Chapter 3

Polymers at interfaces

3.1 Interfaces in polymer blends

When we have immiscible polymer blends — which is the most common circumstance, since it is so difficult to mix dissimilar polymers — materials will consist of some arrangement of droplets or other domains of one phase within a matrix of the the other coexisting phase.

It can be advantageous to prepare such "physical blends", as the heterogenous local structure can give desirable macroscopic physical properties if the domain sizes are not too large. For example, a rubbery polymer material with micron-sized droplets of a glassy polymer will be stiffened by the inclusions; a glassy polymer matrix with micron-size droplets of a rubbery polymer may be toughened.

An detailed account of how these desirable properties come about is beyond the scope of these lectures. However, it is clear that the nature of the interface between immiscible polymers is a key ingredient in understanding such demixed blends. In particular, the width of the interface, i.e., the thickness over which the polymers at the interface intermingle, is a fundamental parameter. If the interface is broad enough that the polymers are entangled across the interface, then we may intuitively expect the interface to be strong — certainly compared to the case where the interface is so sharp that the two phases are only bonded together by weak dispersive (van der Waals) interactions.

We now give a scaling argument for the width of the interface between demixed polymers. We suppose that the phase separation is strong, in the sense that the compositions of the two coexisting phases are nearly pure A and pure B. We begin by assuming the interface is infinitely sharp; now ask, what would be the typical excursion that a polymer immediately adjacent to the interface might make into the other phase?

We expect that such an excursion would be a fluctuation, typically observed if the cost to produce it were of order kT. Since only kT is at stake, the subchain making the excursion must adopt configurations that are only weakly perturbed from being random walks. The cost of the excursion is then of order χn, where n is the length of the subchain. The distance h the subchain penetrates into the other phase scales as the size of the subchain coil.

Thus we have

$$\chi n \sim kT$$
$$h^2 \sim nb^2 \tag{3.1.1}$$

Combining these results, we have

$$h \sim b(kT/\chi)^{1/2} \tag{3.1.2}$$

We can also make a scaling argument for the surface tension at this A-B interface. The A and B monomers are intermixed over a region of thickness h, so the interaction energy density is of order χ/Ω_0 in this region (here Ω_0 is the volume of a monomer). Thus the interfacial tension scales as

$$\gamma \sim h\chi/\Omega_0 \sim kT(b/\Omega_0)(\chi/kT)^{1/2} \tag{3.1.3}$$

A more precise calculation (using the mean-field approximation) by Helfand and Tagami gives the result

$$\gamma = kT(b/\Omega_0)(\chi/6kT)^{1/2}$$
$$h = 2b(kT/6\chi)^{1/2} \tag{3.1.4}$$

Now a typical value for χ for a weakly immiscible polymer pair might be $10^{-2}kT$ or so, such that to achieve $\beta\chi N = 2$ would require $N = 100$, i.e., short chains of less than 100 monomers would be miscible. Then the resulting interfacial thickness is rather large relative to monomeric dimensions, $h = 20b/\sqrt{6} \approx 8.2b$.

((Here b is the effective step size for a monomer, defined by $R^2 = nb^2$ where n is the actual number of monomers. Since we write also $R^2 = C_\infty na^2$, where a is the distance between monomers along the chain, we see $b = \sqrt{C_\infty}a$, somewhat larger than a.))

The corresponding surface tensions are rather small compared to typical tensions for small-molecule liquids; for our example of $\chi = 10^{-2}kT$ we have $\gamma = kT(b/\Omega_0)/(10\sqrt{6})$. Now kTa/Ω_0 turns out to be about 23mN/m, a typical small-molecule tension; so we have a value about ten times smaller for our example. This is another consequence of the relatively weak interactions required to demix polymers.

Note also that when χ is of order its critical point value of $2kT/N$, we have an interfacial thickness of order $\sqrt{N}b$, which is to say, of order the radius of the polymers in the blend. When the interface gets to be this broad, the polymers are threatening to mix.

If χ is known for a given polymer blend, then we can infer the interfacial width and tension. On the other hand, if we can measure the interfacial thickness for an immiscible polymer pair, this amounts to a determination of χ. In the next portion of this lecture, we shall describe a scattering technique — reflectivity, using either X-rays or neutrons — for measuring interfacial profiles.

Reflectivity

Reflectivity is scattering applied to flat, stratified samples. Films, coatings, layered phases, and interfaces are all usefully studied by reflectivity. The regularity imposed by the parallel geometry increases the precision with which microscopic length scales can be measured, when compared to conventional small angle scattering.

If a sample is layered, there will typically be reflections from the top surface as well as from buried interfaces. These reflections can interfere at the detector, which ultimately gives information as to the vertical distance between the interfaces. If the interfaces are diffuse, such interference will be damped out when the probing wavelength becomes of order the interfacial thickness.

To analyze reflectivity experiments, we first review the simple case of scalar waves reflecting off a single sharp interface. (By analyzing "scalar waves", we are neglecting effects related to polarization of electromagnetic waves; this analysis is completely correct for neutrons, and turns out to be accurate for X-rays at sufficiently small incidence angles.)

When a incident plane wave impinges on an interface, a reflected wave and a transmitted wave result. All three waves oscillate at the same temporal frequency, because the transmission and

reflection processes do not change the quantum of energy carried by each photon or each neutron — the scattering is "elastic" (energy-conserving). We may write the waves as

$$\psi_i = \exp(ik_i \cdot x - i\omega t)$$
$$\psi_r = R \exp(ik_r \cdot x - i\omega t)$$
$$\psi_t = T \exp(ik_t \cdot x - i\omega t)$$

$$(3.1.5)$$

The incoming wavevector k_i defines the x-z plane; the incident angle $\bar{\theta}_i$ is between k_i and the z axis, and the glancing angle θ_i is between k_i and the x axis.

Across the interface, the index of refraction changes. We write n for the index on the incident side, and n' on the transmitted side of the interface. The wavenumber depends on the index, as

$$\omega = c_0 k / n \qquad (3.1.6)$$

in which c_0 is the phase velocity of the wave in vacuum. We write k and k' for the wavenumber on the incident and transmitted side respectively.

Along the interface, the waves all oscillate together, with the same spatial dependence in the x direction. That is, the field is continuous across the interface. This implies

$$k \sin \bar{\theta}_i = k \sin \bar{\theta}_r = k' \sin \bar{\theta}_t \qquad (3.1.7)$$

Using the dependence of k on refractive index gives Snell's laws,

$$\bar{\theta}_i = \bar{\theta}_r$$
$$n \sin \bar{\theta}_i = n' \sin \bar{\theta}_t \qquad (3.1.8)$$

A beam transmitted into a medium of higher index "bends towards the normal", and bends away from the normal when passing into a medium of lower index.

If the index on the transmitted side of the interface is lower than on the incident side, there is a maximum possible value of $\bar{\theta}_i$, called the critical angle $\bar{\theta}_c$, beyond which the transmitted wave cannot propagate:

$$\bar{\theta}_c = \sin^{-1} n'/n \qquad (3.1.9)$$

For incident angles larger than $\bar{\theta}_c$, there is no solution to the Snell refraction equation, and the beam is completely reflected (as we shall see below). Just below $\bar{\theta}_c$, the transmitted wave travels almost parallel to the interface.

Because we are interested in the amplitude of the reflected wave, and not just the directions of the transmitted and reflected waves, we need one more relation, implied by the continuity of the field and its normal derivative across the interface:

$$1 + R = T$$
$$k \cos \bar{\theta} - R k \cos \bar{\theta} = T k' \cos \bar{\theta}' \qquad (3.1.10)$$

Solving for R, we have

$$R = \frac{k \cos \bar{\theta} - k' \cos \bar{\theta}'}{k \cos \bar{\theta} + k' \cos \bar{\theta}'} = \frac{k_z - k'_z}{k_z + k'_z} \qquad (3.1.11)$$

The reflected intensity is the complex modulus of the reflected amplitude.

The above discussion has been general; now we specialize to consider reflectivity of X-rays and neutrons. It turns out that the indices of refraction for X-rays and neutrons in matter are both slightly less than unity. We define $n = 1 - \delta$, with

$$\delta_X = \lambda^2 \rho_e r_0 / 2\pi$$
$$\delta_N = \lambda^2 c_{\mathrm{mon}} b_{\mathrm{mon}} / 2\pi \tag{3.1.12}$$

In the above, ρ_e is the electron density and r_0 the classical electron radius (2.82×10^{-13}cm), c_{mon} the monomer concentration and b_{mon} the scattering length for a monomer.

The scattering length is a sum over all the nuclei in the monomer; neutrons scatter from nuclei, whereas X-rays scatter from electrons. Neutrons scatter relatively strongly from hydrogen and deuterium, with scattering lengths of 0.667×10^{-12}cm and -0.374×10^{-12}cm respectively. Note the change in sign; this is why "deuterium labeling" can be used to effectively change the contrast for neutron scattering.

Typical wavelengths for X-ray and neutron scattering experiments would be perhaps 1.5Å and 3Å respectively. For any reasonable values of electron density and monomer concentration, δ_X and δ_N are much smaller than unity. Because $n < 1$ for X-rays and neutrons in matter, a beam incident from vacuum onto matter will have a critical angle; but because n is nearly unity, the critical angle will be very small.

We can expand Snell's law of refraction for small grazing angle θ (we now work in terms of θ, as is customary for reflectivity), which leads to

$$\theta^2 = \theta'^2 + 2\delta = \theta'^2 + \theta_c^2 \tag{3.1.13}$$

From this we can identify $\sqrt{2\delta}$ as θ_c, the critical angle (at which θ' would vanish). From the above we can write the transmitted beam grazing angle as

$$\theta' = \sqrt{\theta^2 - \theta_c^2} \tag{3.1.14}$$

Because the grazing angle is small, $k_z \approx k\theta$, so that we can convert from θ to k_z just by multiplying by k; hence

$$k'_z = \sqrt{k_z^2 - k_c^2} \tag{3.1.15}$$

in which $k_c = k\theta_c$.

So the critical angle as promised is very small (less than a degree typically). And, as we shall see below, it is usually desirable to operate at small grazing angles (because this probes the interface on the desired range of length scales in the z direction), but well above the critical angle (so that the reflected intensity is weak). The reflected amplitude then becomes

$$R = \frac{k_z - \sqrt{k_z^2 - k_c^2}}{k_z + \sqrt{k_z^2 - k_c^2}} \tag{3.1.16}$$

This result is called the Fresnel reflection coefficient.

$R(k_z)$ becomes a complex number of unit modulus for k_z below k_c; thus the reflection is perfect beyond the critical angle. For k_z well above the critical angle, we can expand to find

$$R \approx k_c^2 / (4k_z^2) \tag{3.1.17}$$

Above the critical angle, the reflected amplitude falls off sharply.

For an interface with structure, we can think of it as a succession of interfaces between differentially thin slabs, each with an interface, each resulting in a weak reflected wave. Because the

index is nearly unity everywhere and we stay well above the critical angle, we can ignore both diffraction effects (bending of the transmitted beam) as well as multiple reflections of the reflected beam (analogous to the Born approximation).

Thus the incident wave proceeds almost undisturbed into material, and generates set of weak reflections from each layer. We add up the amplitudes of the scattered waves from each thin interface, with a phase shift $\exp(iqz)$ with $q = 2k_z$ the scattering wavevector, arising from path length difference just as for small-angle scattering. The reflected amplitude dR from one layer is proportional to the change in k_c^2 across the interface, which is proportional to the change in scattering density ρ_e or c_{mon} (since $k_c^2 = 2k^2\delta$ and δ is proportional to the scattering density).

Putting this all together, we have

$$I = |R|^2 \propto (k_c/q)^4 \left| \int dz\, \rho'(z)e^{iqz} \right|^2 \tag{3.1.18}$$

In the above, $\rho(z)$ is the scattering length density normalized to the bulk value deep in the sample (which we use to define k_c). Hence $\rho'(z)$ is the normalized "density of interface".

The result of an interface with structure is to modulate the Fresnel reflectivity law (the falloff of scattered intensity as q^{-4} for angles well above the critical grazing angle), with the modulus squared of the form factor (Fourier transform) of the interfacial profile. Consider an example first of a sharply defined layer of thickness a on top of a thick substrate, in which the scattering length density of the layer is some fraction α of that of the substrate.

The normalized interface density $\rho'(z)$ for this problem is the sum of two delta functions, one at the top of the layer ($z = 0$ and one at the bottom ($z = -a$):

$$\rho'(z) = \alpha\delta(z) + (1 - \alpha)\delta(z + a) \tag{3.1.19}$$

Then we have

$$\int dz\, \rho'(z)e^{iqz} = \alpha + (1 - \alpha)e^{-iqa} \tag{3.1.20}$$

and hence

$$
\begin{aligned}
I &= (k_c/q)^4 \left(\alpha^2 + (1 - \alpha)^2 + 2\alpha(1 - \alpha)\cos qa \right) \\
&= (k_c/q)^4 \left((1 - A) + A\cos qa \right)
\end{aligned}
\tag{3.1.21}
$$

with $A = 2\alpha(1 - \alpha)$. The Fresnel law is modulated by the interference between the front and back interfaces; if the change in scattering length density is the same from vacuum to layer as from layer to substrate, $A = 1/2$ and the modulation completely suppresses the intensity periodically.

The modulation period tells us the thickness of the layer. Note however that as for small-angle scattering, the intensity is not sufficient to determine $\rho'(q)$, but only its modulus — phase information needed to reconstruct $\rho(z)$ from $\rho'(q)$ is once again missing. Thus for reflectivity as well as for small-angle scattering, structure determination requires modeling of the interfacial structure and validation by comparison to data. But because the structure is known to be one-dimensional (assuming the sample was properly prepared!), the modeling task is significantly easier; and because of the strong interference between different interfaces, the signal has more structure to account for, which helps to constrain the model.

If the interfaces are not infinitely sharp but instead are blurred out with a characteristic width b, the Fresnel oscillations do not persist to arbitrarily high q, but decrease in amplitude, dying away when the wavelength probed by the reflectivity ($\lambda_q = 2\pi/q$) becomes as small as the blurring width b. To see this, we represent $\rho'(z)$ as the sum of two normalized Gaussians,

$$\rho'(z) = \alpha\exp(-z^2/2b^2)/\sqrt{\pi b^2} + (1 - \alpha)\exp(-(z + a)^2/2b^2)/\sqrt{\pi b^2} \tag{3.1.22}$$

The required Fourier integrals can be performed by our usual tricks of completing the square in the exponent and shifting the integration variable, to obtain

$$I = (k_c/q)^4 \left((1 - A) + A \cos qa\right) \exp(-q^2 b^2) \tag{3.1.23}$$

As promised, the oscillations, indeed the entire Fresnel reflectivity, dies away when $qb > 1$. If one of the interfaces was sharp and one was diffuse, the oscillations would decay away but the Fresnel q^{-4} reflectivity would persist.

3.2   Single polymers at interfaces

One important role for polymers in complex fluids is to modify the properties of surfaces. Polymers can be adsorbed or chemically attached to surfaces of materials or colloidal particles to change the wettability of the surface, or to modify the attractive forces between particles in a suspension.

Colloidal suspensions, such as inks or paints (in which the pigment particles are suspended in a carrier fluid), must be designed to be stable against flocculation, which results when dispersive forces are sufficiently strong to cause particles to stick together when they come into contact. We shall discuss the origins and magnitudes of dispersive forces in later lectures. For now, it suffices to remark that dispersive forces are generically attractive, and can only be eliminated by careful matching of the particle and suspending fluid. This is usually impossible, however, when the choice of particle and fluid are dictated by other concerns.

One successful strategy is to provide the colloidal particles with a loosely adsorbed layer of polymer, chosen so that the suspending fluid is a good solvent. Then the adsorbed polymer layers can serve as "bumpers" for the particles, providing a repulsive interaction to counteract the dispersive attractions. In this and the following lecture, we shall investigate various kinds of adsorbed polymer layers, to determine the thickness of the resulting layer, the monomer concentration profile, and the force required to compress the layer by some amount. With these results, the strength and range of repulsive forces provided by adsorbed polymer layers can be estimated.

Weak uniform adsorption

The simplest approach to building an adsorbed polymer layer is for the surface to be made weakly attractive to the monomers. This method was used in ancient times in the formulation of inks, which are polymer-stabilized suspensions of pigment (carbon black) in water.

Intuitively, a polymer near a weakly attractive surface should adopt a confined conformation, with loops of some length projecting into the solvent. A carpet of such loops may provide repulsive interactions with another such carpet on a second surface. We want to know, in terms of the properties of the surface, polymer, and solvent, how tall and how dense is the adsorbed layer?

To estimate the thickness of such an adsorbed layer, we begin by making a Flory argument, for a single chain attracted to a surface. We suppose that the binding energy of a monomer is ϵkT, small compared to kT, and that the attraction operates over a monomeric distance δ. Following the usual formula for such estimates, we write the free energy per chain as the sum of two terms: an estimate of the entropy loss due to confinement, and of the energy gain due to surface attractions:

$$\beta F/\text{chain} = \frac{R_e^2}{h^2} - \frac{\epsilon N \delta}{h} \tag{3.2.1}$$

The second term results from assuming that the N monomers are uniformly distributed over a layer of thickness h, such that a fraction δ/h of them are within interaction range of the surface. The first term is the same confinement entropy estimate we made when considering chain swelling. Note that the confinement is only in the direction normal to the surface; the chain is free to adopt random-walk conformations in the plane of the surface.

Minimizing with respect to h, we obtain the scaling relation

$$h \sim \frac{b^2}{\epsilon \delta} \tag{3.2.2}$$

Presuming that the interaction range δ is of order b, we see that the layer thickness is of order b/ϵ. If ϵ is much less than unity (weak absorption), the layer will be thick compared to a monomeric

length, but thin compared to R_e. If the binding energy is of order kT per monomer, the thickness will be monomeric — the chain will not wander away from the surface to gain entropy, since there is only of order one degree of freedom per monomer to be gained by wandering.

Note that the binding energy scales as

$$\beta F/\text{chain} = \frac{N\epsilon^2\delta^2}{b^2} \tag{3.2.3}$$

So for example if $\epsilon = 1/10$ and $N = 1000$ (and $\delta/b = 1$), the layer is $10b$ thick, whereas R_e is about $30b$, and the binding energy is about $10kT$. So even though the attraction per monomer is small, the chain as a whole is rather strongly bound to the surface. Weakly adsorbed polymers are difficult to wash off by mere dilution, without disrupting the attractions by a change of solvent.

End grafted chains; image methods

A different strategy for assembling an adsorbed polymer layer is "end grafting", which is to attach chains by one end, either by chemical bonding or a strongly attractive short-range potential. For example, we may terminate a hydrocarbon polymer with a dipolar group, such as a carboxylic acid or sulfonate group with its counterion; such an endgroup will prefer to sit at an interface, relative to being bathed in nonpolar solvent. Or, we can terminate the polymer with a short length of a second polymer, for which the solvent is poor. In either case, the endgroup will serve to anchor the polymer at the interface by adsorption.

With end grafting, we arrange things so that the interaction between monomers and the surface is repulsive. A single chain end-grafted to a surface is free to adopt random-walk configurations, with the constraint that the chain path always begins at the surface, and never crosses the surface. Intuitively, we may expect the monomers of such a chain to be spread out over a region of size R_g, displaced away from the surface because of the constraint of not crossing. Certainly such chains would not be confined to a thin adsorbed layer, so the height of a "bumper" built from such chains could potentially be taller than for uniform adsorption.

It turns out that random walks near uncrossable interfaces appear frequently in many different contexts. We now describe a useful method for dealing with such random walks, called the "image method". Suppose we want to perform averages over the configurations available to an ideal random walk, which is obliged to start next to a wall, and cannot cross the wall. To keep things simple, we consider only a one-dimensional random walk; At each timestep, the walker either takes a step towards the wall, or away from it, each with probability $1/2$. The walker starts at $z = z_0$ and is not permitted to reach $z = 0$. We can draw the "world-line" of these walks in two dimensions, with "time" (steps) on the vertical axis.

We would like a scheme for automatically throwing away any walk that arrives at the wall. This can be achieved, by launching a walker at $z = z_0$ and an "antiwalker" at $z = -z_0$; both are "free random walkers", unaware of the constraint of the wall. Consider the probability distribution of the free walkers, minus that of the antiwalkers, as a function of z and n. The antiwalker can follow the same paths available to the walker (displaced by $2z_0$); in fact, it is useful to pair up a given path for the walker, with its mirror image for the antiwalker. If the walker never reaches the wall, the walker stays on the positive side of the wall, the antiwalker on the left. Walkers on such paths contribute to the probability distribution on the positive side of the wall. But if the walker ever arrives at the wall, he meets the antiwalker and annihilates. (We may say that thereafter, we pair up the path for the walker with the same path for the antiwalker — not the mirror image — and they cancel forever after in the probability cloud of walkers and antiwalkers.) Thus walkers that reach the wall contribute nothing thereafter to the probability distribution.

This amounts to saying that the probability distribution of walkers $P_W(z, n)$ starting at z_0 that respect the uncrossable wall is given by

$$P_W(z, n) = P(z, z_0, n) - P(z, -z_0, n) \tag{3.2.4}$$

in which $P(z, z_0, t)$ is the probability distribution for free random walks. By translational symmetry, we have $P(z, z_0, n) = p(z - z_0, n)$, and by reflection symmetry we have $p(z, n) = p(-z, n)$. Together, these give $P(0, z_0, n) = P(0, -z_0, n)$, so that $P_W(z, n)$ vanishes at $z = 0$.

If the initial distance z_0 of the walker from the wall is small (one Kuhn length, for example), the difference is well approximated by a derivative with respect to the launching point of walker and antiwalker, and we have approximately

$$P_W(z, n) \approx -2b\partial_z p(z, n) \tag{3.2.5}$$

in which $p(z, n)$ is the free random walk probability distribution

$$p(z, n) = \frac{\exp(-3z^2/2nb^2)}{(2\pi nb^2/3)^{1/2}} \tag{3.2.6}$$

Semicrystalline polymers; Gambler's Ruin

One important context in polymer physics where we encounter random walks near a wall, is the structure of the interface between a crystalline lamella and the adjacent melt in a semicrystalline polymer. The ground state of crystalline polymers are extended chain crystals, with parallel chains in all-trans or helical conformations, packed into a regular array. However, it turns out that crystallizable polymers in practice almost never crystallize completely. Instead, when a crystallizable molten polymer is cooled, small crystals nucleate, and grow much faster in the directions normal to the parallel chain stems, resulting in crystalline lamellae (layers).

Crystal growth in the directions normal to the chain stems is relatively easy because only a small portion of chains ahead of the growth front must be "combed out" to become parallel stems ready to add to the crystal. The tangles and loops present in that region of melt are swept to the adjacent melt, and become part of a carpet of loops above and below the lamella. Crystal growth is extremely slow normal to the layers because it is very difficult to extend the loops and remove the tangles in the adjacent melt in order to extend the parallel chain stems and thicken the lamella.

The final state of crystalline polymers consists of lamellae separated by amorphous regions, which are unable to crystallize either because they are too thin for new crystals to nucleate, or because they are too much beset by trapped entanglements that were swept out of the adjacent lamellae when they crystallized. (The details of this picture are a subject of current research.) A typical crystalline polymer may only be 50 percent crystalline, with lamellae of thickness of order 100Å interleaved with amorphous layers of comparable thickness.

If the lamella grows slowly enough, the carpet of trapped loops may be rather random, characteristic of a low free energy state of maximum entropy. If the chains are long, such that chain ends are rarely encountered, every chain stem that exits a lamella must re-enter the lamella elsewhere, or cross through the adjacent amorphous layer to reach the next lamella.

Let us first make the approximation that the next lamella is very far away, so that we have essentially just one crystal-melt interface, made of loops. And, let us suppose that these loops are noninteracting, ideal random walks (we will consider this assumption further, below). We may make an analogy to a classic problem in probability theory, called the Gambler's Ruin.

Consider a compulsive gambler with an initial stake of $1, who repeatedly plays a game in which he bets $1, and with equal probability wins 1 or loses $1, until he goes bust. The question is,

what is the likelihood that the gambler goes bust on the nth round of the game? (In the analogy, the initial stake of \$1 corresponds to the polymer chain starting one step above the surface, the winnings of the gambler after k steps corresponds to the position of the chain above the surface, and "going bust" corresponds to the return of the chain to the lamella.)

In our lecture on random walks, we showed that the probability distribution for free random walkers satisfies a diffusion equation. This is equally true for random walkers obliged not to cross a wall; we have

$$\partial_n P = D\partial_z^2 P + \delta(n)\delta(z - z_0) \tag{3.2.7}$$

In the above, we have added a "source term", which injects a walker at z_0 at "time" $n = 0$.

We can use this equation to examine the "survival probability", i.e., the fraction of an ensemble of gamblers still playing the game after n rounds. The fraction of surviving gamblers is $S(n) = \int_0^\infty dz\, P(z, n)$. We can derive an equation for $S(n)$ by integrating the PDE for $P(z, n)$ with respect to z, obtaining

$$dS/dn = -\left. D\partial_z P\right|_0 \tag{3.2.8}$$

This equation expresses the conservation law in terms of the diffusive flux of walkers into the absorbing boundary; $-D\partial_z P$ is the flux into the wall, which decreases the number of surviving walkers (gamblers).

Of course, we can also compute $S(n)$ directly by integrating the image method solution over all positive z. It is clear that $S(n)$ must decay with "time" n, as the equal and opposite diffusive clouds of the walkers and antiwalkers on opposite sides of the wall broaden and increasingly cancel out. By either approach, we find that $-dS/dn$ scales as $n^{-3/2}$, so that $S(n)$ itself decays as $n^{-1/2}$.

With this result, we can investigate the average time to go bust. Note that $-dS(n)/dn$ can be interpreted as the probability that a gambler goes bust on the nth round (the reduction of $S(n)$ on the nth round is $S(n) - S(n + 1) \approx -dS/dn$). In terms of the carpet of loops, $-dS/dn$ is the probability that a loop has length n. So the average time to go bust is

$$\bar{n} = -\int_0^\infty dn\, n\, dS/dn \tag{3.2.9}$$

which diverges, because $n\, dS/dn$ decays only as $n^{-1/2}$. Perhaps this result explains in part the allure of gambling; all gamblers go bust, but some take a very long time to do so.

Tie chains; cashing out; first-passage time

Now we consider the effect of a second lamella, some distance L above the first. If the random chain configuration reaches the second interface, a "tie chain" results, connecting the lower and upper lamellae. In terms of the gambler analogy, if a gambler is lucky enough that his winnings exceed L dollars, he is permitted to "cash out" and leave the casino. We would like to know how likely is this unlikely event.

The direct approach to answer this question is complicated. We could try to compute the time-dependent probability distribution for an ensemble of walkers launched one step from the lower boundary, with absorbing conditions on both the lower and upper boundaries. Then, we could integrate the flux at each boundary with respect to time, to see how many walkers exit through each boundary. Note that we cannot use image methods for problems with two absorbing boundaries (or rather, image methods are not convenient, because to enforce both absorbing boundary conditions requires an infinite sequence of antiwalkers and antiantiwalkers and so on, each a reflection of previous images in one of the two mirror interfaces).

There is a simpler way. Imagine supplying a new gambler, with his starting stake of $1, onto the casino floor at regular time intervals (every minute, following P. T. Barnum's dictum). Eventually, a steady state will be reached: gamblers will continually go bust or cash out, at a fixed total rate of one per minute, balancing the influx of new suckers. To compute the fraction of gamblers who cash out, we need only find the steady-state probability distribution of winnings, from which we can compute the steady-state flux out each boundary.

To carry out this scheme, we change the time-dependent source $\delta(n)\delta(z - zz - 0)$ in the PDE for $P(z, n)$ to a steady-state source $r\delta(z - z_0)$. Then in the steady-state limit, the time derivative vanishes, and we have simply

$$0 = D\partial_z^2 P(z) + r\delta(z - z_0) \tag{3.2.10}$$

On either side of the source, which corresponds to a steady injection of walkers at z_0 at a rate r, the differential equation is simply $P''(z) = 0$, which means $P(z)$ is linear. $P(z)$ vanishes at both absorbing boundaries. Putting this together, we have

$$P(z) = \begin{cases} P_0 z/z_0 & 0 \le z \le z_0 \\ P_0(L - z)/(L - z_0) & z_0 \le z \le L \end{cases} \tag{3.2.11}$$

The presence of the source implies a discontinuity in slope at z_0, as can be verified by integrating the differential equation for $P(z)$ from $z_0 - \delta$ to $z_0 + \delta$, resulting in

$$D \partial_z P(z)|_{z_0 - \delta}^{z_0 + \delta} = -r \tag{3.2.12}$$

which is consistent with the above "rooftop" solution if we take the value P_0 such that DP_0/z_0 plus $DP_0/(L - z_0)$ equals r, i.e., such that the sum of the fluxes out both boundaries equals the incoming rate. This gives

$$P_0 = rz_0(L - z_0)/DL \tag{3.2.13}$$

The fluxes out the boundaries at $z = 0$ and $z = L$ are DP_0/z_0 and $DP_0/(L - z_0)$ respectively. The fraction of walkers exiting the far boundary is then

$$f = \frac{1/(L - z_0)}{1/z_0 + 1/(L - z_0)} = z_0/L \tag{3.2.14}$$

Returning now to the problem of semicrystalline polymers, we have typical values of interlamellar spacing and thickness about equal, and of order 100Å. For polyethylene, we have a Kuhn length of about 14Å, so if we take the "injection point" (initial location of the walker) as $z_0 = b$, we have $f = 0.14$. This fraction of tie chains is sufficient to link adjacent lamellae. (Note that lamellae may also be tied together by loops from adjacent lamellae that entangle across the amorphous space; it is more complicated to compute this probability of indirect coupling of lamellae in this fashion.)

We can use this same steady state to infer the mean survival time of the walkers. Because we are supplying walkers at a fixed rate r, the number W of walkers present at any given time is the mean lifetime $\bar{n}$ times the supply rate r. We compute the number present by integrating $P(z)$ over the entire range, which gives $W = P_0 L/2$. Using our result for P_0 above, we have then

$$\bar{n} = z_0(L - z_0)/2D \tag{3.2.15}$$

If we put $D = b^2/6$ as appropriate for a freely jointed polymer random walk in three dimensions, and take $z_0 = b$ as before, we have $\bar{n} = 3L/b$ (assuming $L >> z_0$). With the values above for typical crystalline lamellae and amorphous layer thicknesses, we then have $\bar{n} \approx 20$ Kuhn segments as the mean length of a loop or tie chain.

Finally, we return to consider the reasonableness of approximating the loops at the crystal-melt interface by ideal random walks. There are two issues to consider: first, the question of whether the loops should be regarded as "random", i.e., maximally entropic, as they would be if the interface were constructed to minimize the free energy. This is perhaps reasonable if the crystal grows slowly enough that the material ahead of the crystal growth front can reorganize to some extent.

Second, we may ask whether the loops can be thought of as ideal, that is, not interacting with each other. One way in which the loops must interact in principle is through the requirement of constant melt density. It turns out that a carpet of random loops do correspond to a constant density melt, but the value of the density is correct only at a particular areal density of injected loops. This can be recognized by considering an isotropic melt, cut through by a "phantom plane"; on each side, the halfspace is in fact a carpet of loops at constant melt density.

On a simple cubic lattice, it is easy to see that the injection density corresponding to an isotropic melt of loops is 1/6, because in an isotropic melt the probability of a chain taking a step across to the other side of a phantom plane immediately adjacent is 1/6. Now the actual areal density of injected loops is set by the spacing of chain stems in the crystalline lamella, which is determined by the crystal geometry, unaffected by the interfacial structure. The excess of injected chains is resolved by whatever fraction is necessary of "tight loops", adjacently reentering the lamella.

Multiple chains, weakly adsorbed

We return to the problem of chains adsorbed to a weakly attractive interface, this time with many chains present. As the attraction of the surface for the monomers is increased, a surface in equilibrium with a solution of chains at some finite concentration must eventually saturate, with all available surface sites occupied by monomers. Further increases in the surface attraction can have no effect on the adsorbed mass per unit area, nor on the shape or extent of the monomer concentration profile away from the surface. It is this limiting adsorbed layer we would like to describe.

The concentration profile must reach meltlike density near the surface, and fall off somehow as we move away from the interface. Surely it cannot extend much farther than the radius of gyration of the constituent chains; there would be no reason for a chain to stretch to reach the interface, as other less-distorted chains could take its place in filling the surface sites. Because the concentration profile is not uniform, the usual style of Flory argument (which assumes uniform concentration within a region of some characteristic size) cannot be used to analyze this situation.

Instead, we give a different kind of scaling argument, based on enlightened dimensional analysis. We would like to know, what is the size of the correlation blob a distance z from the wall? If we knew this, we would know the monomer concentration $c(z)$, from blob scaling ($c \sim g/\xi^3$ and so forth). Now we argue that $\xi(z)$ cannot depend on microscopic lengths, such as the monomer size; for if we coarse-grained the monomer appropriately, for example changed our description from chemical monomers to Kuhn (flexible) monomers, ξ would not change. And, we argue that $\xi(z)$ cannot depend on the total length of the chain as long as ξ is much smaller than R_g, just as ξ in semidilute solution is not influenced by chain length for chains above overlap concentration.

So, ξ must be of order z itself, because we have no other lengths in the problem that ξ can depend on. This is a statement both about dimensional analysis — whatever expression we give for ξ must have dimensions of length — as well as a statement about what ξ cannot depend on (microscopic lengths and total chain dimensions).

Thus we write the following scaling assumptions:

$$\xi \sim z$$
$$c \sim g/\xi^3$$
$$\xi/l_s \sim (g/n_s)^{3/5}$$

in which the latter two equations correspond to the usual assumptions that the blobs fill space, and are constructed of self-avoiding walks of thermal blobs (size l_s, mass n_s). Combining these assumptions gives

$$c \sim (n_s/l_s^3)(l_s/z)^{-4/3} \tag{3.2.16}$$

which holds down to the scale of a thermal blob ($z \sim l_s$), at which c takes the value n_s/l_s^3, which is the concentration within one thermal blob. (At shorter length scales still, inside of one thermal blob, the concentration profile is again inhomogeneous, finally approaching melt density in a very thin layer near the surface.) The concentration profile is eventually cut off somehow, for z beyond R_g.

Evidently, the concentration profile obtained from uniform adsorption of chains is long-ranged, but not very robust, in that the concentration distant from the surface is quite low. At far distances from the interface, a simple estimate of the repulsive force between two such layers could be made by overlapping two concentration profiles, and estimating the overlap energy as of order kT per blob.

3.3   Grafted polymer brushes

In the previous lecture, we analyzed the behavior of single chains end-grafted to an uncrossable surface. Now, we consider the case of multiple grafted chains at an interface. We want to describe the height and compressibility of the resulting polymer layer, as a function of chain length N, excluded volume parameter v, and grafting density σ (chains per area).

For sufficiently low values of σ, the grafted chains are isolated, and form individual random coils of dimension essentially equal to R_F, the Flory radius of a swollen chain in good solvent. (This low-coverage limit is called the "mushroom" regime, with each chain forming a "mushroom" above the surface.) When the coverage reaches of order $1/R_F^2$, the mushrooms begin to overlap. It then pays for the chains to stretch away from the surface to some extent, forming a "brush" (each chain analogous to a bristle in a hairbrush).

We construct a Flory argument to estimate the height h of the brush, as follows. The free energy per chain we estimate in the usual way, as

$$\beta F/\text{chain} = \frac{3h^2}{2nb^2} + vN\left(\frac{N\sigma}{h}\right) \tag{3.3.1}$$

In the above, the second term is the usual excluded volume estimate, with v the excluded volume parameter, and the monomer concentration estimated as σ chains per area times N monomers per chain, spread out over a layer of thickness h.

Minimizing with respect to h gives the result

$$h = N\left(\frac{v\sigma b^2}{3}\right)^{1/3} \tag{3.3.2}$$

Note that at fixed coverage σ, the layer height is proportional to N, which means if we go on doubling the chain length at fixed σ, we can make the layer arbitrarily tall compared to the Flory radius R_F. In fact, we know that at σ of order $1R_F^2$, we must get h of order R_F, so our result must be consistent with the scaling

$$h/R_F \sim \left(\sigma R_F^2\right)^{1/3} \tag{3.3.3}$$

which expresses how much taller than the native coil size the layer is, as a function of coverage relative to the overlap coverage.

We can also examine the brush using a blob model, which illuminates the structure in a different way. A chain in the brush is envisioned as a linear sequence of correlation blobs, stacked one atop the next. The correlation length ξ is set by the coverage, such that σ is of order $1/\xi^2$. The correlation blobs as usual are taken to be self-avoiding walks of thermal blobs. The total brush height h scales as $n\xi$, where n is the number of blobs per chain. We determine n by requiring that $N/g \sim n$, where g is the number of monomers per blob.

Together, the scaling assumptions are

$$h \sim n\xi$$
$$\sigma \sim 1/\xi^2$$
$$\xi/l_s \sim (g/n_s)^{3/5}$$
$$N/g \sim n$$

Combining these assumptions (together with our usual scaling results for the thermal blob size), we find a scaling result consistent with the Flory argument.

One result that is easy to see from the blob model is that the free energy per chain must scale as kT times the number of blobs. (This is consistent with the estimate from the Flory argument, but the physical origin of the result is less evident there.)

Compressing a brush

From the Flory expression for the brush free energy as a function of height, we can immediately determine the free energy cost of compressing the brush to a height less than the optimum height. We are typically interested in the force per unit area (i.e., pressure) required to compress the brush at fixed coverage (i.e., the chains do not move on the surface, or leave the brush). Noting that the free energy per area F/A is simply σ times the free energy per chain, we have

$$
\begin{aligned}
P = -\partial(F/A)/\partial h &= -kT\sigma\frac{\partial(\beta F/\text{chain})}{\partial h} \\
&= -kT\sigma\left(\frac{3h}{Nb^2} - \frac{vN^2\sigma}{h^2}\right)
\end{aligned}
\tag{3.3.4}
$$

The above result vanishes at the optimum height h^*; it can be expanded to first order in $\delta h = h - h^*$, with the result

$$
P \approx -\frac{9kT\sigma\delta h}{Nb^2}
\tag{3.3.5}
$$

Note that the force is proportional to σ, so that we can get progressively stiffer brushes by increasing the coverage.

The corresponding free energy change (from integrating $dF/A = -Pdh$, or expanding the free energy itself around the minimum) of

$$
\Delta F/A \approx \frac{9kT\sigma\delta h^2}{2Nb^2}
\tag{3.3.6}
$$

Thus if we compress the brush by of order the ideal end-to-end distance Nb^2, which will be significantly less than the total brush height for a brush of several blobs, the change in free energy will be of order kT per chain.

Forces are somewhat less obviously calculated within the blob picture. When a brush is compressed, the blobs must become smaller and more dense, to accommodate the same number of monomers per unit surface area in a shorter brush. The blob size in the compressed brush is therefore not given by the coverage (as $\sigma = 1/\xi^2$). What remains true is that the free energy of formation of the brush is still kT per blob, so the force to compress the brush may be inferred from the increase in the number of blobs per chain on compression, under the assumption of a uniform concentration and hence uniform blob size within the compressed brush.

Growing a brush

Having described the structure of a brush at a given coverage, we may ask about how a brush may be grown or assembled on a surface. There are several possible approaches; one fancy way is to somehow polymerize the chains from initiation sites chemically bound to the surface.

More commonly, brushes are adsorbed from solution onto an initially bare surface. The dynamics of this process can be complicated; for example, the same energetics that lead the chain endgroups to stick to the surface may lead them to stick to each other in solution, forming micellar aggregates. We shall discuss this sort of self-assembly in later lectures. For now, it suffices to say that if the endgroups are bound to the core of an aggregate in solution, the process of adsorbing onto the surface may be slow, because the equilibrium concentration of free chains in solution may be low.

But there is another reason for growth of a brush from solution to be slow. Consider the process by which a chain from solution penetrates a pre-existing, partially constructed brush to adsorb its

endgroup to the surface. Suppose that the chain enters the brush, dragged by its end by a "Maxwell demon" (thermal fluctuation). The work required to drag the chain into the existing brush is equal to kT times the number of blobs created along the chain as it enters.

This leads to an effective potential $U(z)$ that is a linear function of the distance the end has penetrated:

$$\beta U(z) = (h - z)/\xi \tag{3.3.7}$$

Once the endgroup reaches the surface, the chain energy drops abruptly, by the binding energy ϵ. In equilibrium, the free energy change on adsorbing an additional chain from solution will be zero, so that

$$0 = kTh/\xi - \epsilon - kT \log(c\xi^2\delta) \tag{3.3.8}$$

The last term is the change in entropy of mixing of the chain, from solution at concentration c, to the adsorbed state, where the endgroups form an ideal gas at a concentration of one per $\xi^2\delta$, in which δ is the range of the binding interaction. Neglecting the entropy of mixing contribution, the equilibrium coverage is such that the binding energy of the endgroup just recovers the work done in deforming the chain to fit into the brush.

Suppose we fix the concentration of chains at the boundary of the brush to some value c_0, and ask about the steady rate at which chains diffuse up the potential $U(z)$ into the brush and stick. The diffusion equation describing the chain concentration is a biased diffusion PDE,

$$0 = \partial_t P(z, t) + \partial_z J$$
$$J = -D\partial_z P - P(\partial_z U/\zeta) \tag{3.3.9}$$

The concentration current is the sum of two terms: diffusive (first term) and driven or "drift" (second term). The drift current is driven by the gradient in the effective potential for the endgroup position; in absence of diffusion, the drift current would carry the chains downhill in U, away from the surface.

In the above, ζ is the drag coefficient on the chain, such that the drift velocity v times ζ equals the driving force on the chain position $-\nabla U$. By the Stokes-Einstein relation, D equals kT/ζ. (In the present problem, the drag coefficient should be a function of z, proportional to the number of blobs along the chain as it enters the brush, but we shall ignore that dependence for simplicity.)

The steady state of polymers slowly climbing by diffusion into the brush is described by constant current J, which leads immediately to

$$P(z) = A + Be^{-(h-z)/\xi} \tag{3.3.10}$$

with A and B to be determined by boundary conditions of $P = 0$ at $z = 0$ and $P = c_0$ at $z = h$. Imposing the boundary conditions gives after a bit of algebra

$$P(z) = c_0 \frac{e^{z/\xi} - 1}{e^{h/\xi} - 1} \tag{3.3.11}$$

The corresponding current J can then be evaluated as

$$J = -\frac{Dc_0}{\xi \left(e^{h/\xi} - 1\right)} \tag{3.3.12}$$

We can compare this current to the naive estimate of the on-current rate, J_0 of order $-Dc_0/h$ (i.e., diffusing down a linear concentration gradient over the height of the brush). The actual current is much smaller, by a ratio

$$J/J_0 \approx (h/\xi)\exp(-h/\xi) \quad , \quad h >> \xi \tag{3.3.13}$$

Physically, the current is smaller because the chains must "diffuse uphill" in the potential $U(z)$ all the way to the surface, before the end can adsorb and bind the chain. As the brush grows, this leads to progressively slower adsorption kinetics, and can place a practical limitation on how many blobs tall a brush can be.

One way to overcome this kinetic limitation to growing dense brushes is to grow from a semidilute solution of the adsorbing chains, in which the correlation blob is of roughly the same size as the desired size for the blobs in the final brush. Then, the chains everywhere in the solution are already distorted into sequences of blobs, which eliminates the barrier that led to slow adsorption kinetics described above. This scheme can be employed until the blobs become so small that the solution becomes very viscous, so that the diffusive transport of the chains from solution to the surface is sluggish.

Brushes on particles; Daoud-Cotton

So far, we have been describing brushes grown on flat surfaces. Our results to this point are also valid for brushes grown on particles, as long as the brush height is small compared to the particle radius. We can also analyze the opposite limit, in which n polymer chains are grafted to the surface of a small particle, small in the sense that the radius of the resulting polymer brush is much larger than the particle radius. This limit includes the case of "multiarm star polymers", in which n chains are covalently attached to a central grafting point of molecular size.

We can describe the overall size of the resulting polymer "corona", but not the detailed spatial dependence of the concentration, with a Flory argument. We write the total free energy of the assemblage (not per chain, as we have previously) as

$$\beta F = \frac{nR^2}{Nb^2} + vnN\left(\frac{nN}{R^3}\right) \tag{3.3.14}$$

in which we have made the usual approximations for the entropy reduction due to stretching, and the monomer interactions with the average concentration (of order nN/R^3). Minimizing with respect to R gives

$$R/l_s \sim (N/n_s)^{3/5} n^{1/5} \tag{3.3.15}$$

(In the above, we have put R and N in terms of the thermal blob size l_s and mass n_s, by observing that for $n = 1$ we have the original Flory argument for a single swollen chain.)

We see that the size of the corona in the limit $R \gg a$ scales with chain length in just the same way as for a single swollen chain, unlike the case of the planar brush. As the chain stretches away from the particle or grafting point, there is a lot of room to avoid other chains and thereby relax further stretching. Only by increasing n can we increase R, and then only weakly, as $n^{1/5}$.

To find out how the monomer concentration decreases with increasing distance from the particle, we need a more detailed picture of the corona structure. A blob model of the corona was developed by Daoud and Cotton. Similar to the de Gennes blob model of the uniformly adsorbed polymer layer, the key question is to decide what should be the correlation blob size ξ a distance r from the particle.

Daoud and Cotton argued that the blobs at distance r from the surface must be such that n of them are sufficient to fill up the surface area of a spherical shell of radius r. That is, $n\xi^2$ should scale as $4\pi r^2$. We combine this with the usual scaling assumptions for the concentration within a

blob, and for the relation between the number of monomers and size of a blob:

$$n\xi^2 \sim 4\pi r^2$$
$$\xi/l_s \sim (g/n_s)^{3/5}$$
$$c \sim g/\xi^3 \tag{3.3.16}$$

Together, these imply

$$c \sim (n_s/l_s^3)(\xi/l_s)^{-4/3} \tag{3.3.17}$$

We can find the outer dimension of the corona, beyond which the concentration profile must fall off more sharply than the above power law, by requiring that the integral of the concentration profile account for all the monomers in the grafted chains:

$$nN = 4\pi \int_0^R dr\, r^2 c(r) \tag{3.3.18}$$

which, when applied to our scaling result for $c(r)$, reproduces the characteristic size of the corona we found with the Flory argument.

Polyelectrolyte brushes

An important variation on polymer brushes appears when the polymers in the brush are polyelectrolytes, which have some number of chargeable groups along their length. Such polymers are typically soluble in aqueous solvents (water, salt water, water-based acids, water-alcohol mixtures). The chargeable groups consist of a cation-anion pair, one of which is covalently bonded to the chain (here, we assume the anion). The pair can dissociate in aqueous media, leaving the polymer charged.

The mobile cations (typically alkali metals) dissociate from the polymer for two reasons: first, the solvent polarizes around the cation, reducing the binding energy of the cation to the anion; second, the cations can gain translational entropy by unbinding from the anions. A quantitative treatment of this process is complicated; we will return to this topic in later lectures. For now, it suffices to make the assumption that the counterions are free to explore the brush, but are unlikely to stray far outside the brush because of electrical neutrality. That is, if the counterions were to escape far from the brush, it would leave the surface charged, which would result in a constant electric field and hence a constant force on the counterions, which would pull the counterions back into the brush.

Under this simplifying assumption, the brush is in fact electrically neutral on average. However, the counterions constitute an ideal gas within the brush, with osmotic pressure that tends to push the brush to swell and become taller. We can once again estimate this effect with a Flory argument. We write the free energy per unit area as

$$\beta F/A = \sigma\frac{h^2}{Nb^2} + hc\log c \tag{3.3.19}$$

in which c is the concentration of counterions inside the brush.

We determine c in terms of the number of charges per monomer λ of the chains (which depends on how the chemist made them), as

$$c = N\lambda\sigma/h \tag{3.3.20}$$

Minimizing as usual with respect to h yields the scaling result

$$h \sim Nb\lambda^{1/2} \tag{3.3.21}$$

Note that the brush height is now independent of coverage, determined instead by a balance between the osmotic pressure of the counterions and the entropic penalty for stretching the chains.

Brushes made in this way can be strongly stretched for very modest charging, i.e., for λ much less than unity We may compare h to the ideal chain radius, as

$$h/R_e \sim (N\lambda)^{1/2} \tag{3.3.22}$$

so that the stretch ratio h/R_e scales as the square root of the total number of charges on the chain. Thus we can have h/R_e of order 10, with 100 charges per chain, which may be only one charge for every 10 monomers on a chain of 1000 monomers.

3.4   A more detailed look at brushes

In the previous lecture, we presented a Flory argument and scaling picture for grafted polymer brushes. This description suffices for most practical purposes, to estimate properties such as the brush height, formation energy, and work to compress the brush by some finite amount. However, a more detailed look reveals some oversimplified features of the model that can be remedied with a more sophisticated though still manageable theory.

The more detailed theory, called the "strong stretching" theory for reasons we shall make clear below, turns out to be an interesting illustration of self-consistent equations for polymers. For this reason (and because I played some role in developing this approach), we take the time in this lecture to explore the strong stretching theory of polymer brushes.

Beyond Flory theory; qualitative

In the Flory theory for brushes as well as the blob model, we assumed the chains in the brush were uniformly stretched, with their free ends located at the outer extremity of the brush. The monomer density profile is correspondingly constant. If the ends were attached to a thin plate permeable only to solvent, this picture would be fully consistent; the Flory minimization would correspond to balancing of forces on the plate due to chain stretching and osmotic pressure.

Suppose we start with such a brush of chains attached by their "free" end to such a plate, and then we snip just one chain loose from the plate. What will that chain do? Freed from the constraint to stretch alongside its neighbors, and surrounded by a uniform concentration profile, this chain can lower its free energy by contracting back to the grafting surface and forming a random coil. In consequence, the formerly constant concentration profile will now be not quite constant; instead, in the vicinity of the released chain near the grafting surface, a slightly higher concentration will result.

Now we release a second chain; it too contracts, nearly all the way to the surface, but finds when it arrives (if it was nearby the first relaxed chain in the x-y plane) that the concentration is no longer quite constant. The second chain may then settle into a coil slightly displaced from the grafting surface, to avoid the concentration bump from the first chain. And so a bigger bump results.

As we release more chains from the plate, it is clear what must occur: a nonuniform concentration profile must build up over the entire height of the brush, highest near the wall and steadily decreasing in some fashion away from the wall. Indeed, the chains in an actual brush are not attached to some phantom plate, and the only reason they stretch away from the grafting surface is to avoid other chains. The chains stretch because the monomer concentration steadily decreases away from the grafting surface.

Self-consistent theory

To describe this situation quantitatively, we make use of self-consistent field theory. That is, we employ the same approximation we made in describing scattering from chains in a melt; namely, we assert that the chains in the brush may be thought of as interacting with each other only through the average local concentration. As before, we write the full partition function as a product of single chain partition functions, with a final subtraction from the free energy of half the interaction term, to avoid double-counting the monomer-monomer interactions:

$$Z = Z_1^n e^{\beta \int d^3r \, (1/2) U(r)\phi(r)} \tag{3.4.1}$$

in which the single-chain partition function is

$$Z_1 = \sum_{\text{configs}} e^{-\beta \int ds\, U(r(s))} \tag{3.4.2}$$

Now we need to say a bit more about how to do the sum over all configurations of a random walk. If we coarse-grain the random walk at a scale above the Kuhn step, at which the chain is flexible, each step will be approximately Gaussian distributed. So we describe the chain configurations first as a sequence of locations $\{r_1, r_2, \ldots\}$ or equivalently as a sequence of steps $\{\Delta r_1, \Delta r_2, \ldots\}$ in which $\Delta r_i = r_{i+1} - r_i$.

Then the sum over configurations can be written with its appropriate weight factors as

$$Z_1 = \prod_i \int d(\Delta r_i) e^{-3/(2b^2) \sum_i \Delta r_i^2} e^{-\beta \sum_i U(r_i)} \tag{3.4.3}$$

We can write this single chain partition function also in a continuum fashion, as

$$Z_1 = \int Dr(s)\, e^{-3/(2b^2) \int ds\, (\partial r/\partial s)^2} e^{-\beta \int ds\, U(r(s))} \tag{3.4.4}$$

in which $r(s)$ is the continuum limit of r_i, and $\partial r/\partial s$ the limit of Δr_i (Δs equals one, as we go from one step to the next). The notation $\int Dr(s)$ stands for the "integral over all paths $r(s)$", which really is just shorthand notation for the big product of integrals over the values of the r_i.

Strong-stretching limit

We do not yet know what the self-consistent potential $U(z)$ actually is for the brush. We know that it must satisfy the self-consistency condition $U(z) = v\langle c(z)\rangle$, and we know it only depends on z (because the problem is translationally invariant in the x-y plane). We also know from the scaling analysis that if the coverage is high enough, the chains in the brush are strongly stretched, with stretching energies many times kT. This means the chains are far from random walks; the compromise each chain in a brush makes, between stretching and interacting with monomers from other chains, is painful and exacting.

So we are led to guess that the chain configurations that will dominate the path integral (i.e., the sum over configurations) are those that make the exponent as small as possible, achieving the best possible compromise between stretching (the first term) and interactions with other monomers (the second term). To minimize the exponent, we set to zero its functional derivative with respect to $r(s)$, which gives

$$0 = -3/b^2 r''(s) + \nabla U \tag{3.4.5}$$

Sine we are only interested in the z component of the chain path (and U only depends on z), we write

$$3/b^2 z''(s) = \partial U/\partial z \tag{3.4.6}$$

When faced with a newly derived equation, it often pays to recall if the equation has been seen before in some other context, where it may have been previously analyzed, and intuition about it developed. The above equation looks just like classical mechanics of a particle in a potential — Newton's equation — for a particle of mass $3/b^2$, in a potential $-U$. The monomer position z is the particle position, and the monomer index s corresponds to time. Continuing the analogy, we consider the boundary conditions. Our chain is grafted, so we have $z(N) = 0$ (the particle arrives at $z = 0$ in "time" N). The free end, attached to nothing, can have no tension on it; hence $z'(0) = 0$ — the particle starts from rest at time zero.

Guessing the potential

We still do not know what shape $U(z)$ must have, but we can make an inspired guess. From our chain-releasing thought experiment, we might reasonably conclude that chain free ends ought to be found within the brush at all distances from the grafting surface, with some probability. Translating that statement into the language of classical mechanics: the potential $-U(z)$ must be such that particles falling from rest (no tension on the free end) from any distance from the surface must arrive at the surface with the same time of flight (all chains in the brush have the same length).

That is, the potential $-U(z)$ must be such that the period of a particle in the potential is N, independent of the amplitude of the motion. This is the hallmark of a simple harmonic oscillator, as Galileo long ago observed, watching a chandelier swing after being lit. Thus $U(z)$ must be a parabola. The corresponding classical trajectories are cosines (the motion of an oscillator),

$$z(s; z_0) = z_0 \cos(s\pi/2N) \tag{3.4.7}$$

in which the argument of the cosine is chosen to give $z = 0$ at $s = N$. The curvature of the potential $-U(z)$ can be found by the requirement that the above cosine is a solution of the equation of motion, i.e., that a particle of mass $3/b^2$ takes a time N to cover one-quarter of a full oscillation. This leads to

$$U(z) = A - Bz^2$$
$$B = 3\pi^2/(8N^2b^2) \tag{3.4.8}$$

The coefficient A is found by the requirement that $U(h) = 0$ (monomer density goes to zero at the extremity of the brush) and $\int dz\, U(z) = v \int dz\, c(z) = vN\sigma$ (all monomers reside within the brush). This gives

$$A = Bh^2$$
$$2Ah/3 = vN\sigma \tag{3.4.9}$$

which leads to

$$h = (4vb^2\sigma N^3/\pi^2)^{1/3}$$
$$A = (3/2)(\pi\sigma v/2b)^{2/3} \tag{3.4.10}$$

We see that the brush height scales as predicted by the Flory argument, but with a different numerical prefactor.

End density; consistency

It remains to check whether some positive density of free end locations is indeed consistent with a parabolic concentration profile. In fact, it turns out to be possible to say exactly what the end density $\epsilon(z)$ is as a function of z. For present purposes, it suffices to give an argument that some positive $\epsilon(z)$ must work. Consider the contribution to the monomer density made by a single chain launched from some z_0. The chain starts from rest, depositing monomers at each tick of the clock as it travels towards the grafting surface. Because the chain us unstretched at the free end, and most stretched near the wall, the monomers from the chain are more spread out near the wall, and bunched up near the free end.

That is, the contribution $\delta\phi(z; z_0)$ of this chain to the density decreases as z decreases, i.e., as we move towards the wall. The chain lays down monomers further apart when it is more stretched, according to

$$\delta\phi(z; z_0) = (dz/ds)^{-1} \tag{3.4.11}$$

(read the right-hand side as "one over (length per monomer)", or "monomers per length").

Whereas, the monomer density we are trying to build up from the contributions of individual chains increases as we move towards the wall. So if we launch a chain from the outer extremity of the brush, it will "underfill" the profile we are trying to reproduce, leaving room for another chain to be launched from some z_0 slightly closer in, which will again underfill the profile, and so on. So the end density is a positive function — launches of chains everywhere in the brush are required to build up the profile — and our initial assumption is consistent.

The resulting picture of the grafted brush differs from the simple Flory or scaling description in several respects. First, of course the concentration profile is not flat; instead, the concentration gradient is what drives the chains to stretch. Furthermore, the chains can have their free ends anywhere in the brush; there is a large degeneracy of possible configurations, even in the strong stretching limit.

We may make an analogy between chains in a brush, and office workers who commute to Manhattan. They can live close, in the city somewhere; their commute is short, but housing is expensive and apartments are small. Or, they can live in New Jersey, and suffer a long commute but own a big inexpensive house. To the extent that office workers in Manhattan are identical (as are the chains in our brush) the tradeoff between the long commute and the cost of real estate is an even trade; if it weren't, more people would move into or out of the city, making the commute worse or the real estate more expensive, until the tradeoff was perceived as even.

(Of course, office workers are not identical; some are dedicated urbanites, willing to put up with the indignities of city living but not willing to sit in a car for three hours a day. And some are dedicated suburbanites, willing to suffer long commutes to live surrounded by grass. In a brush with short chains (urbanites) and long chains (suburbanites), the short chains will crowd out the long chains near the grafting surface, and break the degeneracy.)

Free energy of assembly; compression

To compute the free energy of assembly of the brush, we could proceed in a straightforward way, by summing over the free end density the stretch free energy of each chain, and integrating the monomer-monomer interactions over the height of the brush. There is a simpler approach. Because the chains in a brush are degenerate with respect to free end location, it must be that the free energy $\Delta F(z_0)$ required to add one chain to the brush with free end at z_0 must be independent of where we put its free end. The simplest place to evaluate ΔF is with $z_0 = 0$ — a chain with no stretch, only excluded volume penalty — whereupon $\Delta F = NA$.

Then we can compute the free energy to assemble the brush, by progressively adding chains to increase the coverage:

$$F/\text{area} = \int_0^\sigma d\sigma' \, NA(\sigma) \tag{3.4.12}$$

Since A scales as $\sigma^{2/3}$, this leads to

$$F/\text{chain} = (1/\sigma)F/\text{area} = (3/5)NA(\sigma) \tag{3.4.13}$$

Now we reconsider what happens when we compress a brush, either against another brush or with a (hypothetical) semipermeable plate. The chains in the brush are stretched, so we do not expect much interpenetration between brushes, hence the two methods of compression are equivalent. The concentration profile must remain parabolic; the monomers in a compressed brush are accommodated by increasing the constant A in the profile to whatever level is necessary to account for all the monomers.

The force per unit area required to compress the brush is simply the osmotic pressure of a polymer solution of the concentration at the extremity of the brush. For a mean-field description of a polymer solution, we write the free energy per unit volume f as

$$\beta f = \beta F/V = (1/2)vc^2 \qquad (3.4.14)$$

in which c is the monomer concentration, and the factor of $1/2$ corrects for "double counting", i.e., we have an interaction energy of kT for every pair of monomers that suffer a near-collision.

Now the osmotic pressure Π is the change in free energy with respect to the system volume at fixed number of polymer chains (or monomers or whatever):

$$\Pi = - \left.\frac{\partial F}{\partial V}\right|_n \qquad (3.4.15)$$

To evaluate this, we recognize that the monomer concentration c can be written as nN/V, where N is the number of monomers per chain, n the number of chains, and V the system volume. Then we have

$$
\begin{aligned}
\beta \Pi &= -\frac{\partial(V\beta f)}{\partial V} \\
&= -\left(\beta f + V\frac{\partial \beta f}{\partial c}\frac{\partial c}{\partial V}\right) \\
&= -\left(\beta f - c\frac{\partial \beta f}{\partial c}\right) \\
&= (1/2)vc^2 \qquad (3.4.16)
\end{aligned}
$$

Simple calculations can be made following these ideas, with the result that the free energy of a compressed brush (h less than the unperturbed height) is

$$\ldots \qquad (3.4.17)$$

By expanding around the equilibrium height, we find that the force at small compressions δh is not linear in δh, but goes as δh^2. This is a consequence of the "softer" concentration profile of the self-consistent brush, which vanishes linearly at the brush extremity.

Corrections to strong stretching; "fuzz"

In a sketch of a polymer trajectory within the brush, we typically draw a random-looking blob of monomers near the free end location, which then stretches out progressively as it heads for the grafting surface. This is accurate, in that there are random fluctuations on top of the classical trajectories. Because the classical particle starts from rest, for a certain length of time (segment of chain) the random displacement $\langle \Delta z^2 \rangle$, which grows as sb^2, exceeds the average displacement of the trajectory.

(To present yet another strained analogy, the motion of the chain near its free end is reminiscent of Wile E. Coyote, in frantic (random) motion as he runs off a cliff. At first, his random motion exceeds the deterministic falling motion to the canyon floor; very soon, however, no amount of stochastic flailing can return him to the edge of the cliff.)

We can construct a scaling relation for the arclength distance and corresponding mean-square displacement at which the stochastic and deterministic displacements become equal. This determines the length scale ξ of "fuzz" in many quantities in the brush, including for example the

sharpness of the break in slope of the concentration profile at the brush edge. The stochastic displacement is

$$\langle \delta z^2 \rangle = sb^2 \tag{3.4.18}$$

whereas the deterministic displacement is

$$\delta z = z_0 - z_0 \cos(\pi s/2N) \approx z_0(\pi s/2N)^2 \tag{3.4.19}$$

Taking z_0 to be of order h, and using the scaling relations above for the brush height, after a bit of algebra we arrive at a crossover arclength s^* scaling as

$$s^*/N \sim (h/R_e)^{-2/3} \tag{3.4.20}$$

As the brush becomes more strongly stretched and h/R_e increases, the fraction of monomers s/N for which random displacements are important decreases. Correspondingly, the spatial extent of these random displacements becomes smaller, as

$$\delta z^*/h \sim (s^*/N)^2 \sim (h/R_e)^{-4/3} \tag{3.4.21}$$

The more strongly stretched are the chains in the brush, the smaller the size of the fuzz relative to the brush height.

This strong-stretching, classical-mechanics approach to grafted polymers has been employed to treat polydisperse brushes, bending rigidity of brushes on flexible surfaces (a model for surfactant bilayers), growth and exchange kinetics, and properties of block copolymer mesophases.