Chapter 1

Thermodynamics and the Phase Diagrams of Block Copolymers in Electric Fields

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Basic electrostatics and some less familiar thermodynamics is reviewed, and useful Claussius-Clapeyron-like equations are derived. They are applied to predict the form of phase diagrams of two systems. The first is a bulk system of body-centered-cubic phase which undergoes a phase transition either to a hexagonal or disordered phase on the application of an electric field. The second is a surface film of cylindrical phase which can be oriented perpendicular to the substrate by the application of a field.

1.1. Introduction

The genesis of this chapter is my collaboration with David Andelman who introduced me to interesting problems in which electric fields were applied to block copolymers, a system with which I was familiar. The first problem considered was that of a bulk, block copolymer system of body-centered-cubic (bcc) phase in a field. Because of the accumulation of polarization charge on the spheres, the free energy of the system increases in an electric field with respect to that of neighboring phases, like the hexagonal phase of cylinders. Eventually a phase transition occurs between them. It took quite a while, and an intensive calculation by Chin-Yet Lin, before the phase diagram became clear to me. After I understood it, I realized that by the use of some elementary thermodynamics I could have, and *should have*, understand the nature of the phase diagram before I began a difficult calculation.

When encountering a second problem concerning a polymer film, the usual form of such systems, I turned again to thermodynamics. I had been used to surface thermodynamics, but no text had prepared me for the

"surface excess displacement field", a concept that threw me at first until I realized that it was simply another excess surface density like those I had encountered previously and reviewed in a series of Les Houches lectures.[1] Again, the thermodynamics provided the general form of the phase diagram of the system in question, a cylindrical phase in this case.

A fortuitous element in these studies is that I have had the pleasure of teaching a junior-level course in Electrostatics and Electrodynamics at the University of Washington for the last couple of years. This has provided me the opportunity to understand the subtleties of polarizable systems which had eluded me when I had first encountered them.

It is in the hope that insights from electrostatics and thermodynamics will prove as useful, and beautiful, to someone else as they are to me that I agreed to write this chapter.

1.2. Review of basic electrostatics in polarizable materials

The two equations which determine the electric field $\mathbf{E}(\mathbf{r})$ when all charges are at rest, that is, the regime of electrostatics, are Gauss' law

$$\nabla \cdot \mathbf{E} = \frac{\rho_c(\mathbf{r})}{\epsilon_0}, \tag{1.1}$$

which is always valid, and

$$\nabla \times \mathbf{E}(\mathbf{r}) = 0, \tag{1.2}$$

which is only valid in the regime of electrostatics. Together, the two equations are simply a statement of Coulomb's law for they have the solution

$$\mathbf{E}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \int d\mathbf{r}' \rho_c(\mathbf{r}') \frac{(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3}, \tag{1.3}$$

which, again, is only valid in electrostatics. The great difficulty with either Eq. (1.1) or Eq. (1.3) is that the local charge density, ρ_c, in a polarizable medium depends upon the electric field itself so that the equations are self-consistent ones. The standard way to proceed is to observe that the largest contribution to the electric field, after any free charges which may be around, is from the induced dipoles of the medium. Let the local dipole moment per unit volume be $\mathbf{P}(\mathbf{r})$. As one knows the electric field produced by an electric dipole, one readily shows that the electric field produced by $\mathbf{P}(\mathbf{r})$ is the same *as if* there were a local bulk charge density

$$\rho_b(\mathbf{r}) \equiv -\nabla \cdot \mathbf{P}(\mathbf{r}) \tag{1.4}$$

and a local surface charge density

$$\sigma_b(\mathbf{r}) \equiv \mathbf{P}(\mathbf{r}) \cdot \hat{\mathbf{n}}, \tag{1.5}$$

where $\hat{\mathbf{n}}$ is a unit normal to the surface. These charges are said to be "bound", as opposed to "free", hence the subscript b. Note that if the dipole density, $\mathbf{P}$, were known then the bound charge density, ρ_b could be obtained from Eq. (1.4). The reverse is not true, however, for ρ_b only gives us the divergence of $\mathbf{P}$, and a vector field is only completely determined by its divergence *and* its curl. We do not know the latter.

One next separates the total charge density, which appears on the right hand side of Eq. (1.1), into a density ρ_f of free charge, which one controls, and bound charge, which one does not:

$$\rho_c = \rho_f + \rho_b = \rho_f - \nabla \cdot \mathbf{P} \tag{1.6}$$

Substituting this into Eq. (1.1) and rearranging we can write Gauss' law in the form

$$\nabla \cdot \mathbf{D}(\mathbf{r}) = \rho_f(\mathbf{r}), \tag{1.7}$$

where we have defined the displacement field

$$\mathbf{D} \equiv \epsilon_0 \mathbf{E} + \mathbf{P}. \tag{1.8}$$

The apparent advantage of this manoeuvre is that the divergence of the displacement is given only by the free charge. We have buried the bound charge by our definitions. But this is just so much hand waving and buys us nothing for at this point we have two equations; the new version of Gauss' law, Eq. (1.7) above and the defining equation of electrostatics, $\nabla \times \mathbf{E} = 0$. But neither of the two fields $\mathbf{E}$ and $\mathbf{D}$ are well defined because we know only the divergence of one and only the curl of the other. This impasse should not be a surprise. We said that the problem was difficult because the charge density, the source of the electric field, depends upon the electric field itself, and we have not hazarded a guess as to the nature of this relationship. Doing so relates the dipole density $\mathbf{P}$ to the electric field $\mathbf{E}$. The choice for most materials, including the ones of interest here, is to make the reasonable assumption that the relation is a linear one; that is

$$\mathbf{P} = \epsilon_0 \chi_e \mathbf{E}, \tag{1.9}$$

where the dimensionless number χ_e is the electric susceptibility. Upon substitution of this into the defining equation for the displacement, Eq.

(1.8), one obtains

$$\begin{aligned} \mathbf{D} &= \epsilon_0(1+\chi_e)\mathbf{E}, \\ &= \epsilon_0\kappa\mathbf{E}, \end{aligned} \tag{1.10}$$

where $\kappa \equiv (1+\chi_e)$ is the dielectric constant of the material. The fields are now well defined. We satisfy the defining equation of electrostatics $\nabla \times \mathbf{E} = 0$ by introducing the electric potential, V,

$$\mathbf{E}(\mathbf{r}) = -\nabla V(\mathbf{r}). \tag{1.11}$$

This leaves only Gauss's law to be satisfied. Substitution of $\mathbf{D} = \epsilon\kappa\mathbf{E} = -\epsilon\kappa\nabla V$ into Eq. (1.7) yields

$$\nabla^2 V + \frac{\nabla\kappa}{\kappa}\cdot(\nabla V) = -\frac{\rho_f}{\kappa\epsilon_0}, \tag{1.12}$$

where I have allowed for the fact that the dielectric constant can vary spatially.

Just how the dielectric constant varies spatially is not obvious. Suppose that there are two distinct monomers, A and B, joined in a diblock copolymer with polymerization index N of which a fraction, f_A, is A monomer. Let the volume of all monomers be v. Then the local volume fraction of A monomers, $\phi_A(\mathbf{r})$, has the average value $\bar{\phi}_A = f_A$, and the local volume fraction of B monomers, $\phi_B(\mathbf{r})$, has the average value $\bar{\phi}_B = 1 - f_A$. If we denote the deviations of the local volume fractions from their average values by $\delta\phi_A(\mathbf{r})$ and $\delta\phi_B(\mathbf{r}) = -\delta\phi_A(\mathbf{r})$ respectively, with $-f_A \leq \delta\phi_A \leq 1 - f_A$, then one can write quite generally the local dielectric constant as

$$\kappa(\mathbf{r}) = \kappa_A f_A + \kappa_B(1-f_A) + (\kappa_A - \kappa_B)g(\delta\phi_A), \tag{1.13}$$

where κ_A and κ_B are the dielectric constants of the pure A and B systems respectively. The function $g(\delta\phi_A)$ is such that the dielectric constant in Eq. (1.13) above is greater than unity, and $g(-f_A) = -f_A$, $g(1-f_A) = 1-f_A$, which guarantees that $\kappa = \kappa_A$ or κ_B when the system is pure. Other than these small restrictions, little can be said about the function $g(\delta\phi_A)$. One obvious choice is simply

$$g(\delta\phi_A) = \delta\phi_A, \tag{1.14}$$

so that Eq. (1.13) becomes

$$\kappa(\mathbf{r}) = \kappa_A\phi_A(\mathbf{r}) + \kappa_B\phi_B(\mathbf{r}). \tag{1.15}$$

It must be emphasized that this is simply a choice, and is not derived from anything basic. One might employ any of an infinite number of other possibilities, such as

$$g(\delta\phi_A) = -f_A + \sin^2 \frac{\pi(\delta\phi_A + f_A)}{2}, \tag{1.16}$$

in which the effect of adding a different monomer would only begin to affect the dielectric constant in second order in the local volume fraction.

1.3. Basic Thermodynamics

Let us recall the basics of thermodynamics. An excellent book on the subject is that of Callen.[2] There are two equations for the energy, U, of a system consisting of N_i molecules of type i in a volume Ω. The first is the Euler form

$$U = TS + \sum_i \mu_i N_i - p\Omega, \tag{1.17}$$

where S is the entropy, T the temperature, p the pressure, and μ_i the chemical potential of the i'th component. The content of this equation is that the energy is extensive; that is, if one doubles the volume, the number of molecules of each component, and the entropy of the system, then one has also doubled the system energy. The second is the statement of the first law,

$$dU = TdS + \sum_i \mu_i dN_i - pd\Omega. \tag{1.18}$$

By differentiating the Euler form directly and comparing the result with the first law, one obtains the Gibbs-Duhem relation

$$SdT + \sum_i N_i d\mu_i - \Omega dp = 0, \tag{1.19}$$

or, defining the entropy per unit volume, $s \equiv S/\Omega$, and the number densities $\rho_i \equiv N_i/\Omega$,

$$dp = sdT + \sum_i \rho_i d\mu_i. \tag{1.20}$$

It is convenient to introduce the energy per unit volume,

$$u \equiv U/\Omega = Ts + \sum_i \mu_i \rho_i - p, \tag{1.21}$$

whose differential is found immediately from the first law, Eq. (1.18),

$$\begin{aligned} dU &= TdS + \sum_i \mu_i dN_i - pd\Omega, \\ &= (Ts + \sum_i \mu_i \rho_i - p)d\Omega + \Omega(Tds + \sum_i \mu_i d\rho_i), \\ &= ud\Omega + \Omega du, \end{aligned} \tag{1.22}$$

to be

$$du = Tds + \sum_i \mu_i d\rho_i. \tag{1.23}$$

Because the temperature is more easily controlled than the entropy, one introduces the Helmholtz free energy via the Legendre transformation

$$\begin{aligned} F &\equiv U - TS, \\ dF &= dU - TdS - SdT, \\ &= -SdT + \sum_i \mu_i dN_i - pd\Omega \end{aligned} \tag{1.24}$$

or the Helmholtz free energy per unit volume

$$\begin{aligned} f &\equiv u - Ts, \\ df &= du - Tds - sdT, \\ &= -sdT + \sum_i \mu_i d\rho_i, \end{aligned} \tag{1.25}$$

where Eqs. (1.18) and (1.23) have been used.

When the system, which consists of a polarizable material, is in the presence of an electric field, the differential contribution to the energy per unit volume is shown in any standard text, such as Griffiths,[3] to be $\mathbf{E} \cdot d\mathbf{D}$ so that Eq. (1.23) becomes

$$du(\mathbf{r}) = Tds + \sum_i \mu_i d\rho_i + \mathbf{E}(\mathbf{r}) \cdot d\mathbf{D}. \tag{1.26}$$

For linear dielectrics, the electrostatic contribution to the energy per unit volume is

$$u_{elec}(\mathbf{r}) = \frac{\kappa \epsilon_0 E^2(\mathbf{r})}{2}. \tag{1.27}$$

One now observes that while the above is useful if one controls the free charge, changes of which are related to changes in the displacement, $d\mathbf{D}$, via Eq. (1.7), more often one controls the voltage. Changes in the voltage are directly related to changes in the electric field, $d\mathbf{E}$. Hence it

is convenient to make a Legendre transformation both with respect to the entropy, as before, but also with respect to the displacement, to produce a thermodynamic potential which is a function of temperature and electric field,

$$f(\mathbf{r}) \equiv u - Ts - \mathbf{E}(\mathbf{r}) \cdot \mathbf{D}(\mathbf{r}), \tag{1.28}$$

$$df(\mathbf{r}) = -sdT + \sum_i \mu_i d\rho_i - \mathbf{D}(\mathbf{r}) \cdot d\mathbf{E}. \tag{1.29}$$

Essentially one is now including the battery in the system, and the last term is the decrease in internal energy per unit volume of the battery due to the work it must do to keep the voltage on the plates constant. The net contribution to the free energy per unit volume of the whole system, which includes the increase in energy of the material and decrease in energy of the battery, is

$$\begin{aligned} f_{elec}(\mathbf{r}) &= -\frac{\kappa\epsilon_0 E^2(\mathbf{r})}{2}, \\ &= -\frac{\mathbf{D}(\mathbf{r}) \cdot \mathbf{E}(\mathbf{r})}{2}. \end{aligned} \tag{1.30}$$

It should be noted that in the case in which the electric and displacement fields vary over the sample, as they do in the cases of interest here, the free energy density of Eq. (1.28) must be averaged over the sample. Similarly, the change in free energy that one wants is the change in free energy, averaged over the sample, when the voltage on the capacitor plates is changed from V to $V + dV$, or equivalently, when the electric field between the plates is changed from E_0 to $E_0 + dE_0$ where

$$dE_0 \equiv \frac{dV}{\ell} = < dE > = \frac{1}{A} \int \frac{dE_z(\mathbf{r})}{dz} d\mathbf{r}. \tag{1.31}$$

where the brackets denote a spatial average and ℓ is the distance between the plates of area A which are perpendicular to the z axis. The amount by which the spatially averaged free energy density changes due to the change in field, dE_0 is $-D_0 dE_0$ with

$$D_0 \equiv \frac{< D\ dE >}{< dE >}, \tag{1.32}$$

so that

$$df = -sdT + \sum_i \mu_i d\rho_i - D_0 dE_0, \tag{1.33}$$

where df is the change in the spatially averaged free energy density. I have assumed that the system is isotropic so that the averaged displacement is in

the z direction as is E_0. For a system of a single species of block copolymer the number of which is fixed, as will be considered below, this becomes

$$df = -sdT - D_0 dE_0. \tag{1.34}$$

The electrostatic contribution to the spatially averaged free energy density from the linear dielectric can now be written

$$f_{elec} = -\frac{D_0 E_0}{2}. \tag{1.35}$$

Now let us consider the coexistence of two phases. They must be at the same temperature T and are between the same capacitor plates and so are subject to the same E_0. Hence the Helmholtz free energy per unit volume is the same in each phase. Let one phase be denoted a and the other b. Consider one point, (T, E_0) on the coexistence curve. The free energies of the two phases are equal, $f_a(T, E_0) = f_b(T, E_0)$. If we move along the coexistence curve to a point $(T + dT, E_0 + dE_0)$, the free energies of the two phases are again equal. Thus the changes in free energies

$$\begin{aligned} df_a &= -s_a dT - D_{0,a} dE_0, \\ df_b &= -s_b dT - D_{0,b} dE_0, \end{aligned}$$

are equal. If we subtract them, we obtain the Claussius-Clapeyron equation for the slope of the phase boundary

$$\frac{dE_0}{dT} = -\frac{\Delta s}{\Delta D_0}, \tag{1.36}$$

where $\Delta s \equiv s_a - s_b$, and $\Delta D_0 \equiv D_{0,a} - D_{0,b}$.

This equation will play an important role in our analysis. It is convenient to recast it slightly. In the polymer system, temperatures usually enter via the dimensionless Flory parameter

$$\chi N = c/T, \tag{1.37}$$

where c is a constant. Further we introduce dimensionless electric and displacement fields

$$\hat{E}_0 \equiv E_0 \left(\frac{\epsilon_0 v_p}{k_B T}\right)^{1/2}, \tag{1.38}$$

$$\hat{D}_0 \equiv D_0 \left(\frac{v_p}{\epsilon_0 k_B T}\right)^{1/2}, \tag{1.39}$$

where $v_p = Nv$ is the volume per polymer chain. In terms of these dimensionless quantities, the Claussius-Clapeyron equation becomes

$$\frac{d\hat{E}_0}{d(\chi N)} = \frac{v_p}{\chi N}\frac{\Delta(s/k_B)}{\Delta\hat{D}_0} + \frac{\hat{E}_0}{2\chi N}. \tag{1.40}$$

1.4. Electric Field Induced Bulk Phase Transition

I want to consider now an interesting situation in which the application of an external field brings about a phase transition. In particular, I will consider a block copolymer system in which the architecture is such that at low temperatures the system is in the body-centered-cubic state. Thus its free energy is lower, *inter alia*, than that of the disordered phase or the hexagonal, cylindrical phase. However, as an electric field is turned on, its free energy increases relative to that of these two phases and, at some value of the electric field, a first-order transition occurs. This is less obvious than one might expect, so let me go through the argument. The contribution to the free energy from the electric field is that of Eq. (1.35) $f_{el} = -D_0E_0/2$. As I said above, E_0 is fixed by the voltage, so we have to evaluate D_0 in the various phases. This quantity was defined above and is repeated here

$$D_0 = \frac{< D(\mathbf{r})\delta E(\mathbf{r}) >}{< \delta E(\mathbf{r}) >}, \tag{1.41}$$

$$= < D(\mathbf{r}) > + \left[\frac{< D(\mathbf{r})\delta E(\mathbf{r}) >}{< \delta E(\mathbf{r}) >} - < D(\mathbf{r}) >\right], \tag{1.42}$$

where $\delta E(\mathbf{r})$ is a small electric field whose spatial average is a small change in voltage divided by the distance between plates. In the disordered phase, this evaluation is simple because there are no correlations. Thus the square bracket above vanishes and

$$\begin{aligned} D_{0,dis} &= < D(\mathbf{r}) >= \epsilon_0 < \kappa(\mathbf{r})E(\mathbf{r}) >, \\ &= \epsilon_0 < \kappa(\mathbf{r}) >< E(\mathbf{r}) >, \\ &= \epsilon_0\kappa_0 E_0, \end{aligned} \tag{1.43}$$

where κ_0 is the spatial average of the dielectric constant. In an hexagonal phase oriented with the normals to the cylinder axes perpendicular to the field, the displacement D_0 takes the *same* value. This follows from the fact that the electric field must be uniform inside and outside the cylinders, and in fact, takes the same value E_0. If one thinks of a sharp boundary between inside and outside the cylinders, then the basic equation $\nabla \times \mathbf{E} = 0$ ensures that the components of the fields on either side of this boundary

are the same, in accord with the above. As the field is constant, there is no correlation between the displacement and the electric field or the dielectric constant and the field, so one finds that

$$D_{0,cyl} = D_{0,dis} = \epsilon_0 \kappa_0 E_0. \tag{1.44}$$

The above argument also applies to a lamellar phase in which the lamellae are aligned so that the normals to the planes are perpendicular to the field. For an arbitrary arrangement, or for the bcc arrangement in particular, the average value of the displacement D_0 differs from the above value as the correlations, the square bracket in Eq. (1.42), are non-zero.

That D_0 should, in general be smaller, than its value in the disordered, hexagonal, and lamellar phases can be understood as follows. In asking for an average of the displacement, we are asking for a average of the dielectric constant. In a conductor, all mobile charges move to the surface of the conductor. There is maximum separation of charge, and the dielectric constant is infinite. If the media were not polarizable at all, there would be no separation of charge so that the electric susceptibility would vanish and the dielectric constant would be unity. Polarizable materials are between these two extremes. In the lamellar and hexagonal phases, the separation of the polarization charge is as large as it can be, appearing on the surfaces of the dielectric facing the capacitor plates, and the dielectric constant is $\kappa_0 > 1$. In the bcc phase, much of the polarization charge is confined to the surfaces of the spheres so that the separation of charge is reduced. Hence one expects that the dielectric constant is less than that of the lamellar and hexagonal phases. The conclusion of this reasoning is easily verified in perturbation theory.[4]

A simple example of the reduction brought about when the polarization charge can not separate maximally is provided by the case of a lamellar phase where there equal amounts of monomers A and B.[5] As noted above, if the lamellae are oriented so that the normals to the planes are perpendicular to the field, then the electric field is the same in all layers. There are no correlations so that $D_0 =< D(\mathbf{r}) >$ and takes the maximum value

$$D_{0,parallel} = \epsilon_0 \frac{\kappa_A + \kappa_B}{2} E_0, \tag{1.45}$$

where I have assumed a strong segregation limit for simplicity. If the lamellae are oriented with their normals parallel to the field, then, it follows from Gauss' law in the absence of free charge that the displacement is the same in each layer, so again there are no spatial correlations and $D_0 =< D(\mathbf{r}) >$.

The electric fields do differ, of course, $E_A = D/\kappa_A$, $E_B = D/\kappa_B$. Then the average electric field,

$$< E >= E_0 = \frac{D}{2\epsilon_0}\left(\frac{1}{\kappa_A} + \frac{1}{\kappa_B}\right), \tag{1.46}$$

so that

$$D_{0,series} = \frac{2\kappa_A\kappa_B}{\kappa_A + \kappa_B}\epsilon_0 E_0, \tag{1.47}$$

which is easily seen to be less than the maximum value $D_{0,parallel}$ of Eq. (1.45). The conclusion of this argument is that the average displacement in the bcc phase is less than that in either the disordered or hexagonal phases. Hence the dielectric contribution to the free energy, $f_{el} = -D_0 E_0/2$, will not be such a large negative number, and the difference of free energies between these phases will decrease. For a sufficiently strong field, a transition will occur, as noted earlier.

We can now determine the general nature of the phase diagram of this system in the electric field, temperature plane as follows. We have chosen an architecture such that for $E = 0$ and $T = 0$, the bcc phase is the stable one. As the temperature is increased at zero field, the system undergoes a first-order transition to the disordered phase at some temperature, or equivalently, some value of the Flory temperature, $\chi N(E = 0)$. At zero electric field, the difference in displacements between the bcc and disordered phases is zero, of course, but the difference in their entropies is non-zero. The Claussius-Clapeyron Eq. (1.40) tells us that the slope of the boundary between these two phases in the E, T plane, $d\hat{E}_0/d(\chi N)$, becomes infinite as the $E = 0$ axis is approached. For non-zero electric fields, there is a non-zero difference in displacement fields between the two phases. Further we have argued above that the value of displacement field is larger in the disordered phase than in the bcc phase. The entropy density is also larger in the disordered phase than in the bcc phase. Hence Δs and $\Delta\hat{D}_0$ are of the same sign. Therefore the Claussius-Clapeyron Eq. (1.40) says that the slope of the boundary, $d\hat{E}_0/d(\chi N)$, will be positive.

The behavior of the boundary between bcc and hexagonal phases is also easily understood. At zero temperature and zero field, the bcc phase was chosen to be the phase of lowest energy. As the electric field increases, the system eventually make a first-order transition to the hexagonal phase. The slope of the boundary between these phases is zero, from Eq. (1.40), as $1/\chi N = 0$. To determine the slope of this boundary at non-zero temperatures, we need to know the sign of the difference of entropy densities. We

recall from mean field theory that, on lowering the temperature, the system passes from the disordered phase to the bcc phase to the hexagonal phase. Hence the entropy of the bcc phase is greater than that of the hexagonal phase. But the displacement is less in the bcc phase than in the hexagonal phase. Thus the signs of Δs and $\Delta \hat{D}_0$ are opposite, and Eq. (1.40) predicts a negative slope.

The range of temperature over which the bcc is stable decreases as the electric field increases, and finally vanishes at a triple point, at which the disordered, bcc, and hexagonal phases coexist. For larger fields, the disordered and hexagonal phases can coexist. As the entropy densities of these two phases differ but their electric displacements do not, the Claussius-Clapeyron Eq. (1.40) tells us that the slope of the boundary between them is infinite.

We now know what the phase diagram should look like in the electric field, temperature plane. The rest is simply calculation. An example of the result of such a calculation[6] for the architecture $f_A = 0.1$ is shown in Fig. 1.1. Because application of the electric field lowers the $Im\overline{3}m$ symmetry of the bcc phase to $R\overline{3}m$, the region of this phase is so labeled in the figure.

1.5. Basic Surface Thermodynamics

We now consider a system of volume Ω which is bounded by a surface of area A. For the moment, the electric field is zero. It is convenient to separate the total energy, U_{tot}, entropy, S_{tot}, etc. into bulk and surface pieces. One does this by defining the bulk densities

$$u_b \equiv \lim_{\Omega\to\infty} \frac{U_{tot}}{\Omega}, \tag{1.48}$$

$$s_b \equiv \lim_{\Omega\to\infty} \frac{S_{tot}}{\Omega}, \tag{1.49}$$

and surface excess densities

$$u_s \equiv \lim_{\Omega,A\to\infty} \frac{U_{tot} - \Omega u_b}{A}, \tag{1.50}$$

$$s_s \equiv \lim_{\Omega,A\to\infty} \frac{S_{tot} - \Omega s_b}{A}. \tag{1.51}$$

Then the total energy, entropy, and so on have the form

$$U_{tot} = \Omega u_b + A u_s + ...+, \tag{1.52}$$

$$= U_b + U_s + ..., \tag{1.53}$$

where the terms not written out correspond to edge terms, point terms, etc. which will be ignored.

The first law for the total system, which in the absence of the surface had been given by Eq. (1.18), now reads

$$dU_{tot} = TdS_{tot} + \sum_i \mu_i dN_{i,tot} - pd\Omega + \sigma dA, \tag{1.54}$$

where σ is the surface tension. If we write

$$dU_{tot} = dU_b + dU_s, \tag{1.55}$$

use

$$dU_b = TdS_b + \sum_i \mu_i dN_{i,b} - pd\Omega, \tag{1.56}$$

and decompose S_{tot} and $N_{i,tot}$ as in Eq. (1.53), we obtain

$$dU_s = TdS_s + \sum_i \mu_i dN_{i,s} + \sigma dA. \tag{1.57}$$

As the excess surface free energy is extensive,

$$U_s = TS_s + \sum_i \mu_i N_{i,s} + \sigma A. \tag{1.58}$$

Just as in the bulk case it was convenient to define an energy per unit volume, here we define an excess energy per unit area

$$u_s \equiv \frac{U_s}{A}, \tag{1.59}$$

$$= T\frac{S_s}{A} + \sum_i \mu_i \frac{N_{i,s}}{A} + \sigma, \tag{1.60}$$

$$\equiv Ts_s + \sum_i \mu_i n_{i,s} + \sigma, \tag{1.61}$$

whose differential is easily found, from Eq. (1.57), to be

$$du_s = Tds_s + \sum_i \mu_i dn_{i,s}. \tag{1.62}$$

In the presence of an electric field, the system develops a displacement field $\mathbf{D}_{tot}$ and we define a bulk average displacement field, $< \mathbf{D}_b >$ and surface displacement field $\mathbf{D}_s$ according to

$$< \mathbf{D}_b > \equiv \lim_{\Omega\to\infty} \frac{\int \mathbf{D}_{tot}(\mathbf{r})d\mathbf{r}}{\Omega}, \tag{1.63}$$

$$\mathbf{D}_s(\mathbf{t}) \equiv \int (\mathbf{D}_{tot}(\mathbf{t}, z) - < \mathbf{D}_b >)dz, \tag{1.64}$$

where $\mathbf{t}$ is the position vector in the plane of the film.

The differential of the surface excess energy now contains a contribution from the electrostatic interactions

$$du_s = Tds_s + \sum_i \mu_i dn_{i,s} + \mathbf{E}(\mathbf{t}) \cdot d\mathbf{D}_s. \tag{1.65}$$

We again introduce a Legendre transform

$$g_s(\mathbf{t}) \equiv u_s - s_s T - \sum_i \mu_i n_{i,s} - \mathbf{E}(\mathbf{t}) \cdot \mathbf{D}_s(\mathbf{t}), \tag{1.66}$$

$$= \sigma - \mathbf{E}(\mathbf{t}) \cdot \mathbf{D}_s(\mathbf{t}), \tag{1.67}$$

$$dg_s(\mathbf{t}) = -s_s dT - \sum_i n_{i,s} d\mu_i - \mathbf{D}_s(\mathbf{t}) \cdot d\mathbf{E}. \tag{1.68}$$

As in the bulk case, we must average this free energy over the film to produce $g_s =< g_s(\mathbf{t}) >$ with a differential

$$dg_s = -s_s dT - \sum_i n_{i,s} d\mu_i - D_{s,0} dE_0, \tag{1.69}$$

where $D_{s,0}$ is an average over the film completely analogous to its definition in bulk, Eq. (1.41),

$$D_{s,0} \equiv \frac{< D(\mathbf{s})\delta E(\mathbf{s}) >}{< \delta E(\mathbf{s}) >}, \tag{1.70}$$

where now the average is over the position vector $\mathbf{s}$. The field $D_{s,0}$ is the surface excess displacement.

For a one component system, the above differential reduces to

$$dg_s = -s_s dT - n_s d\mu - D_{s,0} dE_{ext}. \tag{1.71}$$

From this, one again derives a Claussius-Clapeyron equation by noting that as one moves along a boundary of coexistence between phases a and b, the change in free energy, g, must be the same in either phase. Hence if one plots the phase diagram at fixed temperature in the electric field, chemical potential plane, the slope of the boundary is given by

$$\frac{dE_{ext}}{d\mu} = -\frac{\Delta n_s}{\Delta D_{s,0}}. \tag{1.72}$$

1.6. Electric Field Induced Surface Phase Transition

The system of interest is one of technical application. One makes a cylindrical phase of block copolymer. Because the substrate invariably prefers

one block over the other, the cylinders will lie flat, parallel to the substrate. For technological applications, one would like the cylinders to be aligned perpendicular to the substrate. One way to do this is to apply a field perpendicular to the substrate. As we saw earlier, the electrostatic contribution to the free energy will be larger, negative, if the cylinder axes are parallel to the field. Eventually this electrostatic energy will outweigh any surface contribution to the system and a surface transition will take place. In fact this simple argument makes a prediction: because the gain in electrostatic free energy if the cylinders align is on the order of $E^2 d_0 A$, with d_0 and A the film thickness and area respectively, and because the surface energy gained when the cylinders lie flat is a constant independent of the field or thickness, a transition should occur when $E^2 d_0 A$ attains some critical, constant value. Thus the value of the electric field at the transition is expected to vary as

$$E_c \sim \frac{1}{d_0^{1/2}}. \tag{1.73}$$

We consider the phase diagram at constant temperature in the field, chemical potential plane. As the thickness of the film is expected to be a monotonic function of the chemical potential, we can consider the phase diagram equivalently in the field, thickness plane. At zero electric field, as one increases the film thickness, one encounters surface phases corresponding to m layers of cylinders lying parallel to the substrate within the film, with m increasing by an integer as one passes from one phase to the next. In between these surface phases there is one in which the cylinders are perpendicular to the substrate.[7] It is clear that as one turns on the electric field, the phase space of the perpendicular phase increases, and that of the parallel phases decreases. Furthermore, the displacement field $D_{s,0}$ is expected, by identical arguments to those given above for the bulk case, to be less than that in the perpendicular phase. Hence as one increases the thickness, $D_{s,0}$ will decrease on going from the perpendicular phase into one of the parallel phases, and will increase as the parallel phase is left and the perpendicular phase re-entered. As the excess surface density, n_s increases monotonically as the chemical potential or the thickness is increased, the Claussius-Clapeyron Eq. (1.72) tells us that the slope of the boundary between a parallel phase and the surrounding perpendicular phase will be positive as one enters the parallel phase and negative as one exits it. Thus one expects a phase diagram to appear as a series of wickets, with the region inside each wicket labeled by the number of parallel layers

in it. Furthermore, these wickets must approach the $E = 0$ axis perpendicularly. This follows from the fact that, at $E = 0$, there is no difference in the displacement of the two phases, while there is a non-zero difference in surface densities. Thus the Claussius-Clapeyron equation predicts that the slopes of the phase boundaries are infinite. Finally, Eq. (1.73) predicts that the height of these wickets will decrease with thickness. Again, all that remains is a calculation, but the form of the results is anticipated. Such a result is shown in Fig. 1.2. The inset shows that the peaks of the wickets do indeed decrease as $1/d_0^{1/2}$.

Thus far we have considered phases in which cylinders are aligned either parallel or perpendicular to the substrate. There is one more phase to consider. If the interaction with the substrate is strong, then one would expect that any cylinders that were perpendicular to the substrate in most of the film would be cut off before they reached the substrate itself so that the latter could be covered with the monomer that it preferred. Such a phase is called an intermediate phase and was discussed in the context of films of lamellar-forming diblocks by Pereira and Williams[5] and Tsori and Andelman.[8] A phase diagram for such a system is shown in Fig. 1.3. One anticipates that the slope of the boundary between intermediate and perpendicular phases is negative because the effect of surface fields becomes less important as the film becomes thicker. One also knows that the displacement is smaller in the intermediate phase than in the perpendicular phase because the cylinders are cut off and there is less separation of charge. The negative slope of the phase boundary and the Claussius-Clapeyron Eq. (1.72) tells me that as the perpendicular phase has the larger displacement, it must also have the larger thickness. That is, the very narrow coexistence region in Fig. 1.3 between perpendicular and intermediate phases, one whose finite thickness is too small to be seen in the figure, has tie lines which have a positive slope. This is something which would not have occurred to me, and is an example in which information that one can intuit can be combined with thermodynamic relations to obtain answers to questions one would not even have thought to ask. That is very good indeed!

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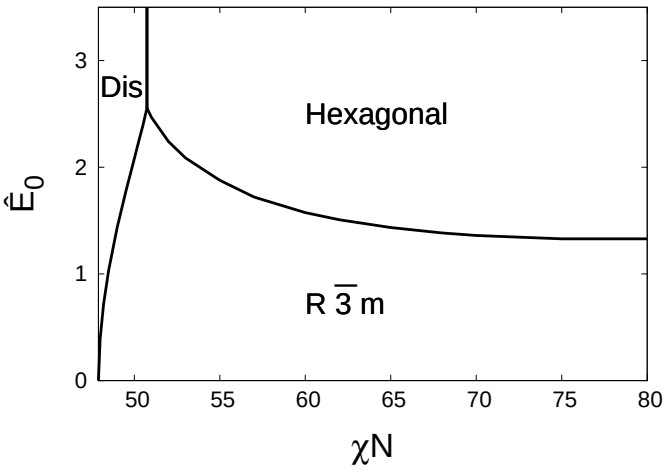

Fig. 1.1. Calculated phase diagram of a diblock copolymer in the presence of an external electric field. It is shown as a function of the dimensionless electric field $\hat{E}_0$ and the dimensionless Flory parameter χN assumed to be inversely proportional to temperature. The fraction of A block in the copolymer is 0.1. For details, see Lin, Schick, and Andelman.[6]

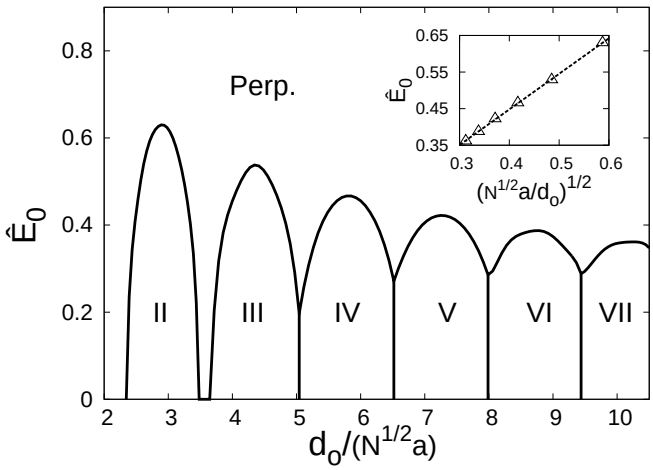

Fig. 1.2. Calculated surface phase diagram of a diblock copolymer adsorbed on a surface in the presence of an external electric field. It is shown at constant temperature as a function of the dimensionless electric field $\hat{E}_0$ and the dimensionless thickness $d_0/N^{1/2}a$ with a the identical Kuhn lengths of the A and B components. Parallel phases are denoted by a roman numeral corresponding to the number of cylinders in the film. The perpendicular phase is marked "Perp". For details, see Lin and Schick.[9]

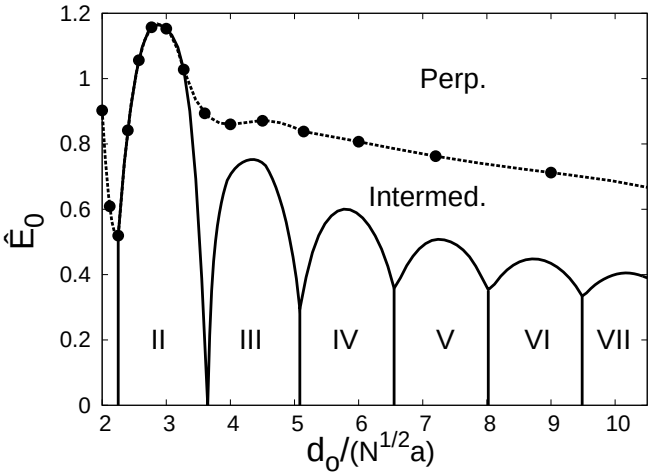

Fig. 1.3. Phase diagram as a function of dimensionless electric field $\hat{E}_0$ and thickness $d_0/N^{1/2}a$ for the same system as that in Fig. 1.2 but with a stronger surface field. The new intermediate phase is labeled "Intermed." For details, see Lin and Schick.[9]

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