Phase Separation in a Grafted Polymer Layer

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We examine equilibrium phase separation in a grafted polymer layer composed of mutually immiscible chains. Under symmetric melt conditions, we predict that there is a transition to a "rippled" phase—a density wave in composition running along the surface. This transition is expected for a molecular weight 2.27 times that for the same species in a simple blend at its demixing threshold. The ripple wavelength is 1.97 times the chain rms end-to-end distance. The lateral rippling is accompanied by a composition oscillation with depth.

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Polymers that have one end permanently attached, or "grafted," to a surface have unique properties.[1-4] If the molecular weight is high enough, then even for a small number of grafts per unit area σ the chains will be strongly perturbed from their ideal random-walk conformations by their excluded-volume interactions. In this paper we consider the equilibrium statistical mechanics of a grafted layer composed of incompatible molecules. Phase separation is inevitable for long chains;[5] the central issue here is to determine the nature of phase separation in the grafted layer. This phase separation is strongly influenced by the mutual deformation of the polymers; accordingly, we find a type of spatial modulation not previously encountered in phase transitions.

We specialize to the case of a polymer melt where demixing interactions are most relevant. The chains are each presumed to displace a fixed volume V; this volume is proportional to the degree of polymerization N. The rms end-to-end distance of such a chain in a melt is $R_E = (3V/a)^{1/2}$, where the "packing length"[6] a is typically of order 10 Å (the radius of gyration is $R_G = R_E/\sqrt{6}$). The layer height is determined by the total chain volume per area of surface as $h = V\sigma$. If $V\sigma \gg (V/a)^{1/2}$, then the chains are extended over a distance far greater than the free radius of gyration. If this condition holds, but still the layer height is much less than the maximum extension of the chains, then at distances less than R_E we can consider the conformations to be random walks, while at longer distances, we can consider the conformation to be essentially one dimensional.

Consider a two-component layer constructed so that the grafted ends are mixed at the grafting surface (for simplicity, we consider the most symmetric case where the two species, denoted A and B, are identical in molecular weight and other respects; the net monomer volume fractions are thus $f_A = f_B = \frac{1}{2}$). This might be done using an ACB triblock where C is short and can be covalently bonded to the surface at temperatures well above the AB demixing transition. We presume that this leads to a situation where the interactions favoring AB demixing are much smaller than the symmetric part of the AB monomer interaction. If the grafted ends could independently wander on the surface, there would be conventional bulk phase separation[5] at $\Lambda V \approx 2$ ($2\Lambda v\phi$ is the free-energy reduction realized by moving a small volume v of A chain from a region with a volume fraction of $\phi_A = \frac{1}{2}$ to a region with $\phi_A = \frac{1}{2} + \phi$). However, if the ends are truly confined, this cannot occur: Any phase separation must occur at shorter length scales. The two short length scales are the layer height, which characterizes the total distance that chains extend vertically, and the free radius R_E, which characterizes the transverse size of conformational fluctuations.

If we consider phase separation on scales of the layer height, we are led to think about a "layered" state,[7] rich in one component at the bottom of the layer, and rich in the other at the top; this is achieved by separating the free ends of the two species vertically. However, phase separation at the much smaller scale of R_E suggests a quite different "rippled" state where the monomer density is modulated along a direction in the plane of the layer. The insets of Figs. 1 and 2 show typical conforma-

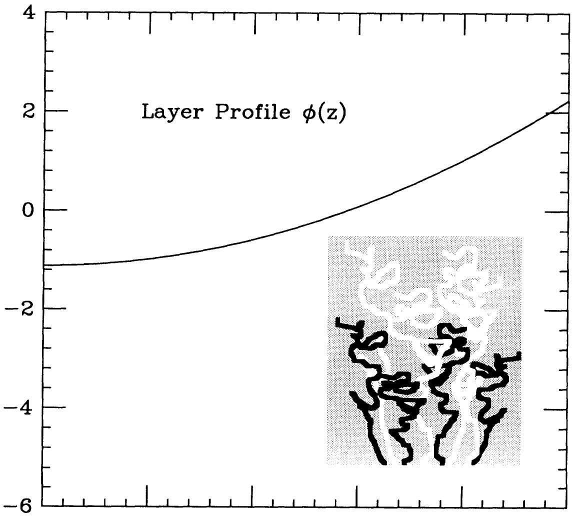

FIG. 1. Inset: The structure of the layered phase. Black chains are near the grafting surface, while the white chains are stretched so that their free ends are nearer the top of the brush. The main figure shows the monomer density difference $\phi(z)$ vs height in units of the layer thickness.

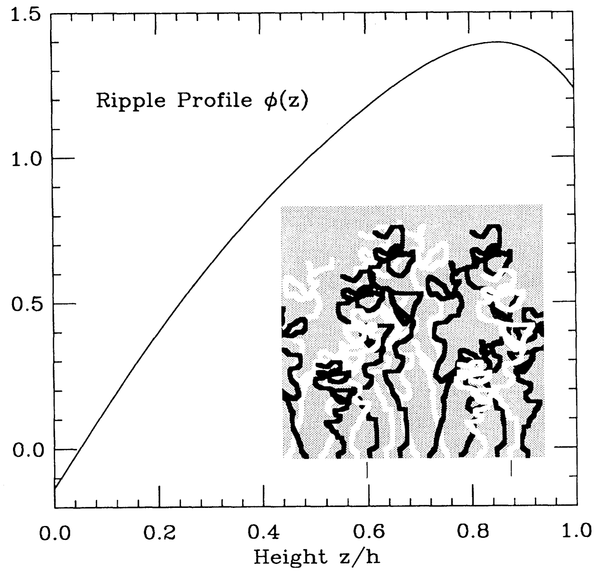

FIG. 2. Inset: The structure of the rippled phase. White and black chains are alternately compressed together and splayed apart along the x direction. A white-rich half wavelength is between the two black tick marks. Along the y direction, out of the page, there is no variation of the structure. Shown on the axes is the oscillating ripple profile $\phi(z)$ vs the height z in units of the layer thickness.

tions of chains in these two types of states. One might argue that the layered phase is preferred due to the smaller amount of A-B interface required. However, we must remember that the layered phase requires the species that is near the surface to be submerged in the tails of the other species. The remainder of this paper addresses the question of which of these states represents the phase-separated grafted layer.

Theory of the two-component brush.— Under the conditions described above, we may consider a free energy per chain that consists of a "stretch" energy (entropy is lost when a chain is extended) and an effective field $p(\mathbf{r})$ due to interactions with surrounding chains:[4,8]

$$S[\mathbf{r}(v)]=\int_0^V dv\left[\frac{a}{2}\left(\frac{d\mathbf{r}}{dv}\right)^2+p(\mathbf{r}(v))\right], \qquad (1)$$

where $\mathbf{r}(v)$ is the position of the vth monomer. The "potential" $p(\mathbf{r})$ is the free-energy cost of placing a unit volume of polymer at position $\mathbf{r}$; in a melt, this is the thermodynamic pressure. Chains that are grafted have one end ($v=0$) constrained to be on the grafting surface ($z=0$). By symmetry, the path which minimizes this free energy must have the form $\mathbf{r}(v)=z(v)\mathbf{z}$, where $\mathbf{z}$ is the unit vector perpendicular to the grafting surface.

This "classical" path satisfies the Euler-Lagrange equation $a\,d^2z/dv^2=dp/dz$, with boundary conditions $z(0)=0$ and $z(V)=z_1$. There is an additional boundary condition which reflects the fact that the end at z_1 is free, and thus cannot support a stretch: $dz/dv|_{v=V}=0$. These conditions determine the form of the pressure to be $p(z)=P[1-(z/h)^2]+\mathcal{O}(1/V)$, where $P=\pi^2a\sigma^2/8$. The trajectories are simply $z(v)=z_1\sin(\pi v/2V)$. The condition that the melt is incompressible determines the number of free ends per unit height to be $d\sigma/dz=(\sigma z/h)(h^2-z^2)^{-1/2}$.

We now consider the fact that our layer is composed of two species of incompatible molecules. Chemical differences give rise to a mixing free energy per chain which is a functional of the (possibly spatially varying) A and B monomer concentrations:

$$\frac{E}{\mathcal{N}kT}=\Lambda\int\frac{d^3r}{\Omega\sigma}\phi_A(\mathbf{r})\phi_B(\mathbf{r}), \qquad (2)$$

where $\phi_A(\mathbf{r})=1-\phi_B(\mathbf{r})\approx\frac{1}{2}$. The area of the surface is Ω; thus the number of chains in the layer is $\mathcal{N}=\Omega\sigma$. The coupling constant Λ has units of an inverse volume: It is related to the Flory χ via $\chi=\Lambda V/N$, where N is the polymerization index of the chains.[9,10]

We must balance this energy against the entropic cost of phase separation. In the case of layering, this entropy is that of the distribution of free ends within the layer. In the case of rippling, the entropy cost is due to more subtle changes in the conformations of chains traveling in different regions of the layer. A great simplification results if we restrict ourselves to the case where the demixing energy of a chain is much less than its elastic stretch energy; quantitatively this is the condition $\Lambda\ll P\approx a\sigma^2$, where P is the pressure at the grafting surface.[7] In this limit we can ignore the effect of any phase separation on the classical trajectories described above.

Transitions to layered and rippled phases.— If we consider phase separation, we must consider the effect of the mixing enthalpy on the statistics of the chain conformations. The statistical weight G for a segment between sites v' and v to run from $\mathbf{r}'$ to $\mathbf{r}$ under the influence of some external potential U is governed by the forced diffusion equation[11]

$$[\partial_v-(1/2a)\nabla^2+U(\mathbf{r})]G(\mathbf{r},\mathbf{r}';v,v')=\delta(\mathbf{r}-\mathbf{r}')\delta(v-v'). \qquad (3)$$

In our situation, the potential U is made up of the pressure $p(z)$, the (much smaller) demixing potential of order $\Lambda(\phi_A-\phi_B)$, and (still smaller) corrections to the chemical potentials of orders $\Lambda^2(\phi_A-\phi_B)^2$ and higher. The motion in the z direction will thus be dominated by the classical motion described above, but in the x-y plane diffusive motion must be considered.

For an A chain, to order $\Lambda(\phi_A-\phi_B)$ the driving potential is a combination of the pressure and the excess local concentration of B monomers (equivalently, the local deficit of A monomers):

$$U(\mathbf{r})=p(z)-\Lambda[\phi_A(\mathbf{r})-f_A]\equiv p(z)-\Lambda\phi(\mathbf{r}).$$

We presume a state uniform in the y direction, but which has x-z structure. If we use the classical trajectory to describe $z(v)$, we can replace v with z as a coordinate. The statistical weight g for the segment of an A chain with classical trajectory between z' and z ($z>z'$) to travel from x' to x in the x direction (where the free end of the *complete* chain is at a height z_1) is determined by

$$\left[\frac{dz}{dv}\partial_z - \frac{1}{2a}\partial_x^2 - \Lambda\phi(x,z)\right]g(x,x';z,z') = \frac{dz}{dv}\delta(x-x')\delta(z-z') . \tag{4}$$

The weights g and G are related by $G = ge^{-S^*}$, where $S^*(z,z';z_1)$ is the portion of the classical (minimal) action (1) corresponding to the portion of the trajectory from z to z', and is of order V.

The quantity $\int dx_1 dy_1 G(\mathbf{r}_0,\mathbf{r}_1;0,V)$ is proportional to the probability that a chain (with the free end grafted to the surface, i.e., $z_0=0$) has its free end at z_1; in the absence of demixing, this quantity is the free-end density $d\sigma/dz_1$. In the absence of demixing, (4) indicates that g does not generate any inhomogeneity in the end distribution; thus $\exp[-S^*(0,z_1;z_1)]$ must be proportional to $d\sigma/dz_1$.[12]

The equation of motion (4) is obtained by expanding the path-integral[11] representation of G around its stationary point (the classical motion). Because the monomer density is uniform in the y direction, and because the pressure does not vary on the scale of the z fluctuations, we are able to consider the y-z motion around the classical trajectory to be free diffusion. This z diffusion may be neglected since it occurs at a scale far smaller than that of the classical motion, and the x-y motion may be separated to yield the one-dimensional equation above.

Now we compute the local concentration of A monomers at a position (x,z); we begin by considering a chain which has its free end at (x_1,z_1). We compute the probability of the monomer $v(z)$ to be at (x,z) by multiplying the weight for a segment of chain to be between $(x_0,0)$ and (x,z) by the weight for the remainder of the chain to be between (x,z) and (x_1,z_1), normalizing the result so that the sum over final positions (x_1,z_1) is unity.[11] This distribution must be integrated over the possible x and z_1 coordinates of the free end. A factor of dv/dz appears in the sum to account for the number of monomers that the chain in question contributes per unit height. This expression now must be integrated over all grafted chains, i.e., over x_0, to obtain the contribution of all chains to the monomer concentration at (x,z); a factor of $f_A = \frac{1}{2}$ is included since only half the chains are of A type.

This gives rise to an expression of the A concentration:

$$\phi_A(x,z) = \frac{\sigma}{2}\int_{z_0=0} d^2r_0 \frac{\int d^3r_1 \int_0^V dv\, G(\mathbf{r}_1,\mathbf{r};V,v)G(\mathbf{r},\mathbf{r}_0;v,0)}{\int d^3r_1'\, G(\mathbf{r}_1',\mathbf{r}_0;V,0)}$$
$$= \frac{\sigma}{2}\int dx_0 \frac{\int_z^h dz_1 (d\sigma/dz_1)(dv/dz)\int dx_1\, g(x_1,x;z_1,z)g(x,x_0;z,0)}{\int_0^h dz_1'(d\sigma/dz_1')\int dx_1'\, g(x_1',x_0;z_1',0)} , \tag{5}$$

where it must be remembered that inside the z_1 and z_1' integrals chains are extended from $z=0$ to $z=z_1$ and $z=z_1'$, respectively. The weights g depend on ϕ; the ϕ which solves this equation is the thermodynamically stable state. For small Λ, the solution is $\phi=0$. Our approach is to expand the right-hand side of this equation in powers of the interaction Λ. Solution of the first-order equation (which will be linear in ϕ) will allow us to determine when a phase transition occurs, and will also indicate the structure of the ordered state.

We assume the perturbation expansion $g = \sum_{n=0}^{\infty} g_n$, where $g_n = \mathcal{O}(\Lambda^n)$. The solution to the forced diffusion equation to order Λ^0 [i.e., (4) with $\Lambda=0$] is simply the free-diffusion Green function:

$$g_0(x,x';z,z') = \left[\frac{a}{2\pi[v(z)-v(z')]}\right]^{1/2} \exp\left[\frac{-a(x-x')^2}{2[v(z)-v(z')]}\right]\Theta(z-z') , \tag{6}$$

where $\Theta(z)$ is the Heaviside unit step function, and $v(z) = (2V/\pi)\sin^{-1}(z/z_1)$. The equation that must be solved to obtain g_1 is

$$\left[\frac{dz}{dv}\partial_z - \frac{1}{2a}\partial_x^2\right]g_1(x,x';z,z') = \Lambda\phi(x,z)g_0(x,x';z,z') ; \tag{7}$$

this has the solution

$$g_1(x,x';z,z') = \Lambda\int_0^{z_1} dz''\int dx''\, g_0(x,x'';z,z'')\phi(x'',z'')\frac{dv}{dz''}g_0(x'',x';z'',z') . \tag{8}$$

This first-order correction is essentially the Born approximation familiar from potential scattering: Higher-order contributions have the form $g_n = \Lambda^n g_0\phi g_0\phi \cdots \phi g_0$.

If we examine $\phi(x,z) = \phi(z)\cos(kx)$, we find that to linear order the self-consistent equation does not mix modes of different momentum k. Thus we are led to a linear integral equation for the order parameter $\phi(z)$:

$$\phi(z) = \frac{\Lambda}{2}\int_z^h dz_1 \frac{dv}{dz}\frac{d\sigma}{dz_1}\left[\int_0^{z_1} dz'\frac{dv}{dz'}\phi(z')\exp\left(-\frac{k^2|v(z)_{z_1} - v(z')_{z_1}|}{2a}\right) - \int_0^h \frac{dz_1'}{\sigma}\frac{d\sigma}{dz_1'}\int_0^{z_1'} dz'\frac{dv}{dz'}\phi(z')\exp\left(-\frac{k^2[v(z)_{z_1} + v(z')_{z_1'}]}{2a}\right)\right] , \tag{9}$$

where $v(z)_{z_1}=(2V/\pi)\sin^{-1}(z/z_1)$ is the classical configuration of a chain with the free end at height z_1. This equation may be solved by expansion of $\phi(z)$ in Legendre polynomials, and thereby reducing (9) to a linear eigenvalue problem, which may be solved numerically.

If we set $k=0$, there is an instability to a layered state at $(\Lambda V)^*=8$ (to 1 part in 10^5), which is 4 times the demixing threshold for the same chains in the bulk. The transition is second order, and slightly beyond the transition $\phi_A-\phi_B\approx(\Lambda-\Lambda^*)^{1/2}\phi(z)$, where $\phi(z)$ is the universal profile shown in Fig. 1. A completely different layering calculation[7] (to be described elsewhere) involving only classical properties of the chains, which uses the difference between the local density of A and B free ends as the order parameter, leads to identical predictions for layering. In this formulation, the demixing of the ends leads to monomer demixing, which lowers the enthalpy. However, end demixing lowers the mixing entropy of the ends. The competition between these two effects drives the phase transition: We find it remarkable that a complete theory of layering can be constructed without any reference to the chain conformation fluctuations.

If we do not restrict ourselves to $k=0$, we find a transition to $\phi(z)\neq 0$ at $(\Lambda V)^*=4.549$; the monomer density difference $\phi(z)$ at the instability is shown in Fig. 2 (for all smaller Λ, the equation above only has the solution $\phi=0$). We note that, given chains that bulk phase separate at $(\Lambda V)^*_{\text{bulk}}=2$, chains of the same species assembled into a grafted layer must be at least 2.27 times as long in order to form ripples.

The rippling transition is second order; the monomer density difference behaves as $\phi_A-\phi_B\approx(\Lambda-\Lambda^*)^{1/2}\phi(z)\times\cos(kx)$ just after the transition. The wave number of the pattern is $k=1.841(a/V)^{1/2}=3.189R_E^{-1}$, corresponding to a wavelength of $2\pi/k=1.970R_E$; we see that the phase separation occurs at a scale far below h, and is due to the diffusive properties of the conformations at short length scales. Evidently this transition preempts the symmetric layering instability since it occurs at weaker coupling (lower molecular weight or smaller Λ). We note that fluctuation effects may modify the details of the transition since it occurs from a state with $k=0$ to one with $k\neq 0$, as in phase separation of a diblock melt.[13] However, our approach is exact for $N\rightarrow\infty$.

The linear self-consistent equation (9) can be alternately obtained from the two-point density correlation function of a single chain in a one-component melt layer, as we will discuss in a future paper. This is an independent check on our calculations, and allows a physical interpretation of the kernel of the integral equation as essentially the scattering function of a labeled chain in a melt brush.

We expect the phase transition discussed here to be controllable in a number of ways. First, altering the relative compositions, packing lengths, and molecular weights[14] should drive first-order transitions between different ordered states. Our method may be systematically extended to higher order in ϕ to predict these transitions. Second, varying the A-B proportions *within* each chain should alter the relative stability of the rippled and layered states. Finally, we expect further distinctive properties in the regime where the composition is strongly modulated, but where the mixing energy remains much smaller than the stretching energy.[7]

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