \propto \sin \theta \exp(-\beta K/2\theta^2) \quad (2.1.7)$$

(The prefactor of  $\sin \theta$  results from the differential solid angle,

$$d\Theta = \sin \theta d\theta d\phi \quad (2.1.8)$$

which is the area of a small patch on the unit sphere at inclination angle  $\theta$ , over which  $\theta$  varies by  $d\theta$  and  $\phi$  varies by  $d\phi$ .)

The bond angles fluctuate, so our previous expression for the successive tangent directions becomes

$$t_n = t_0 \prod_{i=1}^n \cos \theta_i + \delta t_1 \sin \theta_1 \prod_{i=2}^n \cos \theta_i + \dots \quad (2.1.9)$$

Upon averaging, we have

$$\langle t_n \cdot t_0 \rangle = \exp(-n \log(1/\langle \cos \theta \rangle)) \quad (2.1.10)$$

in which we have used the fact that the different  $\theta_i$  are all independent of each other, and of the azimuthal deflections  $\delta t_i$ .

If the potential is reasonably stiff, such that the angular deflections are small, then we can expand the cosine as

$$\langle \cos \theta \rangle \approx \langle 1 - \theta^2/2 \rangle \quad (2.1.11)$$

and likewise replace  $\sin \theta$  in  $P(\theta)$  with  $\theta$  itself. Then the average we need is

$$\langle \theta^2 \rangle = \frac{\int d\theta \theta^3 \exp(-\beta K/2\theta^2)}{\int d\theta \theta \exp(-\beta K/2\theta^2)} \quad (2.1.12)$$

If angular deflections are small, we can extend the range of integration to infinity (the integrand is negligible there anyway). Then, making the change of variable  $y = \beta K/2\theta^2$  results in

$$\langle \theta^2 \rangle = (2/\beta K) \frac{\int_0^\infty dy y \exp(-y)}{\int_0^\infty dy \exp(-y)} = 2/\beta K \quad (2.1.13)$$

Using this, we have

$$\log(1/\langle \cos \theta \rangle) = -\log \langle \cos \theta \rangle \approx -\log(1 - 1/\beta K) \approx 1/\beta K \quad (2.1.14)$$

So finally, we have

$$\langle t_n \cdot t_0 \rangle = \exp(-n/L_p) \quad (2.1.15)$$

in which  $L_p = \beta K$  is the “persistence length” (here measured in whatever repeat units were used to define the successive tangents and angles). We note that the persistence length increases as the polymer becomes stiffer (i.e., as  $K$  increases).

We can identify the persistence length of the previous model, the freely rotating dihedral chain, by noting that  $\beta K$  (which is  $L_p$ ) is in that case the same as  $-1/\log(\cos \theta)$ . So for a small bond angle, such that  $\cos \theta$  is nearly unity and the log is very small (and negative), the persistence length would reasonably be large.

### Mean-square end-to-end distance

The end-to-end vector  $R$  connecting the two ends of a wormlike chain should for short chains grow linearly with length, while for long chains should behave like a random walk. To see this, we compute the end-to-end vector from the tangent, by integrating along the arclength:

$$R(n) = \int ds t(s) \quad (2.1.16)$$

(For convenience, we are taking a continuum limit, in which the repeat unit index  $i$  is replaced by arclength position  $s$ , according to  $s = na$ , where  $a$  is the length of a repeat unit.)

Then the mean-square end-to-end distance is

$$\begin{aligned} \langle R(n) \cdot R(n) \rangle &= \int_0^n ds \int_0^n ds' \langle t(s) \cdot t(s') \rangle \\ &= \int_0^n ds \int_0^n ds' e^{-|s-s'|/L_p} = 2 \int_0^n ds \int_0^s ds' e^{-(s-s')/L_p} \end{aligned} \quad (2.1.17)$$

In the above, the arclength distance between the two tangents is  $|s - s'|$ , and we break the integral into two equal halves (one with  $s > s'$ , the other with  $s < s'$ ) to get rid of the pesky absolute value sign.

The integral is now elementary to perform, and a bit of algebra leads to

$$\langle R(n) \cdot R(n) \rangle = 2L_p^2 (n/L_p - 1 + \exp(-n/L_p)) \quad (2.1.18)$$

For short chains such that  $n$  is much less than  $L_p$ , we can expand the exponential to second order, to find that  $\langle R^2(n) \rangle$  is approximately  $L^2$  (that is, that the end-to-end distance is as for a straight rod). For long chains, the first term in parenthesis dominates, and we have  $\langle R^2(n) \rangle$  approximately equal to  $2nL_p$ ; that is, the mean-square end-to-end distance grows only linearly with chain length, as for a random walk.

### Contour length, Kuhn length, $C_\infty$

In the previous section, we analyzed two models, and found that long polymer chains with different flexibility can have quite different mean-square end-to-end distances. The more flexible a long chain is, the smaller its dimensions are. A traditional measure of this effect is provided by the “characteristic ratio”  $C_\infty$ , defined as the ratio of  $\langle R^2 \rangle$  as it is for a given type of long chain (hence the subscript  $\infty$ ), to what it would be if every repeat unit in the chain were freely jointed. The ratio  $C_\infty$  is always larger than unity.

The definition of  $C_\infty$  presupposes an agreed-upon definition of a chain repeat unit, which can sometimes be confusing (in polyethylene, is it every carbon, or every two carbons? What about polypropylene? What about random copolymers?). Anyway,  $C_\infty$  is customarily defined as

$$C_\infty = \frac{\langle R^2 \rangle}{Nl^2} \quad (2.1.19)$$

in which  $l$  is the bond length. By this definition, the segment length of a carbon-carbon bond in PE (taking a segment as one carbon, not one ethylene) is  $1.54\text{\AA}$ .

The maximum extended length of the chain  $R_{max}$  can be written in terms of this bond length  $l$  as

$$R_{max} = Nl \cos(\theta/2) \quad (2.1.20)$$

in which  $\theta$  is the deflection angle between successive bonds, i.e.,  $\cos \theta = t_i \cdot t_{i+1}$ .

It is more physically meaningful to define for a polymer chain an equivalent freely jointed chain, in which we choose the effective number of steps  $N^*$  and effective step length  $b^*$  in such a way that the maximum length  $N^*b^*$  equals the actual maximum length  $R_{max}$ , and the mean-square end-to-end distance  $N^*b^{*2}$  equals the actual  $\langle R^2 \rangle$ . We have

$$\begin{aligned} b^* &= \langle R^2 \rangle / R_{max} \\ N^* &= R_{max}^2 / \langle R^2 \rangle \end{aligned} \quad (2.1.21)$$

The length  $b^*$  is called the Kuhn length, which is independent of the definition of the repeat unit, and is a good measure of the distance over which a chain forgets its direction.

In terms of the characteristic ratio, the above can be written

$$\begin{aligned} b^* &= \frac{C_\infty l}{\cos(\theta/2)} \\ N/N^* &= \frac{C_\infty}{\cos^2(\theta/2)} \end{aligned} \quad (2.1.22)$$

Since  $C_\infty$  is always greater than unity and  $\cos(\theta/2)$  is always less than unity, the equivalent freely jointed chain always has fewer units of greater length than the real chain.

Sometimes it is convenient to count actual monomers, rather than Kuhn monomers consisting of  $N/N^*$  segments; in this case, we define a statistical segment length  $b$ , such that the mean-square end-to-end distance of the actual chain  $R^2$  is equal to  $Nb^2$ , where  $N$  is the actual number of monomers.

Evidently, this definition depends on what we take to be a monomer (which is sometimes unambiguous, i.e., for homopolymers such as polystyrene, and is sometimes ambiguous, as for random copolymers). With this definition, we can think of the chain conformations as freely jointed with  $N$  steps of length  $b$ , but only for chains that are either unperturbed random walks, or weakly stretched such that they are far from their fully extended length. The statistical segment length can be related to the characteristic ratio by

$$b^2 = C_\infty l^2 \quad (2.1.23)$$

## 2.2 Probing single chains: pulling

[Reading: CR, Chapter 2, sections 2.5–2.6, 2.8]

To find out about the properties of a material, interact with it and see what happens. The two most straightforward ways to interact with a polymer are to pull on it, and to look at it. Of course, polymers are small, so we can neither grab the end directly, nor see a polymer with our eyes. (Although, with fluorescently labeled DNA attached to microbeads manipulated with an optical tweezer and viewed in a microscope, we can do both.) But there are indirect ways to pull on one end of a polymer with respect to the other — by placing the polymer in solution, and applying an extensional flow, for example.

### Pulling force

If we pull the ends of a random-walk polymer chain well apart from each other, we bring the chain into a set of unlikely conformations, that it would only rarely visit in equilibrium. We have reduced the entropy of the chain by pulling on it. From our general discussion of external parameters coupled to statistical systems, we recall that the force “conjugate to” a given external parameter is given by the derivative of the entropy with respect to the parameter.

So what is the entropy of a polymer chain with a specified end-to-end vector? Recall that the probability of the chain end being found at  $R$  for an unbiased random walk is

$$P(R) \propto \exp(-3R^2/2Nb^2) \quad (2.2.1)$$

(This form is Gaussian, as the central limit theorem says it must be, with a width chosen in such a way that  $\langle R^2 \rangle = Nb^2$ .)

Now  $P(R)d^3R$  is the fraction of polymer configurations in which the chain winds up within the small volume  $dV = d^3R$  around  $R$ , out of all possible polymer configurations. So the change in entropy, upon constraining the location of the chain end to this small volume, is

$$1/k\Delta S = \log(P(R)dV) = -\frac{3R^2}{2Nb^2} + \log dV \quad (2.2.2)$$

The corresponding force is given by the thermodynamic derivative,

$$f = -\frac{T\partial S}{\partial R} = \frac{3kTR}{Nb^2} = \frac{3kTR}{R_e^2} \quad (2.2.3)$$

(where  $R_e^2 = Nb^2$  is the mean-square end-to-end distance). This is the force of a harmonic spring of zero rest length, with spring constant  $3kT/Nb^2$ . Because the springlike response results from entropy effects, we call this an “entropic spring”.

If we bias the random walk with an applied external force  $f$ , the energy acquires a term  $-R \cdot f$ , so that the probability distribution becomes

$$P(R) \propto \exp(-3R^2/2Nb^2 + \beta f \cdot R) \quad (2.2.4)$$

The most likely value of  $R$  under tension is the one that maximizes the exponent, which again gives  $f = 3R/(Nb^2)$ .

### Stretch blobs and scaling

The entropic spring for shorter chains is progressively stiffer, scaling as  $1/N$ . For any given force  $f$ , there is a chain segment short enough that the end-to-end distance is perturbed by an amount of “relative order unity”, i.e., by about the root-mean-square end-to-end distance  $R_e$  itself.

To see this, put  $R = R_e$  in the force law, and solve for  $R_e$ , to obtain

$$R_e = \frac{3kT}{f} \quad (2.2.5)$$

As the applied force becomes larger, the size of the marginally perturbed segment decreases.

The free energy change of this length of this marginally perturbed segment (with  $R = R_e$ ) is

$$\Delta F = -T\Delta S = 3kT/2 \quad (2.2.6)$$

which is to say, “of order  $kT$ ”. In other words, the chain segment of length such that a given force perturbs its typical size by a factor of order unity, stores about  $kT$  worth of free energy under the deformation.

This specially chosen size of chain segment is called a “stretch blob”. We can regard a longer chain stretched out by this same force as a succession of stretch blobs, arranged in a (more or less) straight line. Let  $g$  be the number of effective segments in the stretch blob, so that the entire chain consists of  $N/g$  such blobs.

Each blob has an typical end-to-end distance  $\xi$ , such that  $\xi^2$  is of order  $gb^2$  (that is, the blob is marginally perturbed from being a random walk). The total end-to-end separation  $R$  of the full chain is then of order  $N/g$  times  $\xi$ . Finally, the free energy stored in the entire stretched chain is of order “ $kT$  per blob”, or  $(N/g)kT$  altogether. That is, we expect

$$\begin{aligned} \xi^2 &\sim gb^2 \\ R &\sim (N/g)\xi \\ \Delta F &\sim (N/g)kT \end{aligned} \quad (2.2.7)$$

When these assumptions are combined, we obtain

$$\begin{aligned} N/g &\sim (R/R_e)^2 \\ \xi^2/Nb^2 &\sim (R_e/R)^2 \\ \Delta F &\sim kT(R/R_e)^2 \end{aligned} \quad (2.2.8)$$

That is, 1) the number of blobs is of order the “stretch ratio”  $R/R_e$  squared (the stretch ratio is the ratio of the proscribed end-to-end distance  $R$  to the mean end-to-end distance  $R_e$ ); 2) the blob size compared to the unstretched coil size goes as the inverse stretch ratio squared; and 3) the free energy stored in deformation is  $kT$  times the stretch ratio squared, or  $kT$  times the number of “stretch blobs” (marginally perturbed segments).

The above argument is a “scaling argument”, in which we are concerned with how a set of interrelated quantities with some given parameter (here, the stretch ratio, or equivalently the stored free energy in  $kT$  units). By “scaling”, we mean the power law or other functional dependence the quantities have on the parameter. In cases where there is only one parameter varying, we can often determine the scaling by some combination of physical arguments (as here) augmented by dimensional analysis, without doing any calculation, and without keeping track of numerical prefactors (the omission of the prefactors is what is meant by the  $\sim$  relation.)

Scaling arguments are very useful in several ways:

- They are easier to work out than full calculations.
- They can be useful in assessing which physical effects to neglect and which to focus on, in designing a model simple enough to analyze.
- They constrain the behavior of a more precise calculation; if the calculation violates the scaling argument, a mistake has been made.

### Freely jointed chain

The freely jointed chain model turns out to be simple enough that we can compute the force-extension relation exactly from the partition function, while capturing the expected finite extensibility of a real chain. To represent a freely jointed chain under constant tension  $f$ , we introduce a simple expression for the potential energy  $U$ , as

$$U = -R \cdot f \quad (2.2.9)$$

in which  $R$  is the fluctuating end-to-end vector,

$$R = a \sum_k n_k \quad (2.2.10)$$

in terms of the step length  $a$  and set  $\{n_k\}$  of unit vectors describing each step.

The partition function  $Z$  is

$$Z = \int \prod_k dn_k e^{\beta a \sum_k f \cdot n_k} \quad (2.2.11)$$

Because each step is independent, coupled only to the biasing force  $f$ , the multidimensional integral over all  $n_k$  factors into a product of integrals over each step:

$$Z = \left( \int dn e^{\beta f a \hat{z} \cdot n} \right)^N \quad (2.2.12)$$

in which we have taken the force to point along the  $z$  axis.

Correspondingly, the mean end-to-end displacement  $R$  along the  $z$  axis is

$$\langle R \rangle = \frac{aN \int dn e^{\beta f a \hat{z} \cdot n} \hat{z} \cdot n}{Z} \quad (2.2.13)$$

The fully extended length of the chain is evidently  $aN$ .

The dependence on the force appears in terms of the dimensionless group  $\beta f a$ , which compares the orientational energy of a single steps under tension  $f a$  to the thermal energy. When  $\beta f a$  is small, the individual steps are only weakly oriented, and the chain is a weakly biased random walk. When  $\beta f a$  is large, the individual steps are strongly biased to point along  $\hat{z}$ , and the chain approaches its fully extended length. To simplify the notation, we define  $x = \beta f a$ .

The integrals  $\int dn$  over the unit sphere of possible directions for the step can be written in spherical coordinates as  $\int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta$ . Since the Boltzmann factor  $e^{x \cos\theta}$  is independent of  $\phi$ , the integrals over  $\phi$  cancel in the numerator and denominator of the expression for  $\langle R \rangle$ . The integral over  $\theta$  can be recast as an integral over  $\cos\theta = \mu$  (because  $\sin\theta d\theta = d(\cos\theta) = d\mu$ ), where  $\mu$  runs from -1 to 1. The partition function becomes

$$Z = \left( \frac{1}{2} \int_{-1}^1 d\mu e^{x\mu} \right)^N = \left( \frac{\sinh x}{x} \right)^N \quad (2.2.14)$$

Here we have introduced a constant factor  $1/2$  in each partition integral, which amounts to defining the zero of free energy as the unperturbed random walk (for which  $x \rightarrow 0$  and  $Z \rightarrow 1$ ).

Note that we can write  $R$  in terms of a derivative of  $Z$ , as

$$\frac{\langle R \rangle}{a} = N \langle \mu \rangle = \frac{\partial \log Z}{\partial x} = N (\coth x - 1/x) \quad (2.2.15)$$

This result gives the force-extension law in an “inverse” form; we would like to write  $f$  as a function of  $\langle R \rangle$ , but the function on the right-hand side cannot be inverted in terms of common functions.

However, we can explore the force-extension law by plotting it, and we can investigate the small- and large-force limits of the force-extension law, by taking the limits of small and large  $x$ . For large  $x$ , the function  $\coth x - 1/x$  is approximately  $1 - 1/x$ , and so  $\langle R \rangle$  approaches the fully extended length  $Na$ , with corrections of order  $1/(\beta a f)$ .

For small  $x$ , we expand  $\coth x$  as  $1/x + x/3 + \dots$ , which leads to

$$\langle R \rangle \approx (1/3)N\beta f a^2 \quad (2.2.16)$$

We can invert this linear force-distance relation to write

$$f = \frac{3kT}{Na^2} R \quad (2.2.17)$$

This entropic spring constant  $K = 3kT/(Na^2)$  is exactly what we obtained by considering the entropy of a random walk as a function of the end-to-end vector. We can also argue that this force should be the derivative of the free energy with respect to the end-to-end vector,  $f = -\partial F/\partial R$ , which we can integrate to obtain

$$\Delta F = \frac{3kT}{2Na^2} R^2 \quad (2.2.18)$$

which is again the entropic cost of requiring the end-to-end vector to take a certain value.

More generally, we can obtain the free energy by taking the log of the partition function  $Z = e^{-\beta F}$ , which gives

$$F = -kT \log Z = -NkT \log \left( \frac{\sinh x}{x} \right) \quad (2.2.19)$$

The free energy defined this way equals  $E - TS$ , i.e., it includes the energy  $-R \cdot f$ . We can obtain the entropic part of the free energy  $-TS$  by subtracting the energy from  $F$ , and regarding the combination as a function of  $R$ :

$$-TS(R) = F(f) + Rf \quad (2.2.20)$$

Practically speaking, to compute the entropy using this result we select a value of  $f$ , compute the corresponding values of  $F$  and  $R$  and hence  $S$ . To obtain the function  $S(R)$ , we generate a table of values  $\{f_i\}$  and the corresponding values  $\{R_i\}$  and  $\{S_i\}$ , and then the pairs  $\{R_i, S_i\}$  as numerically defining the function  $S(R)$ . Plotted this way, we find that  $S(R)$  monotonically increases from zero (the entropy was defined with respect to the unstretched chain), and diverges logarithmically at maximum extension (when the number of configurations becomes vanishingly small).

## 2.3 Scattering and the size of polymers

[Reading: CR Chapter 2, Sections 2.4 and 2.8] Single polymer molecules are too small to see with the unaided eye. However, we can use scattering of X-rays, neutrons, or light to “look” at the average shape of a polymer. These experiments are all variations on scattering a well-defined wave from an object whose size is comparable to the wavelength of the incident radiation. To understand how to interpret such experiments, we need to describe the scattering of waves. Because polymer coils fluctuate in their conformation, we must perform averages over the possible conformations in order to predict the results of scattering experiments.

### Radius of gyration

The end-to-end distance provides one measure of the size of a fluctuating polymer chain. However, it only depends directly on the location of the two ends, not on the intervening monomers. Another more democratic measure of the size of the coil is the radius of gyration, defined by

$$R_g^2 = 1/N \sum_i (R_i - \bar{R})^2 \quad (2.3.1)$$

in which  $\bar{R}$  is the position of the center of mass, defined by

$$\bar{R} = 1/N \sum_i R_i \quad (2.3.2)$$

Thus the radius of gyration is the average of the square distance from each monomer to the center of mass.

It turns out that another equivalent expression for the gyration radius is

$$\begin{aligned} R_g^2 &= 1/2N^2 \sum_{i,j} (R_i - R_j)^2 \\ &= 1/2N^2 \sum_{i,j} ((R_i - \bar{R}) - (R_j - \bar{R}))^2 \\ &= 1/2N^2 \sum_{i,j} ((R_i - \bar{R})^2 - 2(R_i - \bar{R})(R_j - \bar{R}) + (R_j - \bar{R})^2) \\ &= 1/N \sum_i (R_i - \bar{R})^2 - \left[ 1/N \sum_i (R_i - \bar{R}) \right]^2 \\ &= 1/N \sum_i (R_i - \bar{R})^2 \end{aligned} \quad (2.3.3)$$

Viewed this way, the radius of gyration is an average of the square distance from any monomer to any other monomer.

We can compute the mean square radius of gyration for a flexible polymer, by performing the average over configurations of the second expression, as follows:

$$\begin{aligned} \langle R_g^2 \rangle &= 1/2N^2 \int ds ds' \langle (R(s) - R(s'))^2 \rangle \\ &= 1/N^2 \int_0^N ds \int_0^s ds' (s - s') b^2 \\ &= Nb^2/6 \end{aligned} \quad (2.3.4)$$

In the above, we used the fact that  $\langle (R(s) - R(s'))^2 \rangle$  is the mean-square end-to-end distance of the polymer strand between monomers  $s$  and  $s'$ , which is  $|s - s'|$  monomers long, and so has mean-square end-to-end distance  $|s - s'|b^2$ . (We then divide the square region of integration into two identical regions,  $s > s'$  and  $s < s'$ , to replace the inconvenient absolute value  $|s - s'|$  with  $s - s'$ , in the integration  $\int_0^N ds \int_0^s ds'$ .)

Remarkably, the radius of gyration emerges from a consideration of scattering of waves (light, X-ray, or neutrons) from a weakly scattering object, as we shall demonstrate in the next section.

## Scattering

One very important probe of small objects is to scatter various kinds of radiation from them. The radiation can be monochromatic light from a laser, collimated single-energy neutrons from a nuclear reactor or a spallation source, X-rays from a laboratory rotating anode source or a synchrotron.

In each case, the essential physics is that the incident radiation can be regarded as a plane wave impinging on a small but macroscopic region of the sample, which scatters a certain amount of the radiation in various directions as an outgoing wave, where the scattered intensity is measured by a detector far from the sample. The wave electromagnetic for the case of light and X-rays, and a quantum-mechanical “matter wave” for the case of neutrons, but the mathematical description for all three is similar.

A reasonable mental image is to think of waves in a water tank generated by an immersed vertical plate oscillating up and down at a regular frequency; the waves travel along with planar wavefronts until they reach some small object held fixed in the water, whereupon a pattern of circular scattered waves emanates from the scatterer (small object).

We write the incoming wave as a plane wave, with amplitude at location  $\mathbf{x}$  equal to

$$A_{in} = A_0 e^{i\mathbf{k}\cdot\mathbf{x}} e^{-i\omega t} \quad (2.3.5)$$

(To obtain a real-valued wave, we may for example take the real part of the above expression.) This expression represents a traveling plane wave. The planar wavefronts are perpendicular to the “wavevector”  $k$ , which can be seen by noting that two points  $x$  and  $x + \delta x$  have the same phase (value of the exponent) if  $k \cdot \delta x = 0$ , i.e., if the two points are displaced perpendicular to the wavevector.

Two points displaced by  $\lambda$  normal to the wavefronts (i.e., in the direction of  $k$ ) have the same amplitude, with phase displaced by  $2\pi$ , from which we find

$$|k|\lambda = 2\pi \quad (2.3.6)$$

We can see that the wave travels in the direction of  $k$ , because the origin ( $x = 0$ ) is a point of zero phase at time zero, whereas at later times a point of zero phase along the  $k$  direction satisfying

$$k \cdot x = \omega t \quad (2.3.7)$$

Thus the plane of zero phase moves in the  $k$  direction with velocity  $\omega/|k|$ .

This wave strikes a sample located at the origin, with some finite extent away from the origin described by its “scattering density”  $\rho(\mathbf{x})$ . For light, the scattering density is proportional to difference in refractive index; for X-rays, scattering density is proportional to the electron density and hence ultimately to the atomic number of atoms present; and for neutrons, the scattering density is mainly a function of the number of hydrogen and deuterium atoms present.

Here  $\mathbf{k}$  is the wavevector of the wave, and  $\omega$  its temporal frequency; that is, the field (electromagnetic, or matter wave) oscillates with frequency  $\omega$ , and the wavelength — distance between

successive peaks in the wave — is such that  $k\lambda = 2\pi$ , or  $\lambda = 2\pi/k$ . The length  $k$  of the wavevector  $\mathbf{k}$  is called the wavenumber. Note that the wavevector points in a direction perpendicular to the wavefronts, because any two points separated by some  $\Delta\mathbf{x}$  perpendicular to  $\mathbf{k}$  have the same phase.

(In writing a wave as a complex exponential, we are making use of a mathematical convenience in the case of electromagnetic waves, for which the actual fields are real; we should quietly take the real part of any wave amplitude at the end of a calculation.)

In any case, an outgoing spherical wave emanates from each scattering point  $\mathbf{x}_s$ , with an amplitude at location  $\mathbf{x}$  equal to

$$\delta A_{out}(\mathbf{R}, \mathbf{x}) = A_0 \rho(\mathbf{x}) e^{i\mathbf{k}\cdot\mathbf{x}} e^{-i\omega t} \frac{e^{ik|\mathbf{R}-\mathbf{x}|}}{|\mathbf{R}-\mathbf{x}|} \quad (2.3.8)$$

in which  $|\mathbf{R}-\mathbf{x}|$  is the distance from the scatterer at  $\mathbf{x}$  to the observation point at  $\mathbf{R}$ . The above expression describes spherical wavefronts, with the phase  $k|R-x|$  growing linearly with distance in all directions away from the scatterer at  $x$ . The wavefronts at time  $t=0$  are spherical shells with radii  $2\pi n/k$ , for  $n=0, 1, 2, \dots$

The factor  $|R-x|$  in the denominator enforces the requirement that the intensity of the spherical wave (which is given by the square of the amplitude), integrated over the entire spherical shell at some fixed distance  $d$  from the scatterer, will be independent of  $d$ . The total scattered intensity is conserved, corresponding either to the energy of the scattered wave (for electromagnetic waves) or the probability of observing a particle (for quantum-mechanical matter waves). Hence the intensity in any given direction falls off as the inverse square of the distance, and the scattering amplitude falls off inversely with distance.

The sample, though macroscopic, is small (microns for light, millimeters for X-rays, up to centimeter for neutrons, depending on the collimation and focussing of the beam, limited by the incident wavelength), and the detector is far away (many centimeters to a few meters). So we expand  $|\mathbf{R}-\mathbf{x}|$ , writing

$$\begin{aligned} |\mathbf{R}-\mathbf{x}| &= \sqrt{\mathbf{R}^2 - 2\mathbf{R}\cdot\mathbf{x} + \mathbf{x}^2} \\ &\approx R(1 - 2\mathbf{R}\cdot\mathbf{x}/R^2)^{1/2} \approx R - \mathbf{n}\cdot\mathbf{x} \end{aligned} \quad (2.3.9)$$

in which  $\mathbf{n}$  is a unit vector that points in the same direction as  $\mathbf{R}$ .

The small change in distance to the detector as we move over the sample is negligible in the denominator, but not in the exponent, where it has the effect of changing the phase of the scattered wave received at the detector. (If we change the path length from scatterer to detector by of order a wavelength, the phase of the scattered amplitude is changed significantly relative to other scattered waves.) So we use the above expansion to write the outgoing wave from a scattering point as

$$\delta A_{out}(\mathbf{R}, \mathbf{x}) = A_0 \rho(\mathbf{x}) e^{i\mathbf{k}\cdot\mathbf{x}} e^{-i\omega t} \frac{e^{-i\mathbf{k}\cdot\mathbf{x}}}{R} = \frac{A_0 e^{-i\omega t}}{R} \rho(\mathbf{x}) e^{-i\mathbf{q}\cdot\mathbf{x}} \quad (2.3.10)$$

Here we have absorbed into the amplitude  $A_0$  the constant phase factor  $e^{ikR}$ , which is the “reference phase shift” from the origin to the detector, independent of the displacement  $x$  of the various scatterers from the origin.

In the above,  $\mathbf{q}$  is the scattering wavevector, defined by

$$\begin{aligned} \mathbf{q} &= \mathbf{k}' - \mathbf{k} \\ \mathbf{k}' &= k\mathbf{n} \end{aligned} \quad (2.3.11)$$

That is, the scattered wavevector  $\mathbf{k}'$  has the same wavelength as the incident wave, but points towards the detector; and the scattering wavevector connects the tip of the incident wavevector (which points forwards) to the tip of the scattered wavevector. By analyzing this geometry, we can show that

$$q = \frac{4\pi}{\lambda} \sin(\theta/2) \quad (2.3.12)$$

where  $\theta$  is the deflection angle between the incoming wavevector  $k$  (direction of the incoming beam) and the outgoing wavevector  $k'$  (direction from the sample to the detector).

From the scattered amplitude, we can see that two scatterers at  $x$  and  $x+\delta x$  scatter “coherently” — with the same phase at the detector — if  $q \cdot \delta x = 0$ . By drawing the paths perpendicular to the incoming plane wavefronts from the source to the scatterers, and the paths perpendicular to the outgoing wavefronts from the scatterers to the detector, we can see directly that two particles displaced perpendicular to  $q$  have the same path length.

In contrast, if we draw the corresponding paths for a pair of particles displaced along  $q$ , we find that the paths are not the same length. The geometry, and the phase factor  $e^{iq \cdot x}$ , tell us that particles displaced along  $q$  by a length  $\pi/q$  will scatter “incoherently” — out of phase — at the detector. The magnitude of  $q$  determines the necessary displacement for particles to scatter out of phase. Roughly speaking, particles displaced by less than  $\pi/q$  along the  $q$  direction scatter coherently. Thus the magnitude of  $q$  determines the length scale over which scattering probes inhomogeneities in the sample, since particles closer than  $\pi/q$  scatter coherently, as a single scattering entity.

As the scattering angle  $\theta$  is varied (by moving the detector in an arc around the sample), the direction of  $q$  changes, and its magnitude varies over a certain range of values. The smallest magnitude corresponds to the smallest angle  $\theta$ , which is limited in practical situations by how close the detector can come to the forward direction, without being damaged by the intense, unscattered main beam.

Every point in the sample scatters, so the total scattered amplitude at the detector is the sum over all points in the sample. If the scattering amplitude is strong, so that a scattered wave may be scattered again by some other scatterer before it exits the sample, then it is not simple to sum up the scattering contributions. This is called “multiple scattering”, and experimenters work hard to avoid it by adjusting things so that the scattering amplitude is not too strong (by doing such things as index matching the sample, using thin samples, and so on).

If we have weak scattering, it is a good approximation to assume that waves are not multiply scattered (this is called the Born approximation), so that the amplitude at the detector is

$$A_{out} = \frac{A_0 e^{-i\omega t}}{R} \int d^3x \rho(\mathbf{x}) e^{-i\mathbf{q} \cdot \mathbf{x}} = \frac{A_0 e^{-i\omega t}}{R} \rho(\mathbf{q}) \quad (2.3.13)$$

in which  $\rho(\mathbf{q})$  is the Fourier transform of the scattering density  $\rho(\mathbf{x})$ . Some authors use a tilde, as in  $\tilde{\rho}(\mathbf{q})$ , to distinguish the Fourier transform from the original function; others, as here, use the letter chosen for the argument ( $q$  and  $k$  for wavevectors,  $x$  and  $r$  and such for positions) to distinguish between the original function and the transform.

Detectors, it turns out, measure not wave amplitudes but rather wave intensities. The intensity  $I$  of a wave is the complex modulus of the amplitude,  $I = |A|^2$ . To see this, write the amplitude  $A$  as

$$A = a \exp(i\phi) \exp(-i\omega t) \quad (2.3.14)$$

in which the amplitude front factor  $a$  and the phase  $\phi$  are both real. All oscillatory waves observed at a given point, for example the sum of the scattered waves at the detector, can be written this way, because all complex numbers can be written this way.

Now the actual field amplitude in the case of electromagnetic waves is the real part of these complex exponentials; so the field intensity at the detector is

$$I = a^2 \cos(\phi - \omega t)^2 \quad (2.3.15)$$

which oscillates extremely rapidly (at the frequency of the light). The detector responds to the short-time average of this field, which is  $\bar{I} = a^2/2$ . (For quantum mechanical matter waves, the wave amplitude actually is a complex number, and the probability of detecting a particle is proportional to the complex modulus of that amplitude, so the result is the same as for electromagnetic waves, up to the factor of 1/2.)

So, assuming we have weak scatterers (no multiple scattering), the detector measures a signal proportional to the modulus squared of the Fourier transform of the scattering length density:

$$I(q) = \frac{A_0^2}{R^2} \rho(\mathbf{q})\rho(-\mathbf{q}) \quad (2.3.16)$$

(In the above, we have used the fact that the complex conjugate  $\rho^*(\mathbf{q})$  of the Fourier transform of a real-valued field  $\rho(\mathbf{x})$ , is equal to  $\rho(-\mathbf{q})$ .) The signal is also proportional to the square of the incident amplitude  $A_0$ , and dies off as  $1/R^2$  (the inverse square law for wave intensity).

Note that even if we could measure  $I(q)$  with perfect accuracy, we could not infer the density of scatterers  $\rho(x)$ . This is because we cannot simply “take the square root” of the real-valued  $I(q)$ , to obtain  $\rho(q)$  which is in general complex, and hence cannot invert the Fourier transform to find  $\rho(x)$ . The “phase information” has been lost; we know  $|\rho(q)|$ , but not its complex phase. As a result, comparison of theoretical predictions of the structure of the scatterers to experimental measurements of  $I(q)$  is almost always a matter of “forward modeling”. A guess is made as to the structure, perhaps with some adjustable parameters, which are then varied to give the best fit to  $I(q)$ . Thus we may say that the scattering is consistent with some model, but cannot rule out that some rather different arrangement of scatterers could produce very similar results.

### Scattering from single ideal chains

Here we compute the expected scattering intensity from a dilute solution of ideal flexible chains. Because the solution is dilute, we may regard the relative location of chains as completely random; therefore, the scattering from different chains is completely incoherent, which means that the intensities from different chains add together.

To see this, consider the simple case of two equal strength point sources scattering into a detector, with random phases relative to each other; the amplitude at the detector could be written

$$A = A_0 \exp(-i\omega t) (1 + \exp(i\phi)) \quad (2.3.17)$$

Then the average intensity (averaged over the random phase) would be

$$\begin{aligned} \langle I \rangle &= A_0^2 \langle (1 + \exp(i\phi))(1 + \exp(-i\phi)) \rangle \\ &= A_0^2 (1 + 0 + 0 + 1) \end{aligned} \quad (2.3.18)$$

The crossterms vanish under averaging over the relative phase, and we get the same result as if we had simply added the intensities. If the two scatterers had scattered coherently, with the same relative phase (i.e.,  $\phi = 0$ ), we would have had an intensity of  $4A_0^2$  rather than  $2A_0^2$ . This difference becomes more pronounced if we have  $N$  particles, rather than just two. If the  $N$  particles scatter incoherently, the intensity is proportional to  $N$ ; whereas, if the particles all scatter coherently, the intensity is proportional to  $N^2$ .

In a typical scattering geometry, the scattering volume illuminated by the source and imaged onto the detector would contain very many chains, even for a quite dilute solution, so that the instantaneous intensity at the detector would result from the incoherent scattering from many chains, each in a different configuration. Because there are many chains scattering at once, the intensity would represent an average over the chain conformations. If the sample were extremely dilute, or the scattering volume very small, it may be that so few chains scatter at any moment, that the scattered intensity is not averaged instantaneously. In this case, the intensity at the detector would fluctuate in time, and the time-averaged intensity would restore the average over chain conformations.

To perform the average over conformations of the scattering from a single chain, we introduce the density for a single chain as

$$\rho(x) = \int ds \delta(x - r(s)) \quad (2.3.19)$$

The corresponding Fourier transform is

$$\rho(q) = \int d^3x \exp(-iq \cdot x) \rho(x) = \int ds \exp(-iq \cdot r(s)) \quad (2.3.20)$$

This is evidently a fluctuating object; we want the average intensity, from many different chains in the scattering volume.

So we compute the average intensity, as

$$\langle I \rangle = \frac{A_0^2}{R^2} \int ds ds' \langle \exp(-iq \cdot (r(s) - r(s'))) \rangle \quad (2.3.21)$$

We need the average for the integrand. To compute it, we use the fact that we know the distribution function for the separation  $R = r(s) - r(s')$ ; it is a Gaussian, proportional to  $\exp(-3R^2/2|s - s'|b^2)$ . So we write

$$\langle \exp(iq \cdot (r(s) - r(s'))) \rangle = \frac{\int d^3R \exp(-3R^2/2|s - s'|b^2) \exp(iq \cdot R)}{\int d^3R \exp(-3R^2/2|s - s'|b^2)} \quad (2.3.22)$$

We deal with the Gaussian integral in the numerator by “completing the square”; that is, write

$$\begin{aligned} -3R^2/2nb^2 + iq \cdot R &= -3/2nb^2 (R^2 - 2inb^2/3q \cdot R) \\ &= -3/2nb^2 \left( (R - inb^2/3q)^2 + (nb^2/3)^2 q^2 \right) \end{aligned} \quad (2.3.23)$$

in which  $n$  equals  $|s - s'|$ . Then we can change variables in the numerator integral to  $R' = R - inb^2/3q$ , whereupon the integral is the same Gaussian as the denominator, times  $\exp(-b^2q^2n/6)$ . The final result is

$$\langle \exp(iq \cdot (r(s) - r(s'))) \rangle = \exp(-b^2q^2n/6) \quad (2.3.24)$$

Using this result in the expression for  $\langle I \rangle$ , we have

$$\langle I \rangle = \frac{A_0^2}{R^2} \int ds ds' \exp(-b^2q^2|s - s'|/6) \quad (2.3.25)$$

And remarkably, we have seen this exact integral before, in the context of the mean-square end-to-end distance of semiflexible chains. Applying that result here, we have finally

$$\begin{aligned} \langle I \rangle &= \frac{A_0^2}{R^2} N^2 g(q^2 R_g^2) \\ g(x) &= 2(x - 1 + \exp(-x))/x^2 \end{aligned} \quad (2.3.26)$$

The function  $g(x)$  is called the Debye function, and describes the average scattering from dilute ideal polymer chains. In the limit of small wavenumber, where small means  $q^2 R_g^2$  much less than unity, all of the monomers in the polymer scatter coherently (i.e., in phase), and the scattering intensity is proportional to  $N^2$  (the amplitudes add, and the intensity goes as the amplitude squared).

As the wavenumber increases, different portions of the chain begin to scatter out of phase with each other. We see this by expanding  $g(x)$  for small  $x$  as

$$g(x) \approx 1 - x/3 \dots \quad (2.3.27)$$

This means that when  $q^2$  starts to be comparable to  $R_g^2$ , the scattering intensity decreases. By this means, we can measure the size of polymer coils in solution, as long as the coil size is in the range of accessible scattering wavenumbers.

### Scattering and fractal dimension

The scattering  $I(q)$  for a dilute polymer solution, proportional to  $g(q^2 R_g^2)$ , does not have very much structure; basically, it has a characteristic length ( $q R_g = 1$ ) and a power-law falloff at large  $q$ , as  $q^{-2}$ . Here, we consider an argument for the form of the falloff, which reveals something about the short-range structure of random walks.

We have argued previously that at a given wavevector  $q$ , scatterers closer to each other than  $2\pi/q$  will scatter “coherently”, i.e., the spherical waves emanating from these scattering points will arrive at the detector with nearly the same phase. So the selection of  $q$  determines the “resolution” with which we examine the sample.

So consider an ideal polymer chain of  $N$  total steps, and imagine the walk as a sequence of  $N/n$  subchains, of  $n$  steps each. Each of the subchains is itself a random walk, with a characteristic size  $R(n)$  scaling as  $\sqrt{nb}$ . If we adjusted  $q$  such that  $qR(n)$  was of order unity, which is to say  $q$  scaling as  $n^{-1/2}/b$ , then each subchain would scatter coherently.

The  $N/n$  different subchains, separated by distances larger than  $1/q$ , would scatter incoherently, i.e., their intensities would add linearly at the detector. As a result, the scattered intensity at the detector would scale as  $N/n$  times  $n^2$ , or  $Nn$ . Writing this in terms of  $q$ , we have  $I(q)$  scaling as  $N/(q^2 b^2)$ , in agreement with our calculation.

This argument can be generalized, for other types of random arrangement of scatterers. The key ingredient how the number and mass of subunits of the collection of scatterers depends on the spatial “resolution” or length scale  $1/q$ . Suppose we have a random collection of scatterers of total mass  $M$ , with the property that if we “coarse-grain” the random collection on a length scale  $\xi$ , there are of order  $M/m$  subunits, each of mass  $m$ , with  $m(\xi)$  scaling as  $(\xi/a)^{D_f}$ .

Here we call  $D_f$  the “fractal dimension”; it tells how the mass of a randomly constructed object depends on its size relative to the size  $a$  of its constituents. (For the ideal random walk, we had  $R(n)$  scaling as  $\sqrt{nb}$  or equivalently  $n(R)$  scaling as  $(R/b)^2$ , so  $D_f = 2$  in this language.) Not all collections of scattering points are fractals; scaling of this form is a rather special property, that indicates that the random structure is “self-similar” — it “looks the same” under different magnifications, or “has no characteristic length scale” other than the size of the constituent and the size of the entire object.

When we do have a fractal, though, the scattering at wavelengths  $1/q$  smaller than the size of the entire object again scales as the number of subobjects  $M/m$  times the coherent scattering  $m^2$  from each; with  $m$  scaling as  $(qa)^{-D_f}$ , this leads to  $I(q)$  scaling as  $M/(qa)^{D_f}$ . Hence when we observe a power-law dependence of scattering, it can sometimes be interpreted as a measure of the “fractal dimension” of the collection of scatterers.

### Structure factor and form factor

Scattering is a very versatile probe of microscopic structure, which we will revisit in various forms in later lectures. Now, we consider the common example of scattering from a fluid of pointlike particles. In a fluid, the particle locations are not completely random, but are correlated in some way, because the molecules cannot strongly overlap, but are held by attractive interactions into close contacts. The resulting structure of the fluid is described by the pair correlation function,

$$g(r, r') = \rho^{-2} \langle \rho(r) \rho(r') \rangle \quad (2.3.28)$$

in which  $\rho(r)$  is the concentration of particles at  $r$ , with average value  $\rho$ .

The function  $g(r, r')$  measures the joint probability of having a particle at  $r$  and a second particle at  $r'$ . Because a homogeneous fluid is translationally invariant,  $g(r, r')$  actually only depends on the separation vector  $r - r'$  (there are no distinguished locations in the fluid). Likewise, for an isotropic fluid,  $g(r, r')$  does not depend on the direction of the separation vector  $r - r'$ , but only on its length  $|r - r'|$ .

For large separations  $|r - r'|$ , the two points  $r$  and  $r'$  are uncorrelated — a particle will be present at  $r'$  without regard to whether another particle is present at  $r$ . Hence the average  $\langle \rho(r) \rho(r') \rangle$  for large separations can be factored as  $\langle \rho(r) \rangle \langle \rho(r') \rangle$ , which equals  $\rho^2$ . The front factor of  $\rho^{-2}$  in the definition of  $g(r, r')$  is chosen so that  $g(r, r')$  approaches unity for large separations.

We have shown earlier that the scattered intensity  $I(q)$  from a collection of pointlike scatterers is proportional to the average  $\langle \rho(q) \rho(-q) \rangle$ . This average in turn can be related to  $g(r, r')$  using Fourier transforms:

$$\begin{aligned} I(q) &\propto \langle \rho(q) \rho(-q) \rangle \\ &= \int dr \int dr' e^{-iq \cdot (r - r')} \langle \rho(r) \rho(r') \rangle \\ &= \rho^2 \int dr' \int dr e^{-iq \cdot r} g(r) \\ &= N \rho \int dr e^{-iq \cdot r} g(r) \end{aligned} \quad (2.3.29)$$

In the above, we reverse the order of integration, and shift the integration variable  $r$  by  $r'$ . The integral  $\int dr'$  then gives a factor of  $V$  (the illuminated scattering volume);  $\rho V$  equals  $N$ , the total number of scatters. The result says that the scattered intensity is proportional to the number of scatters, times the Fourier transform of the pair correlation function.

A similar argument can be made for particles that are not pointlike, but have a scattering density profile. For convenience, suppose the particles are spherically symmetric, with a density profile given by  $f(r)$ . We can regard the particles as composed of tiny pointlike scattering bits. The scattering intensity is still proportional to the Fourier transform of the pair correlation function  $g(r, r')$  of the pointlike scattering bits.

We can write this pair correlation function in terms of the density profile  $f(r)$  and pair correlation function of the particles  $g_0(r, r')$ , as

$$g(r) = \int dr_1 \int dr_2 f(r_1) f(r_2) g_0(r + r_1 - r_2) \quad (2.3.30)$$

The above relation expresses the fact that the probability of finding a scattering bit at the origin and at  $r$ , requires there to be a particle near the origin and near  $r$ , such that the density profile of the first particle overlaps the origin, and the second particle overlaps  $r$ .

We evaluate the Fourier transform of  $g(r)$ , as

$$\begin{aligned}
 g(q) &= \int dr e^{-iq \cdot r} \int dr_1 \int dr_2 f(r_1) f(r_2) g_0(r + r_1 - r_2) \\
 &= \int dr_1 \int dr_2 \int dr_0 e^{-iq \cdot (r_0 + r_2 - r_1)} f(r_1) f(r_2) g_0(r_0) \\
 &= S_0(q) f(q) f(-q) = S_0(q) |f(q)|^2
 \end{aligned} \tag{2.3.31}$$

In the above, we define  $r_0$  by  $r_0 = r + r_1 - r_2$ , and shift the integral  $\int dr$  to an integral  $\int dr_0$ , thus separating the multiple integral into a product of Fourier transforms. The structure factor  $S_0(q)$  is the Fourier transform of  $g_0(r)$ , the pair correlation function of the particle centers.

Since the scattering intensity  $I(q)$  is proportional to  $g(q)$ , we have

$$I(q) \propto S_0(q) |f(q)|^2 \tag{2.3.32}$$

That is, the scattering intensity is proportional to the product of the particle structure factor, and the square of the “form factor”  $f(q)$  (Fourier transform of the particle density profile).

## 2.4 Single chains in real solvents

Up to now, we have considered only effects of flexibility on the conformations of a polymer chain, and said nothing about how conformations would be affected by interactions between monomers, or between the monomers of a chain and surrounding solvent.

Two monomers, distant along the chain but located close by in space, have some effective interaction potential  $U(r)$  that influences their relative position. This potential incorporates the effects of the intervening solvent, which can originate both in direct energetic interactions, as well as changes in the solvent configurational entropy induced by the presence of the monomers.

Qualitatively, the interaction potential will have a repulsive “hard core”, which imposes a high energetic cost for configurations in which two monomers overlap. The potential may also have an “attractive well”, a lower energy when the monomers are located close by, without intervening solvent. Such an attraction can have many different microscopic origins, but typically has a range of order the size of a monomer (unless interactions between charges contribute).

If the monomers were not bonded together to form a chain, but instead were simply free to move about in dilute solution, the potential  $U(r)$  would alter the probability  $P(r, r_0)$  of finding a second monomer at  $r$  near a given monomer at  $r_0$ .

When the distance between  $r$  and  $r_0$  is large, the probability  $P(r)$  must become equal to the average monomer concentration  $c$  — the monomer at  $r_0$  can have no effect on the concentration at distant points  $r$ . This motivates the definition of the pair correlation function  $g(r)$  as

$$P(r, r_0) = cg(|r - r_0|) \quad (2.4.1)$$

Roughly speaking, we expect  $g(r)$  to go like  $\exp(-\beta U(r))$ , because the probability of placing a second monomer near a given monomer (now at the origin) should be proportional to this Boltzmann factor.

For a potential  $U(r)$  with just a repulsive core and no attractive well, the effect of the potential on  $g(r)$  is clear; monomers are never found in the repulsive core, leading to an “excluded volume”. If a potential has both attractive and repulsive parts, a more detailed analysis than we present here finds that a useful measure of the effective size of the excluded volume is given by

$$v = \int d^3r (1 - \exp(-\beta U(r))) \quad (2.4.2)$$

The virial coefficient  $v$  measures the average change in  $g(r)$  (by our simple estimate) from what it would be if there were no interactions at all (i.e.,  $g(r) = 1$ ). Depending on the strength of attractive contributions to  $v$ , we may have the following cases:

- $v \approx v_0$ , where  $v_0$  is the excluded volume of a pair of monomers. For spherical monomers of hard-core radius  $a$ , this is  $v_0 = 4\pi/3(2a)^3$  (the monomers cannot approach closer than  $2a$ ). A solvent that induces no attractive interactions between monomers is called “athermal”.
- $v$  significantly less than  $v_0$ , but still positive. This is the case when the monomers feel some attraction, but not enough to overwhelm the hard-core contribution to  $v$ . Such a solvent is called a “good” solvent, though in some sense it should be called a “not-so-good” solvent, because it could be “better” by being athermal.
- $v = 0$ . This is the special case when the attractive and repulsive contributions cancel. Then, we have no pairwise interaction between monomers. At this special point, as we shall see below, chains behave as ideal random walks. Such a solvent is called a “theta” solvent.

- $v < 0$  but  $|v| < v_0$ . Attractions overwhelm repulsions; this is called a “poor” solvent, and leads to chain conformations of collapsed globules, but with some solvent present within the globule.
- $v \approx -v_0$ . Attractions are so strong that solvent is essentially repelled from within the globule. Such a solvent is called a “nonsolvent”.

It is convenient to consider the virial coefficient for an “effective monomer”, i.e., a Kuhn step. Because the chain is persistent in its direction, we should think of a Kuhn step as roughly cylindrical in shape, with length  $b^*$  and diameter  $d$  (where the monomers, say, are spheres of diameter  $d$ ). The excluded volume of two randomly oriented cylindrical monomers involves an average over their relative orientation.

When the angle between the two cylinders is  $\theta$ , the excluded volume is  $b^{*2}\theta d$  (the excluded volume is a parallelepiped of height  $d$  and side length  $l$ ). Averaging over  $\theta$  gives  $v = 2b^{*2}d/\pi$ . The answer scales as  $b^{*2}d$  rather than the (smaller) volume  $b^*d^2$ .

### Interaction effects on polymer size

Now we turn to consider the effect of monomer interactions on the conformations of the entire chain. We begin by estimating how likely are close approaches of monomers in a random walk, if no special measures are taken to avoid them.

First we note that a polymer in an ideal random-walk conformation is mostly empty space. We loosely define the “pervaded volume” of a polymer chain as the volume of a sphere sufficient to contain the conformation. (We sidestep questions of whether this definition should be precisely  $4\pi/3R_g^3$ , or  $R_e$  instead of  $R_g$ , or with or without the  $4\pi/3$ .) Additionally, we speak of the “displaced volume” of a chain as the space its monomers take up in solution; this volume  $\Omega$  equals  $N^*v_0$  (here again,  $N^*$  is the number of Kuhn monomers).

Now the fraction  $\phi$  of pervaded volume actually occupied by the chain scales as

$$\phi \sim \Omega/R_e^3 \sim N^{*-1/2}v_0/b^{*3} \quad (2.4.3)$$

which is small for long chains and smaller for stiff chains (since  $v_0/b^{*3}$  goes as  $(d/b^*)^2$ ).

But although the polymer coil is mostly empty space, there are a large number of monomer-monomer contacts within the coil. To count them, we consider one given monomer, observe that the expected number of other monomers within its excluded volume would be  $cv_0$ , where  $c$  is the monomer concentration within the pervaded volume, if the monomers were placed randomly. The concentration  $c$  satisfies  $cv_0 = \phi$ , so per monomer, we have an average of  $\phi$  contacts. Taking all monomers together, then, we have  $N\phi/2$  contacts (every contact counted twice). Though  $\phi$  was small (as  $N^{-1/2}$ ),  $N\phi$  is large (as  $N^{1/2}$ ).

What is the free energy cost of these contacts? If they were indeed overlaps between monomers, the energetic cost would be enormous. However, the literal overlap of two monomers can be avoided by local rearrangements, leading to “near misses” between two sections of chain. For example, one chain may rearrange two adjacent effective monomers in a “crankshaft motion” to swing a colliding monomer out of the way. This local rearrangement reduces the conformational entropy of the chain, by an amount of order  $kT$  since conformation of one freely jointed segment is no longer randomly selected (the freely jointed steps are less random by about one “decision”)

Another way for a polymer chain to avoid collisions is by adopting “fluffier”, more open conformations, for instance by separating its two ends as if under an external force. We know that a chain can roughly double its typical end-to-end distance at a cost of only about  $kT$ , which would avoid

a lot of contacts between monomers at a single stroke. So the question arises, what is the optimal strategy for the chain to maximize its entropy — should it remain an ideal random walk but make many local adjustments to avoid collisions, or should it adopt less prevalent fluffier conformations which preclude collisions?

A simple and ingenious argument was given by Flory to determine the optimum size for a chain in solution; one writes an estimate for the free energy of the chain, assumed to have a size  $R$  to be determined, as the sum of an “energy” cost for collisions, and an entropy cost for adopting a larger size:

$$\beta F = N^2 v / R^3 + 3/2 R^2 / R_e^2 \quad (2.4.4)$$

In the above, the second term is the same entropy change we wrote when considering the stretching of a chain; here, we assert that the entropy cost of making the chain “fluffier” scales the same way.

The first term is an estimate of the number of collisions  $N\phi$ , with a cost of  $kT$  per collision. This “energy” cost of collisions is actually entropic as well, to some extent, because of the entropy cost of the local rearrangement required to turn a collision into a near miss.

We choose  $R$  to minimize  $F$ :

$$0 = -3N^2 v / R^4 + 3R / R_e^2 \quad (2.4.5)$$

We cast the above in terms of the “stretch ratio”  $R/R_e$ , by rearranging to write

$$\begin{aligned} R/R_e &= (N/N_s)^{1/10} \\ N_s &= (b^{*3}/v)^2 \end{aligned} \quad (2.4.6)$$

in which  $N_s$  is the “swelling length”. Equivalently we may write

$$R = R_s (N/N_s)^{3/5} \quad (2.4.7)$$

in which  $R_s$  is the ideal end-to-end distance of a subchain of  $N_s$  monomers, i.e., the size of a thermal blob.

For sufficiently long chains, such that  $N$  is much larger than  $N_s$ , the Flory estimate finds that the optimum size of the polymer coil is larger than  $R_e$ , the ideal random-walk size, by a weak power law of  $N$ . Nonetheless, the difference between  $N^{1/2}$  and  $N^{3/5}$  can be distinguished, in scattering determinations of  $R_g$  versus  $M$  for chains in good solvent.

Note that  $N_s$  may be many monomers, if the chain is rather stiff [since  $v$  goes as  $b^{*2}d$ ,  $N_s$  goes as  $(b^*/d)^2$ ] or if the solvent is not very good (since  $v$  becomes small). Recall that we are working in terms of effective freely jointed segments, each of which consists of  $C_\infty / \cos^2(\theta/2)$  monomers, with step length  $b^*$  of  $C_\infty l / \cos(\theta/2)$ . Assuming that the monomers of the chain are roughly spherical, so that  $l$  and  $d$  are of the same order, we have that  $b^*/d$  is of order  $C_\infty / \cos(\theta/2)$ , and  $N_s$  corresponds to about  $(C_\infty / \cos(\theta/2))^2$  monomers.

Values of  $C_\infty$  of 5 or so are not uncommon, and with a typical deflection angle  $\theta$  of 60 degrees,  $\cos(\theta/2)$  equals  $\sqrt{3}/2$ . Thus  $N_s$  is of order  $100/3 \approx 30$  or so. so that even at  $N = 10^4$  monomers (a molecular weight of  $10^6$ g/mol in polystyrene) the ratio  $N/N_s$  is only about 300, and  $R/R_e$  is  $(300)^{1/10}$  or about 2. This may seem a small effect, but often we are interested in the pervaded volume, which scales as  $R^3$ , whereupon the swelling effect is larger. For example, we often want to know what is the “overlap concentration”, at which the individual coils of a dilute solution begin to pervade the entire space within the solvent. The overlap concentration marks the boundary between dilute and overlapping chains, which overlap leads to entanglement, large increases in solution viscosity, and other phenomena. Chain swelling results in a smaller overlap concentration, by a factor of 8 in the above example.

If we have a chain shorter than  $N_s$ , the above equation gives a nonsensical result, that the dimension of the chain is smaller than the ideal random walk. Indeed, if we have  $v = 0$ , the above argument would imply that  $R$  equals zero, which is certainly wrong. In fact, we should recover  $R/R_e$  equal to unity for  $N$  much smaller than  $N_s$ ; so clearly something is missing from the above argument.

What is missing, is the entropic cost of confining the chain to a smaller volume than it would otherwise pervade as an ideal random walk. We can give a scaling argument to estimate this entropic cost. Suppose we wanted to confine a chain into a volume of size  $R$  less than the ideal  $R_e$  for the chain. We can break the chain up into  $N/n$  subchains of  $n$  monomers, where  $n$  is chosen so that the subchains would just fit into the confined volume; that is, so that  $nb^2$  is of order  $R$ .

We can regard the entire chain as a random walk of subchain units. However, if we want to confine the chain into the volume of size  $R$ , the walk cannot be random; we place the first subchain into the volume, and the next subchain must likewise be placed into the volume, when it could have made a random step elsewhere. Each subchain gives up of order  $kT$  of free energy to return to the confining volume; the cost for the entire chain is  $N/nkT$ , or  $kTR_e^2/R^2$ .

We add this term to the Flory estimate for the chain free energy:

$$\beta F = \frac{3R^2}{2R_e^2} + \frac{N^2v}{R^3} + \frac{3R_e^2}{2R^2} \quad (2.4.8)$$

Now, minimizing with respect to  $R$  gives

$$(R/R_e)^5 - (R/R_e) = (N/N_s)^{1/2} \quad (2.4.9)$$

This equation describes the crossover between a swollen “self-avoiding” chain, and an ideal chain at theta condition. As  $v$  becomes small,  $N_s$  becomes large; for  $N$  much less than  $N_s$ ,  $R/R_e$  approaches unity, while for  $N$  much greater than  $N_s$ ,  $R/R_e$  scales as  $(N/N_s)^{1/10}$ .

The ingenuity of the Flory estimate is in writing the estimate of the interaction energy completely neglecting correlations, i.e., assuming the monomers to be randomly placed within the pervaded volume, while at the same time estimating the configurational entropy cost of a fluffier coil as for an ideal chain, i.e., without regard to what interactions between the monomers would do to the configurations. Each of these is a heuristic estimate; the surprising conclusion is that taken together, they give a serviceable approximation to the actual behavior of chains.

## 2.5 Polymer-polymer blends

In this lecture we construct a simple model that describes the free energy changes that occur when blends of two polymers mix or demix. We begin by considering a mixture of two small-molecule solvents. A detailed theory of the statistical mechanics of such a mixture would be daunting; the molecules have shape, internal modes, complicated interaction potentials; and their conformations at liquidlike densities would be extremely difficult to count.

So, we resort to a simplified model, that captures the essential physics of small-molecule mixtures; namely, a “lattice liquid”. We idealize the molecules as identical-sized spheres, and count the available configurations by obliging the molecules to reside within cells in a regular simple-cubic lattice. Every cell contains one molecule.

In the same spirit as the Flory theory of the size of a polymer chain, we estimate the free energy  $F$  of the lattice liquid as the sum  $E - TS$  of two terms: a simple “random mixing” estimate of the interaction energy  $E$  between neighboring molecules, and a corresponding estimate of the configurational entropy  $S$  in placing the molecules on the lattice.

On the lattice, each cell has  $Z$  neighbors with which it interacts; we assign an energy cost  $\chi$  to each pair of unlike neighbors. Every cell can be regarded as “owning” half of its bonds for counting purposes. Each bond can have unlike neighbors in two ways, if the first cell is type A and the second type B, or vice versa. Per cell, the average energy is then

$$E/N = (Z/2)\chi(\phi_A\phi_B + \phi_B\phi_A) = Z\chi\phi_A\phi_B \quad (2.5.1)$$

in which  $\phi_A = N_A/N$  is the fraction of  $N$  total sites occupied by  $N_A$  molecules of type A.

The configurational entropy we estimate by counting the number of ways  $\Omega$  of placing  $N_A$  molecules of type A and  $N_B$  of type B onto  $N$  total lattice sites, which is just  $N!/(N_A!N_B!)$ . The entropy is then  $S = k \log \Omega$ ; using the Stirling expansion, we have

$$\begin{aligned} S/k &= N \log N - N - (N_A \log N_A - N_A) - (N_B \log N_B - N_B) \\ &= (N_A + N_B) \log N - N_A \log N_A - N_B \log N_B \\ &= -N_A \log N_A/N - N_B \log N_B/N \end{aligned} \quad (2.5.2)$$

Thus the entropy per site is

$$S/(kN) = -\phi_A \log \phi_A - \phi_B \log \phi_B \quad (2.5.3)$$

Combining these two estimates, we have

$$\beta F/N = \beta\chi\phi_A\phi_B + \phi_A \log \phi_A + \phi_B \log \phi_B \quad (2.5.4)$$

Now we investigate the phase behavior implied by this free energy, as a function of  $\phi_A = \phi$  (with  $\phi_B = 1 - \phi$ ). The first term is a parabola with maximum of  $\beta\chi/4$  at  $\phi_A = \phi_B = 1/2$ ; the second term is concave up, with a minimum at  $\phi_A = \phi_B = 1/2$ . Evidently the first term favors demixing and the second favors mixing.

We can plot  $\beta F/N$  as a function of  $\phi$ : as  $\chi$  increases, the first term eventually splits the minimum at  $\phi = 1/2$  into a pair of minima, which progressively separate as  $\chi$  increases. These minima correspond to coexisting phases, the location of which are determined by the common tangent construction. The free energy of coexisting phases with a specified average value of  $\phi$ , determined by a linear mixing rule along the common tangent connecting the two phases, is evidently lower than any homogeneous point on the curve  $F(\phi)/N$ .

The locus of inflection points on the free energy define the spinodal, which represents the limit of stability of the single phase to spontaneous concentration fluctuations about the imposed average concentration. For points on the concave-down portion of the curve  $F(\phi)/N$ , the free energy can be made smaller by separating the homogeneous phase into two phases slightly richer and poorer in  $\phi$ . The free energy is thus unstable to small variations in the average concentration. Whereas, for points on the concave-up portion of the curve, separating the homogeneous phase into two phases slightly richer and poorer in  $\phi$  leads to a higher free energy; thus the free energy is stable to small perturbations.

The spinodal is easier to calculate than the binodal, as it satisfies

$$0 = \partial^2 \beta F / \partial \phi^2 = -2\beta\chi + 1/\phi + 1/(1-\phi) \quad (2.5.5)$$

which rearranges to

$$2\beta\chi\phi(1-\phi) = 1 \quad (2.5.6)$$

Because of the symmetry on exchange of A and B, which corresponds to  $\phi$  exchanged with  $1-\phi$ , it turns out to be convenient to focus on the difference between  $\phi$  and the symmetric value  $1/2$ , by defining  $\phi = 1/2 + \delta\phi$ . Then  $\phi(1-\phi)$  becomes  $(1/2 + \delta\phi)(1/2 - \delta\phi)$  or  $1/4 - \delta\phi^2$ , whereupon the spinodal equation is

$$\delta\phi^2 = (\beta\chi/2 - 1)/2\beta\chi \quad (2.5.7)$$

Evidently, the spinodal consists of a pair of real roots, as long as  $\beta\chi$  is greater than 2. This defines the critical point for the demixing. As the temperature decreases,  $\beta\chi$  increases, which increases the strength of the repulsive interactions relative to the entropy of mixing. The mixture separates into two coexisting phases.

Now we modify this treatment to deal with mixtures of two long flexible polymers A and B, with  $n_A$  and  $n_B$  segments respectively. We assume the A and B monomers to be the same size, such that they fit into the cells of the lattice as we assumed for the small-molecule mixture. But unlike the mixture of two small molecules, the polymers have a great deal of conformational freedom; it would appear to be challenging to count the number of these conformations, to account for the associated conformational entropy.

Here, we resort to an approximation, introduced by Flory (and justified later in a theoretical treatment by Edwards): we assume that the set of conformations available to a polymer in the mixed melt is the same as when the polymers are demixed. Why should this be true? First consider the case of A and B polymers of identical length; then, as long as the interactions between the A and B monomers are weak enough not to perturb the conformations very much, conformations in the A-B mixture can simply be thought of as identical to conformations in the pure A state, with a certain number of the chains randomly chosen to be labeled B.

If the lengths of the A and B polymers are not identical, but both are long, the argument is slightly different. Then, we say that if the interactions between A and B monomers are weak enough, then the conformations of both kinds of chains in the melt, whether mixed or unmixed, must essentially be ideal random walks. The reasoning is as follows: chains in a melt must constantly make small adjustments to avoid other chains; there is no distinction, if the chains have identical local structure, between avoiding an A chain or a B chain, or between avoiding distant portions of the same chain or avoiding other chains.

Thus (Flory argued, and Edwards proved) chains in the melt adopt essentially ideal random-walk configurations, whether in a pure state or in a mixed state. Since the same set of conformations is available to the chains in the mixed or pure state, there is no change in the conformational entropy upon mixing, which eliminates the need to count the number of chain conformations. This

argument assumes “conformational identity” between the two species of polymers; which would not be so if the two chains had different stiffness, or different diameters. In such a case, there could (and would) be a change in the conformational entropy upon mixing, which would lead to an excess free energy as a result of the relative ease or difficulty of packing chains of different stiffness or diameter together in the same melt.

What remains to count are the number of ways to locate the chains on the lattice. Each chain has one translational degree of freedom, which we may regard as the location of the center of mass, or the front end. The fraction of sites containing the center of mass of an A type chain is  $\phi_A/N_A$  (only one out of every  $N_A$  sites with an A monomer contains a front end monomer).

For long chains the concentration of ends is very small, essentially an ideal gas. There is a negligible chance that randomly chosen locations for A ends and B ends will coincide. We may therefore estimate the translational entropy of each species separately, as the log of the number of ways to choose  $n_A$  sites for the A ends among all  $N$  lattice sites (and similarly for the B type chains).

We have

$$\begin{aligned} S/k &= \log(N!/n_A!(N-n_A!)) \\ &\approx (N \log N - N) - (n_A \log n_A - n_A) - ((N-n_A) \log(N-n_A) - (N-n_A)) \\ &= -n_A \log n_A/N - (N-n_A) \log(N-n_A)/N \end{aligned} \quad (2.5.8)$$

in which we have used the Stirling approximation as usual.

Now write the entropy per site, in terms of  $\phi_A$ , as

$$\begin{aligned} S/(kN) &= -\phi_A/N_A \log \phi_A/N_A - (1 - \phi_A/N_A) \log(1 - \phi_A/N_A) \\ &\approx -\phi_A/N_A \log \phi_A/N_A \end{aligned} \quad (2.5.9)$$

This is a quite general result for the entropy per site of an ideal gas of lattice concentration  $\phi_A/N_A$  (here, the concentration of ends). In the above, we have blithely dropped terms linear in  $\phi$ , because they do not affect the common tangent, or indeed any aspect of the phase behavior. Linear terms in  $\phi$  added to the free energy correspond only to constant shifts in the chemical potential of species A relative to B.

We estimate the interaction energy in exactly the same way as before, whereupon we have

$$\beta F/N = \chi \phi_A \phi_B + \phi_A/N_A \log \phi_A/N_A + \phi_B/N_B \log \phi_B/N_B \quad (2.5.10)$$

Carrying out the same exercise to find the spinodal, we obtain for the symmetric case  $N_A = N_B$

$$\delta \phi^2 = (\beta N_A \chi / 2 - 1) / 2 \beta N_A \chi \quad (2.5.11)$$

Now the critical point is  $\chi = 2kT/N_A$ , a much weaker interaction, much less than  $kT$  per monomer. This has several important consequences. First of all, it means that even very small repulsive monomer-monomer interactions are sufficient to demix polymers, because there are so many interactions per chain, but only one translational degree of freedom. That is, the entropy loss in separating a symmetric polymer blend is of order  $kT \log 2$  per *chain*, but the interaction energy in the mixed state is of order  $\chi$  per *monomer*.

Furthermore, it means that in most practical circumstances, the effective monomer-monomer interactions are weak compared to  $kT$ . This is part of the justification for the approximation that chain conformations are ideal random walks even in the mixed state, largely unperturbed by A–B interactions.

For typical polymers,  $\chi$  is on the order of  $10^{-2}$  to  $10^{-3}$ , in units of  $kT$  per “reference volume”  $v$ , commonly taken as  $v = 0.1\text{nm}^3$ . At a density of  $1\text{g/cm}^3$ , this is the volume of a unit of about  $60\text{g/mol}$ , which is a typical monomer molecular weight. Thus a volume large enough that the excess energy is of order  $kT$ , is 100 to 1000 typical monomers. This simple estimate illustrates the great difficulty of determining  $\chi$  from molecular scale simulations or atomistic modeling.

### Remarks on interactions

In our estimate of the energy of mixing, we blithely assumed that only contacts between unlike monomers cost energy. More reasonable is to assume that contacts between A monomers have an attractive energy  $\epsilon_{AA} < 0$ , contacts between B monomers  $\epsilon_{BB} < 0$ , and between A and B monomers  $\epsilon_{AB} < 0$ . The random-mixing interaction energy per site would then be estimated as

$$E/N = (Z/2)(\phi_A^2\epsilon_{AA} + 2\phi_A\phi_B\epsilon_{AB} + \phi_B^2\epsilon_{BB}) \quad (2.5.12)$$

Note that the pure phases now have nonzero interaction energy, with  $E/N$  equal to  $(Z/2)\epsilon_{AA}$  in pure A and likewise in pure B. Thus, the energy of mixing — the difference in energy per site in the mixed versus the pure states — is

$$\begin{aligned} E/N &= (Z/2)(\phi_A^2\epsilon_{AA} + 2\phi_A\phi_B\epsilon_{AB} + \phi_B^2\epsilon_{BB}) - \phi_A(Z/2)\epsilon_{AA} - \phi_B(Z/2)\epsilon_{BB} \\ &= Z(\epsilon_{AB} - \epsilon_{AA}/2 - \epsilon_{BB}/2)\phi_A\phi_B \end{aligned} \quad (2.5.13)$$

Only the combination of interaction energies  $Z(\epsilon_{AB} - \epsilon_{AA}/2 - \epsilon_{BB}/2)$  appears in the mixing energy, which motivates the definition

$$\chi_{AB} = Z(\epsilon_{AB} - \epsilon_{AA}/2 - \epsilon_{BB}/2) \quad (2.5.14)$$

If the interaction energy between A and B is less favorable than the A–A and B–B interactions that were disrupted when A and B monomers were brought from the pure phases to the mixed phase, i.e., if  $\epsilon_{AB}$  is less negative than the average of  $\epsilon_{AA}$  and  $\epsilon_{BB}$ , then the net interaction is repulsive.

In the case of noncharged, nonpolar polymers (no permanent dipoles and no free charges), the main source of interaction is dispersive or “van der Waals” interactions. A key feature of these interactions is that to good approximation, the interaction energy between a molecular unit of type A and one of type B at a given distance (closest approach, say) is the product of a quantity (the “molecular polarizability”) pertaining only to A, times an analogous factor for B:

$$\epsilon_{AB} = \delta_A\delta_B \quad (2.5.15)$$

The quantity  $\delta_A$  is called the “solubility parameter” for A, and is tabulated for a wide range of molecules and molecular groups.

For interactions for which this is true, we find

$$\chi_{AB} \propto (\delta_A - \delta_B)^2 \quad (2.5.16)$$

In other words, the interaction between A and B is *always* repulsive, and proportional to the difference in polarizability between the two species. The result is that “like prefers like”, there is always some repulsive interaction between unlike species, and the strategy to get two polymers to mix is to make them as similar in terms of solubility parameter as possible.

But this cannot be the entire story with regard to interactions between polymers, because there are examples of polymers that mix readily which are evidently quite different in terms of polarizability. It turns out that in many of these cases, the mechanism at work is hydrogen bonding

interactions. The essence of a hydrogen bond, so named for the bonds that occur between molecules in liquid water and ice, is an electrostatic attraction between a somewhat positively charged hydrogen (stripped to some extent of its electron, which participates in a polarized covalent bond with some other atom) and a some other negatively charged atom (oxygen, in the case of water).

In a hydrogen bond, there is a “donor” (the positively charged hydrogen) and an “acceptor” (the negatively charged atom); they play distinct, asymmetric roles in the bond. Now a molecule or molecular group can be an effective hydrogen bond donor, acceptor, both, or neither. Water is a good donor (at the H) and a good acceptor (at the O); ether and carbonyl oxygens are good acceptors; “acidic” hydrogens such as those in  $-\text{CHCl}-$  (where the chlorine strips the electron from the hydrogen) are good donors.

In the same spirit as writing  $\epsilon_{AB} = \delta_A \delta_B$  for nonpolar dispersive interactions, we can write the interaction energy for hydrogen bonding as

$$\epsilon_{AB}^{(H)} = d_A a_B + d_B a_A \quad (2.5.17)$$

in which  $d_A$  and  $a_A$  are some measure of the “donor strength” and “acceptor strength” of species A, and likewise for B. (We may think for example of the maximum and minimum electrostatic potential on the surface of closest approach of species A, as a rough measure of donor and acceptor strength.)

Applying Eq. (2.5.14) for  $\chi$  with  $\epsilon_{AB}$  given by Eq. (2.5.17), we find after a bit of algebra

$$\chi = Z(d_A - d_B)(a_A - a_B) \quad (2.5.18)$$

Unlike the result for  $\chi$  from attractive dispersive interactions, this result is not the square of a difference. We can make the above expression negative, by choosing monomer A to be a good hydrogen bond donor but a poor acceptor, and B a poor hydrogen bond donor but a good acceptor. For such a case, only the mixed state can form strong hydrogen bonds, and the excess free energy of mixing can be negative as a result.

## 2.6 Semidilute solutions

In this lecture we describe polymer chains in solution in a good solvent at finite concentration, and how the conformations and properties of the polymer chains vary with concentration. Our approach will be to construct a scaling description of the polymer conformations.

We begin with a single chain in dilute solution, described in Lecture 2.4, which we may regard as a self-avoiding walk of thermal blobs. The free energy cost of overlapping two thermal blobs is of order  $kT$ . The dilute solution may be regarded as an ideal gas of chains.

As we concentrate the solution, we reach the “overlap concentration”  $c^*$  where the fraction of volume pervaded by the individual chain coils approaches unity. The overlap concentration scales as  $N/R_e^3$  ( $N$  monomers per chain, distributed somehow within a pervaded volume of order  $R_e^3$ ).

As we increase the concentration  $c$  to beyond  $c^*$ , we may regard the chains as composed of subchains of  $g$  monomers, such that the subchains, as self-avoiding walks of thermal blobs, have overlap concentration  $c$ . The subchain has a coil dimension denoted as  $\xi$ , called the correlation length. We refer to the subchain coil as a “correlation blob”. The correlation blobs, which at overlap concentration are the size of the swollen chains, become progressively smaller as the concentration increases.

The conformation of a complete chain is then a Gaussian random walk of correlation blobs (which are themselves self-avoiding walks of thermal blobs, which are themselves Gaussian random walks of Kuhn steps). The reason the chain is a Gaussian rather than a self-avoiding walk of correlation blobs, is that there is no particular reason for a chain to avoid its own blobs, when the entire solution is full of blobs, all of which must be contended with.

As we increase the concentration further, eventually the correlation blobs become as small as the thermal blob size, at a concentration denoted  $c^{**}$ . At this point, the chain conformations are Gaussian on all scales above the Kuhn length; a subchain large enough to avoid itself, is already interacting with other chains, and there is no particular reason for self-avoidance.

Consequently, chains are largest in dilute solution, shrink progressively in the semidilute regime (between  $c^*$  and  $c^{**}$ ), and behave as Gaussian random walks at and above  $c^{**}$ , with conformations as in the melt.

### Osmometry

Another way to observe the effects of chain swelling and self-avoidance is to measure the affinity the solution has for additional solvent, using osmometry. An osmometer is a U-shaped tube with the two arms separated by a membrane, which is permeable to solvent but not to solute (here, polymer). Initially, equal volumes of solution and pure solvent are loaded into the two arms. Because the interactions between monomers are net repulsive, the free energy is decreased when solvent passes across the membrane to dilute the solution. Solvent continues to pass through the membrane until the height of the fluid column on the solution side rises enough that the hydrostatic pressure difference across the membrane prevents further dilution.

The equilibrium condition is that the exchange of a small volume of solvent across the membrane gives zero net change free energy:

$$0 = \rho gh + \partial F / \partial V \quad (2.6.1)$$

We have written the solution free energy per unit volume  $F/V$  as a function of polymer volume fraction  $\phi = nNv_0/V$  ( $n$  the number of chains,  $N$  the number of monomers per chain,  $v_0$  the monomer excluded volume). Thus  $F = Vf(nNv_0/V)$ , so that the expression for the osmotic pressure we seek is

$$\Pi = \partial F / \partial V = f(\phi) - \phi \partial f / \partial \phi \quad (2.6.2)$$

How many correlation blobs are there per chain, as a function of concentration? At overlap concentration, a chain consists of only one correlation blob, of size  $R_e$ , so we have

$$c^* \sim \frac{N}{R_e^3} \quad (2.6.3)$$

At higher concentrations, there are  $g$  monomers per blob; the concentration within the blob is  $c$ , so that

$$c \sim \frac{g}{\xi^3} \quad (2.6.4)$$

The blobs are presumed to be swollen, so that

$$\xi \sim R_s \left( \frac{g}{N_s} \right)^{3/5} \quad (2.6.5)$$

Here we assume  $g > N_s$ , which is equivalent to assuming that the concentration  $c$  is less than  $c^{**}$ , at which the blob shrinks to the size  $R_s$ . The chain in dilute solution is likewise swollen, so that

$$R_e \sim_s \left( \frac{N}{N_s} \right)^{3/5} \quad (2.6.6)$$

We can combine these scaling assumptions to determine how the number of blobs and the size of the correlation blobs scale with increasing concentration. Since all the scaling relations are power laws, we may expect dimensionless quantities such as  $\xi/R_e$  and  $N/g$  to scale as some power of  $c/c^*$ . To combine our scaling assumptions, we begin by combining the expressions for  $c$  and  $c^*$ , as

$$\frac{c}{c^*} \sim \left( \frac{g}{N} \right) \left( \frac{\xi}{R_e} \right)^3 \quad (2.6.7)$$

We can likewise take the ratio of the scaling assumptions for  $\xi$  and  $R_e$ , to relate the ratios  $\xi/R_e$  and  $g/N$ , as

$$\frac{\xi}{R_e} \sim \left( \frac{g}{N} \right)^{3/5} \quad (2.6.8)$$

This relation can be used to replace either  $g/N$  or  $\xi/R_e$  in the expression for  $c/c^*$ . Putting these results together, we have

$$\begin{aligned} \frac{g}{N} &\sim \left( \frac{c}{c^*} \right)^{-5/4} \\ \frac{\xi}{R_e} &\sim \left( \frac{c}{c^*} \right)^{-3/4} \end{aligned} \quad (2.6.9)$$

In the semidilute regime, the scaling assumption that the free energy is “ $kT$  per correlation blob”, so that

$$\frac{F}{V} \sim \frac{kT}{\xi^3} \sim \frac{kT}{R_e^3} \left( \frac{c}{c^*} \right)^{9/4} \quad (2.6.10)$$

The corresponding osmotic pressure  $\Pi$  then scales in the same way. In the dilute regime, the free energy of the solution is that of an ideal gas of chains, for which

$$\frac{F}{V} = \frac{kT\phi}{NV} \log(\phi/N) \quad (2.6.11)$$

The corresponding osmotic pressure is that of an ideal gas,

$$\Pi = \frac{kT\phi}{Nv} \quad (2.6.12)$$

The expressions for the osmotic pressure in the dilute and semidilute regimes must match up at the overlap concentration. The semidilute result gives  $\Pi$  of order  $kT/R_e^3$  or  $kTc^*/N$ , which indeed agrees with the dilute result (recalling that  $\phi = cv$ ). The dependence of the osmotic pressure on concentration throughout the dilute and semidilute regimes must be a “crossover function”, of the form

$$\Pi = \frac{kT}{R_e^3} p(c/c^*) \quad (2.6.13)$$

with  $p(x)$  a dimensionless function such that  $p(x) \sim x$  for  $x \ll 1$ , and  $p(x) \sim x^{9/4}$  for  $x \gg 1$ .

We note that the osmotic pressure becomes independent of chain length in the semidilute regime (this may be verified directly from the various power law dependences). Physically, this must be the case because the free energy and the osmotic pressure are both “ $kT$  per correlation blob”, and the blob size is only a function of  $c/c^{**}$ , independent of chain length. In fact, asserting that this must be so is one route to figuring out what power law must appear in  $p(x)$  at large  $x$ .

### Confinement and stretching in good solvent

Scaling descriptions in terms of “blobs” can also be usefully constructed to describe polymers in good solvents under various sorts of deformation, both as single chains and in semidilute solution. Here we consider two cases: a single chain in good solvent under tension, and a single chain in good solvent confined between two plates.

For a single chain in good solvent under tension, we again represent the conformation as a linear sequence of marginally perturbed subchains or “stretch blobs”. However, in contrast to our previous treatment of an ideal chain under tension, the stretch blobs are self-avoiding walks of thermal blobs. As before, we denote the size of the blob by  $\xi$  and the number of monomers in a blob by  $g$ .

The ingredients of our scaling treatment are

$$\begin{aligned} \xi &\sim R_s(g/N_s)^{3/5} \\ R_e^* &\sim R_s(N/N_s)^{3/5} \\ R &\sim (N/g)\xi \\ \Delta F &\sim (N/g)kT \end{aligned}$$

In the above, the scaling relations correspond to the following physical assumptions:

- the stretch blobs are self-avoiding walks of thermal blobs;
- the unstretched chain of end-to-end dimension  $R_e^*$  is likewise a self-avoiding walk of thermal blobs;
- the stretched chain is a line of stretch blobs;
- the stretching free energy is  $kT$  per blob.

When these assumptions are combined, we obtain

$$\begin{aligned} N/g &\sim (R/R_e^*)^{5/2} \\ (\xi/R_e^*)^2 &\sim (R_e^*/R)^3 \\ \Delta F &\sim kT(R/R_e^*)^{5/2} \end{aligned}$$

We find results similar in structure to the ideal-chain case — everything can be expressed in terms of the “stretch ratio”  $R/R_e^*$  — but the power laws are different, as a result of the swelling effect. In particular, the “entropic spring” is no longer harmonic; instead, it is progressively harder to stretch the chain to larger deformations, because the diminishing self-avoidance of the deformed chain helps less and less to push the chain outwards.

If we confine a single swollen chain between plates, we may regard the resulting chain conformations again as a self-avoiding walk of correlation blobs; in this case, the blob dimension is set by the plate spacing  $h$ . The scaling assumptions are then

$$\begin{aligned}\xi &= h \\ \xi &\sim R_s(g/N_s)^{3/5} \\ R_e^* &\sim R_s(N/N_s)^{3/5} \\ \Delta F &\sim (N/g)kT\end{aligned}$$

with the result that

$$\Delta F \sim kT(R_e^*/h)^{5/3} \tag{2.6.14}$$

As the chain is confined, the blob size becomes smaller, more and more blobs result, at a free energy cost of  $kT$  per blob.

## 2.7 Fluctuations, scattering, and mean-field approximation

In previous lectures, we introduced scattering as a means to investigate the structure of individual chains in solution. Then, we described the phase behavior of polymer-polymer blends. In the present lecture, we combine these two topics, and discuss what is to be learned by scattering from a binary polymer blend.

On average, in the single phase region, the concentration within a A–B polymer blend is uniform, with no evident droplets of a distinct phase from which to scatter. However, the mixing is not perfectly uniform; there are at any given moment regions rich in polymer A or B. The spatial extent of these concentration fluctuations grows large in the vicinity of the critical point. At the critical point, the osmotic compressibility — which governs the ease with which concentration fluctuations can appear — diverges. The spatially large fluctuations scatter coherently at small wavenumbers, giving rise to large intensity small-angle scattering.

We know that scattering is proportional to modulus squared of the Fourier transform of the scattering density, which for concentration fluctuations in a binary melt (for which the mass density is essentially constant) should somehow be proportional to the local difference in concentration between A and B monomers. So we focus on calculating the following matrix of correlation functions:

$$S_{\alpha\beta}(r, r') = \langle \delta\phi_\alpha(r) \delta\phi_\beta(r') \rangle \quad (2.7.1)$$

in which  $\alpha$  and  $\beta$  each take on the values A or B, and  $\delta\phi_\alpha(r)$  is the local deviation of the concentration of species  $\alpha$  at  $r$ .

Because the melt is incompressible, the sum of the local volume fractions of A and B monomers must be always unity, so that  $\delta\phi_A(r) + \delta\phi_B(r)$  must be zero everywhere. (This imposes a relation between the different components  $S_{\alpha\beta}$ , namely  $S_{AA} = -S_{AB} = S_{BB}$ , which we shall eventually enforce, below.)

### Correlation and response functions

It turns out to be very useful to consider what at first sight is an unrelated problem, namely, the calculation of the response of the local concentration  $\phi_\alpha(r)$  at  $r$  to an “external field”  $W_\beta(r')$  applied at  $r'$ . By an external field, we mean an imposed potential that attracts monomers of type  $\beta$  to  $r'$ . The effect of such a potential is to add a term to the system energy, of the form

$$\Delta E = \sum_\gamma \int d^3r W_\gamma(r) \phi_\gamma(r) \quad (2.7.2)$$

This can be written in another useful way, as a sum over the contributions of each chain to the concentration:

$$\Delta E = \sum_\gamma \sum_{i \in \gamma} \int_0^N ds W_\gamma(r_i(s)) \quad (2.7.3)$$

If the potential is weak —  $W_\beta$  is taken to be small enough that its perturbing effect is small — then the response of the concentrations to its imposition should be first-order in  $W_\beta$ , allowing us to define a matrix of response functions  $R_{\alpha\beta}(r, r')$ :

$$\langle \delta\phi_\alpha(r) \rangle = - \int d^3r' R_{\alpha\beta}(r, r') W_\beta(r') \quad (2.7.4)$$

In writing the response functions this way, we are saying little except that the response is linear. (And, we adopt a sign convention that is aimed at getting a positive result for  $R$ , since positive

values of  $W$  disfavor positive values of  $\delta\phi$ .) We are, however, allowing for the possibility that a potential imposed at a point  $r'$  on species  $\beta$  could perturb the concentration of species  $\alpha$  at a point  $r$  some distance away.

Now consider how the addition of such a term to the system energy would alter the partition function. Surprisingly, we do not need to write the partition function very explicitly to observe something useful. We write

$$\begin{aligned} Z &= \sum_{\text{configs}} e^{-\beta E_0[\text{configs}]} e^{-\beta \Delta E} \\ &= \sum_{\text{configs}} e^{-\beta E_0[\text{configs}]} e^{-\beta \sum_{\gamma} \int d^3r W_{\gamma}(r) \phi_{\gamma}(r)} \end{aligned} \quad (2.7.5)$$

Now the perturbing term, the integral in the exponential, can be thought of equally well as a sum over a fine mesh of points in space,

$$\int d^3r W_{\gamma}(r) \phi_{\gamma}(r) \approx \Delta V \sum_j W_{\gamma}(r_j) \phi_{\gamma}(r_j) \quad (2.7.6)$$

where  $\Delta V$  is a differentially small volume.

The point is, derivatives of  $Z$  with respect to  $W_{\beta}(r_j)$  bring down factors of  $\phi_{\beta}(r_j)$  “into the average”; that is,

$$-\frac{1}{\beta \Delta V} \frac{\partial \log Z}{\partial W_{\beta}(r_j)} = \langle \phi_{\beta}(r_j) \rangle \quad (2.7.7)$$

If we take another derivative, with respect to  $W_{\alpha}$  at some other point  $r_k$ , down comes another factor of  $\Delta V \phi_{\alpha}(r_k)$ , leading to

$$\frac{1}{(\beta \Delta V)^2} \frac{\partial^2 \log Z}{\partial W_{\beta}(r_j) \partial W_{\alpha}(r_k)} = \langle \phi_{\beta}(r_j) \phi_{\alpha}(r_k) \rangle - \langle \phi_{\beta}(r_j) \rangle \langle \phi_{\alpha}(r_k) \rangle \quad (2.7.8)$$

(The second term comes from the second derivative hitting the  $Z$  in the denominator of the average.) We describe this result as “derivatives with respect to the potential  $W$  ‘generate’ averages of the field  $\phi$ ”.

Now we can prettify this a bit, by absorbing the factors of  $1/\Delta V$  into a special definition of a “functional derivative”, which just means “derivative with respect to the value of a function at a point”, as opposed to the usual “derivative with respect to the value of some parameter”: we write

$$\frac{1}{\beta} \frac{\delta \log Z}{\delta W_{\beta}(r)} = \langle \phi_{\beta}(r) \rangle \quad (2.7.9)$$

and so forth.

So what we notice is that on the one hand,

$$-\frac{1}{\beta} \left. \frac{\delta \langle \phi_{\alpha}(r) \rangle}{\delta W_{\beta}(r')} \right|_{W=0} = \langle \phi_{\alpha}(r) \phi_{\beta}(r') \rangle = S_{\alpha\beta}(r, r') \quad (2.7.10)$$

in which the second term with the separate average of the two factors of  $\phi$  vanishes because we set  $W = 0$  after taking the derivative, to “turn off the field”.

And on the other hand, if we apply the functional derivative to our linear response expression, we have

$$\left. \frac{\delta \langle \phi_{\alpha}(r) \rangle}{\delta W_{\beta}(r')} \right|_{W=0} = -R_{\alpha\beta}(r, r') \quad (2.7.11)$$

So it must be that

$$\beta S_{\alpha\beta}(r, r') = R_{\alpha\beta}(r, r') \quad (2.7.12)$$

The response function and the correlation function are the same thing, a result that does not depend on any details of the partition function at all.

We may give a plausibility argument for why the response and correlation functions should be proportional, as follows: if fluctuations are common in which a variation in  $\phi_\alpha$  at  $r$  accompanies a variation in  $\phi_\beta$  at  $r'$ , then it is reasonable that an externally applied potential that directly couples to  $\phi_\beta$  at  $r'$  will likewise induce a response in  $\phi_\alpha$  at  $r$ .

## Mean-field theory

Having established the equivalence of the correlation and response functions, we set about computing the response function from the partition function. Now the exact partition function of a system of interacting chains is a complicated beast; we must sum over the set of configurations of all chains, subject to the constraint of fixed density, with configurations weighted by their interaction energy.

The density constraint and the interactions between chains are complicated to enforce exactly. But a serviceable approximation can be made, in which each chain is regarded as interacting with all the others only through two average “potential fields” — the hydrostatic pressure  $p(r)$ , and the chemical potential  $\mu_\alpha(r)$  for monomers of type  $\alpha$ .

In this approximation, called the mean-field approximation, the pressure  $p(r)$  and chemical potential  $\mu_\alpha(r)$  do not fluctuate, but take on an average value that depends on the state of the system. In a homogenous one-phase system, both fields would be spatially uniform. In a two-phase system with an interface separating A-rich and B-rich regions, the potentials would have distinct values in each phase.

What makes the mean-field approximation tractable, is that in the partition function we have only to sum over the conformations of a single representative chain, which can take on all possible random-walk configurations, weighted by their energy in the potential fields:

$$Z \approx \left[ \sum_{\text{A configs}} e^{-\beta \int ds (P(r(s)) + \mu_A(r(s)) + W_A(r(s)))} \right]^{N_A} \left[ \sum_{\text{B configs}} e^{-\beta \int ds (P(r(s)) + \mu_B(r(s)) + W_B(r(s)))} \right]^{N_B} \quad (2.7.13)$$

Approximated in this way, the perturbed value of the concentration  $\phi$  is the linear response of a system of independent chains to the imposed external field  $W$  and the “internal” fields  $P$  and  $\mu$ :

$$\langle \delta\phi_\alpha(r) \rangle = -\beta \int d^3r' S_{\alpha\beta}^{(0)}(r, r') (W_\beta(r') + \mu_\beta(r') + P(r')) \quad (2.7.14)$$

Note that  $S_{\alpha\beta}^{(0)}(r, r')$  must actually be a function only of  $r - r'$ , because of translational invariance. (Below, we shall compute  $S_{\alpha\beta}^{(0)}(r, r')$  explicitly, and see that this is in fact the case.) We can turn the convolution integral in the above equation into a product, by taking the Fourier transform:

$$\langle \delta\phi_\alpha(q) \rangle = -\beta S_{\alpha\beta}^{(0)}(q) (W_\beta(q) + \mu_\beta(q) + P(q)) \quad (2.7.15)$$

The potential fields  $P$  and  $\mu$  are determined by self-consistency conditions. The chemical potential field  $\mu$  represents interactions of the given chain with the average monomer concentration, so we enforce

$$\begin{aligned} \mu_A(r) &= \chi \langle \delta\phi_B(r) \rangle \\ \mu_B(r) &= \chi \langle \delta\phi_A(r) \rangle \end{aligned} \quad (2.7.16)$$

The pressure field  $P$  is chosen to enforce the constraint of constant average density,

$$0 = \langle \delta\phi_A(r) \rangle + \langle \delta\phi_B(r) \rangle \quad (2.7.17)$$

If we think of  $\langle \delta\phi_\alpha(q) \rangle$  as a two-component vector (A and B components), and  $S_{\alpha\beta}^{(0)}(q)$  as a 2x2 matrix, then we are to choose  $P(q)$  in such a way that the vector  $\langle \delta\phi_\alpha(q) \rangle$  points along the direction  $\{1, -1\}$ . That is,  $P$  is chosen to cancel whatever part of  $-\beta S_{\alpha\beta}^{(0)}(W_\beta + \mu_\beta)$  points along  $\{1, 1\}$ . Now we may as well enforce that  $W_\beta$  points along  $\{1, -1\}$ , because any part of this vector that points along  $\{1, 1\}$  can be absorbed into the  $P$  term.

### Solving the self-consistent equations.

Here we present the details of how to solve this tricky little set of equations. We introduce some notation:  $\mathbf{1}$  is the vector  $\{1, 1\}$ ;  $\bar{\mathbf{1}}$  is  $\{1, -1\}$ ; we write  $\Phi$  for the vector of  $\delta\phi_\alpha$ ,  $\mathbf{S}^{(0)}$  for the matrix of correlation functions.

First, we need to find  $P$ . So we impose the condition that there is no component of the vector  $\Phi$  in the  $\mathbf{1}$  direction. We write  $\mathbf{W}$  as

$$\mathbf{W} = (W/2)\mathbf{1} + (\bar{W}/2)\bar{\mathbf{1}} \quad (2.7.18)$$

which implies  $W = W_A + W_B$  and  $\bar{W} = W_A - W_B$ . The term proportional to  $\mathbf{1}$  can be absorbed into  $P$ .

Likewise, we impose the condition that  $\Phi$  has no component along  $\mathbf{1}$ , by writing

$$\Phi = \phi\bar{\mathbf{1}} \quad (2.7.19)$$

We have

$$\phi\bar{\mathbf{1}} = -\beta\mathbf{S} \cdot (\bar{W}/2\bar{\mathbf{1}} - kT\chi\phi\bar{\mathbf{1}} + P\mathbf{1}) \quad (2.7.20)$$

We find  $P$  by taking the dot product of  $\mathbf{1}$  with the above equation, to obtain

$$0 = \mathbf{1} \cdot \mathbf{S} \cdot \bar{\mathbf{1}}(\bar{W}/2 - kT\chi\phi) + \mathbf{1} \cdot \mathbf{S} \cdot \mathbf{1}P \quad (2.7.21)$$

Solving for  $P$ , we have

$$P = -(\bar{W}/2 - kT\chi\phi)\Delta/\Sigma \quad (2.7.22)$$

in which we have defined

$$\begin{aligned} \Delta &\equiv \mathbf{1} \cdot \mathbf{S} \cdot \bar{\mathbf{1}} = S_{AA} - S_{BB} \\ \Sigma &\equiv \mathbf{1} \cdot \mathbf{S} \cdot \mathbf{1} = S_{AA} + 2S_{AB} + S_{BB} \\ \bar{\Sigma} &\equiv \bar{\mathbf{1}} \cdot \mathbf{S} \cdot \bar{\mathbf{1}} = S_{AA} + 2S_{AB} + S_{BB} \end{aligned} \quad (2.7.23)$$

Now we compute  $\phi$  by taking the dot product of  $\bar{\mathbf{1}}$  with the equation, to obtain

$$2\phi = -\beta(\bar{\Sigma} - \Delta^2/\Sigma)(\bar{W}/2 - kT\chi\phi) \quad (2.7.24)$$

Solving for  $\phi$ , we have

$$\phi = -\beta S\bar{W} = -\beta(\Sigma/D - 2\chi)^{-1}\bar{W} \quad (2.7.25)$$

in which  $D$  is the determinant of  $S$ ,  $D = S_{AA}S_{BB} - S_{AB}^2$ . This result is sometimes called (for historical reasons, which we need not explain here) the ‘‘random phase approximation’’ or RPA result for the response function.

For the case of homopolymer blends, the correlation matrix  $\mathbf{S}$  is diagonal, so that  $\Sigma = S_{AA} + S_{BB}$  and  $D = S_{AA}S_{BB}$ , whereupon

$$\phi(q) = -\beta S_{eff}(q) \bar{W}(q) = -\beta (1/S_{AA}(q) + 1/S_{BB}(q) - 2\chi)^{-1} \bar{W}(q) \quad (2.7.26)$$

Observe that the response can become quite large if the denominator comes close to vanishing; we shall see below that this happens when we are close to the critical point.

Note that  $\bar{W}$  couples to the concentration difference), because of incompressibility:

$$W_\alpha \phi_\alpha = (W_\alpha - W_\beta) \phi = \bar{W} \phi \quad (2.7.27)$$

It remains to calculate the independent-chain correlation functions  $S_{\alpha\beta}^{(0)}$ . For homopolymers (which are either all A monomers, or all B monomers) there are no correlations for non-interacting chains between the locations of A monomers and B monomers; hence  $S_{AB}$  vanishes. So we focus on  $S_{AA}$  and  $S_{BB}$ .

$$\begin{aligned} S_{AA}^{(0)}(r, r') &= \langle \phi_A(r) \phi_A(r') \rangle \\ &= \sum_{i, j \in A} \int ds \int ds' \langle \delta(r - r_i(s)) \delta(r' - r_j(s')) \rangle \end{aligned} \quad (2.7.28)$$

in which we have used

$$\phi_A(r) = \sum_{i \in A} \int ds \delta(r - r_i(s)) \quad (2.7.29)$$

Now the average of the product of delta functions asks the question, if the  $s$ th monomer on chain  $i$  is at  $r$ , how likely is it to find the  $s'$ th monomer on chain  $j$  at  $r'$ ? First of all, for independent chains, there are no correlations unless  $i = j$ . Then, the correlation can only depend on the difference in positions  $r - r'$ , not on the absolute position  $r$ ; we expose this by writing

$$\begin{aligned} \langle \delta(r - r(s)) \delta(r' - r(s')) \rangle &= \langle \delta(r - r(s)) \delta((r' - r) - (r(s') - r(s))) \rangle \\ &= \langle \delta(r - r(s)) \rangle \langle \delta((r' - r) - (r(s') - r(s))) \rangle \\ &= 1/V \langle \delta((r' - r) - (r(s') - r(s))) \rangle \end{aligned} \quad (2.7.30)$$

The second equality holds because there is no correlation between where the  $s$ th monomer sits in space, and where the  $s'$ th monomer sits relative to the  $s$ th monomer. The final equality holds because the  $s$ th monomer of the chain is equally likely to be found anywhere in the entire volume.

So we see that indeed  $S(r, r')$  only depends on  $r - r'$ ; taking the Fourier transform, we have

$$S_{AA}^{(0)}(q) = (n_A/V) \int ds \int ds' \langle e^{iq \cdot (r(s) - r(s'))} \rangle \quad (2.7.31)$$

in which  $n_A$  is the total number of A chains. Lo and behold, we have twice before encountered this particular integral; it is the Debye function  $N_A^2 g(q^2 R_g^2)$ , so that

$$S_{AA}^{(0)}(q) = \phi_A N_A g(q^2 N_A b^2 / 6) \quad (2.7.32)$$

So for a homopolymer blend, the scattering is

$$1/S(q) = 1/(\phi_A N_A g(q^2 N_A b^2 / 6)) + 1/(\phi_B N_B g(q^2 N_B b^2 / 6)) - 2\chi \quad (2.7.33)$$

Remembering our expansion of the Debye function, for small  $q$  this is approximately

$$\begin{aligned} 1/S(q) &= 1/S(0) + \frac{q^2 b^2}{12\phi(1-\phi)} \\ 1/S(0) &= 1/(\phi_A N_A) + 1/(\phi_B N_B) - 2\chi \end{aligned} \quad (2.7.34)$$

The scattering intensity is then proportional to a Lorentzian function,

$$\begin{aligned} S(q)/S(0) &= 1/(1 + q^2 \xi^2) \\ \xi^2 &= b^2 S(0)/(12\phi_A \phi_B) \end{aligned} \quad (2.7.35)$$

The scattering in the forward direction diverges as we approach the spinodal condition; as well, the length scale determined by the falloff in the scattering diverges. The scattering signature of a blend near to the spinodal is strong low-angle (low- $q$ ) scattering. The chi parameter can be determined from the shape of the scattering, in particular from the magnitude of  $\xi$ .