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Polymer Solutions under Electric Fields: Ellipsoidal Correlation Holes

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ABSTRACT: An electric field, $\mathcal{E}$, shifts the phase equilibria in polymeric solutions and distorts anisotropically concentration fluctuations in the vicinity of the coexistence curve. I present a statistical theory of birefringent binary polymeric solutions. An explicit form for the structure factor in terms of the molecular anisotropic polarizabilities of the statistical segments, ν_A and ν_B, is given. For polymers A (containing N_A segments) in a monomeric solvent B, it is predicted that in the critical point the anisotropic corrections to the light scattering intensity scales as $N_A^{1/2}\nu_A\mathcal{E}^2$. When $\nu_A > 0$ and $\nu_B < 0$, for polymer A (N_A) plus polymer B (N_B) solution the resulting anisotropy turns out to be dependent solely on the sign of the combination $N_A^{-1/2}\nu_A + N_B^{-1/2}\nu_B$. The theory provides a microscopic argumentation on why an electric field suppresses the separation and why the phase equilibria shift is proportional to $\mathcal{E}^2$. We also predict diamond- and pillowlike forms of the isointensity contours.

1. Introduction

Electrostatic Corrections to the Free Energy of Binary Mixtures. Binary liquid mixtures demix into two coexisting phases when taken into the thermodynamically unstable regime. The spinodal decomposition is accompanied by the critical opalescence—the growth of fluctuations and the increasing of their length scales. In 1964, Debye and Kleboth[1] studied the effects of an electric field on the critical opalescence of low-molecular-weight (nitrobenzene/2,2,4-trimethylpentane) solutions. Besides the induced anisotropy due to orientations of segments (which was well-known for a long time as the Kerr effect or birefringence), they have discovered that an applied field favors the demixing. A negative shift of the transition temperature was found to be proportional to the square of the field intensity. A quantitative explanation of this shift is given by Landau and Lifshitz (1958). The main idea can be represented and resumed as follows.

Let us consider a mixture of monomers A and B, whose molecular dielectric susceptibilities are $\alpha^{(A)}$ and $\alpha^{(B)}$, respectively. An applied field $\vec{E}$ polarizes monomers and interacts with induced polar moments $\vec{P}$. The corresponding electrostatic correction to the free energy

$$H = -\sum_{\text{all}}^{\text{dipoles}} \vec{E}\vec{P}, \qquad P^{(A)} = \alpha^{(A)}E, \qquad P^{(B)} = \alpha^{(B)}E$$

does not depend on positions of monomers. Not being dependent on positions of monomers, this term does not influence the concentration fluctuations. However, besides the term $\vec{P}\vec{E}$, the electrostatic energy includes a contribution due to dipole−dipole interactions. The dipole−dipole interaction between the Ith monomer at point $\vec{r}_I$ and the Jth monomer at point $\vec{r}_J = \vec{r} + \vec{r}_I$,

$$\frac{(\vec{P}_I\vec{P}_J)r^2 - 3(\vec{P}_I\vec{r})(\vec{P}_J\vec{r})}{r^3} \propto P_I P_J$$

summed over all pairs of monomers, also contributes to the total free energy. Once the dipole−dipole interaction is taken into account, the free energy of a binary melt becomes sensitive to relative positions of monomers, i.e., to the concentration patterns. A simple consideration illustrates that the energy of the dipole−dipole interaction of two AB pairs is always smaller than that of AA and BB pairs:

$$(P^{(A)})^2 + (P^{(B)})^2 - 2P^{(A)}P^{(B)} = E^2(\alpha^{(A)} - \alpha^{(B)})^2 > 0$$

Since thermal equilibrium corresponds to the minimum of the free energy, one concludes that (i) an applied electric field suppresses separation of monomers of different chemical nature and the effect is proportional (ii) to the square of the electric field intensity and (iii) to the squared difference of the dielectric susceptibilities of A and B monomers.

Polymer Solutions under an Electric Field. Recently Wirtz, Berend, and Fuller studied experimentally[5] the influence of an electric field on the critical opalescence in polymeric solutions: polymer plus low-molecular-weight solvent. Two phenomena were detected—the anisotropy of the scattering patterns (the circular scattering patterns become ellipsoidal) and a negative shift of the spinodal and coexistence lines (the electric-field-induced remixing in the two-phase region). Though both effects can be explained phenomenologically in terms of electrostatic corrections, i.e., as a consequence of the composition-dependent dielectric constant,[1,2,4] the goal of the present paper is to challenge this point of view. We will show that in polymers a new physics appears due to the linkage of monomers into macromolecular chains. To make this statement sharper, we formulate it as follows. Even if the dielectric constant of a polymer solution would be composition independent (i.e., even when the dipole−dipole interaction is neglected), the contours of the light scattering intensity will still reveal "diamonds", "ellipsoids", or even more complicated forms (Figures 1 and 2). This is the configurational entropy of birefringent chains which is responsible for such a strange behavior of the concentration fluctuations under an electric field.

Statistics of Chains under an Electric Field. In our previous work[12] we described the microphase separation of diblock copolymers under an electric field. In this paper we apply these results to study the phase equilibrium and concentration fluctuations in polymer

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solutions. Let us quote some basic points of the analysis,[12] which are necessary for further discussion.

An electric field $\vec{E}$ not only polarizes segments but also orients them.[13,14] The induced polar moment of a segment $\vec{P}$ depends on its orientation with respect to the field (ref 2, sections 7 and 13). Dipoles of the segment oriented along the perpendicular to $\vec{E}$, $\vec{P}_{\mathrm{l}}$, and $\vec{P}_{\mathrm{p}}$ are different:

$$\vec{P}_{\mathrm{l}} = (\alpha + \nu)\vec{E}, \qquad \vec{P}_{\mathrm{p}} = \alpha\vec{E}$$

Here α and ν are the so-called isotropic and anisotropic parts of the segment molecular polarizability. The cases $\nu > 0$ and $\nu < 0$ correspond to the stronger polarizability along and perpendicular to the bond $\vec{a}$, respectively. The probability for a segment to be tilted along $\vec{a}$ is given by the Gibbs distribution and proportional to

$$\mathrm{e}^{-H/kT} \propto \mathrm{e}^{(\vec{P}\vec{E})/kT} \propto \mathrm{e}^{\nu(\vec{a}\vec{E})^2/a^2kT}$$

For $\nu > 0$ ($\nu < 0$) the probability to be oriented along (perpendicular to) the electric field dominates. As a measure of the induced anisotropy, it is convenient to accept the (Mayer–Saupe) order parameter S—the average square of the cosine of the angle between the statistical segment $\vec{a}$ and the direction of field:

$$\frac{S}{3} = \frac{\langle(\vec{a}\vec{E})^2\rangle}{E^2} = \frac{\int_0^1 \zeta^2 \mathrm{e}^{\xi\zeta^2}\,\mathrm{d}\zeta}{\int_0^1 \mathrm{e}^{\xi\zeta^2}\,\mathrm{d}\zeta} \sim \frac{1}{3}\left(1 + \frac{4}{15}\xi\right), \quad \xi = \nu E^2/kT \tag{1}$$

Here the brackets $\langle\,\rangle$ denote the thermal average. For randomly oriented segments (for Gaussian chains), $S = 1$. The parameter ξ characterizes a tendency of an applied field to tilt segments disoriented by thermal fluctuations: Indeed, kT is a thermal energy per segment and νE^2 is the energy of dipole reorientation in the field. The parameter S has a simple physical meaning in terms of the lattice model: $S/3$ and $1 - S/3$ are the probability for a segment to be oriented along or perpendicular to $\vec{E}$, respectively.

An applied field deforms the gyration spheres of chains into ellipsoids. By definition (1), the gyration radii of A and B chains along and perpendicular to $\vec{E}$ are

$$R_{\mathrm{l}}^{(\mathrm{A})\,2} = R_{\mathrm{A}}^2 S^{(\mathrm{A})}, \qquad R_{\mathrm{p}}^{(\mathrm{A})\,2} = R_{\mathrm{A}}^2(3 - S^{(\mathrm{A})})$$

and

$$R_{\mathrm{l}}^{(\mathrm{B})\,2} = R_{\mathrm{B}}^2 S^{(\mathrm{B})}, \qquad R_{p}^{(\mathrm{B})\,2} = R_{\mathrm{B}}^2(3 - S^{(\mathrm{B})})$$

respectively. Here R_{A} and R_{B} are the gyration radii of A and B chains in the absence of the field. The end-to-end vector $\vec{r}$ distribution function for a birefringent chain is no longer a function of r^2 but depends separately[12] on components of $\vec{r}$ along and perpendicular to the field, r_{l} and r_{p}, as follows:

$$\mathrm{e}^{-(r_{\mathrm{l}}/2R_{\mathrm{l}}^{(\mathrm{A})})^2}\mathrm{e}^{-(r_{\mathrm{p}}/2R_{\mathrm{p}}^{(\mathrm{A})})^2}, \qquad \mathrm{e}^{-(r_{\mathrm{l}}/2R_{\mathrm{l}}^{(\mathrm{B})})^2}\mathrm{e}^{-(r_{\mathrm{p}}/2R_{\mathrm{p}}^{(\mathrm{B})})^2}$$

Since chains are no longer Gaussian, the physics of polymer solutions (in particular, the structure factor and the phase diagram) must be essentially modified.[12]

We will argue that the non-Gaussian statistics of chains reveals itself as "ellipsoidal correlation holes", which can be easily detected by the light scattering on the critical fluctuations. The essential result of the present theory, crucial for its verification, is an explicit form (sections 3 and 4) for the anisotropic corrections to the scattering function

$$S^{-1}(\vec{q},\vec{\mathcal{E}}) = S^{-1}(\vec{q}) + \delta S^{-1}(\vec{q},\vec{\mathcal{E}})$$

Here $S(\vec{q})$ is the scattering intensity in the absence of the electric field. For polymer plus polymer and polymer plus monomer solutions $\delta S^{-1}(\vec{q},\mathcal{E})$ read as

$$\frac{a^2}{135}(q_{\mathrm{l}}^2 - q_{\mathrm{p}}^2)\left(\frac{\nu_{\mathrm{A}}}{\Phi} + \frac{\nu_{\mathrm{B}}}{(1 - \Phi)}\right)\frac{\mathcal{E}^2}{kT} \tag{2}$$

and

$$\frac{a^2}{135}(q_{\mathrm{l}}^2 - q_{\mathrm{p}}^2)\frac{\nu_{\mathrm{A}}}{\Phi}\frac{\mathcal{E}^2}{kT} \tag{3}$$

respectively. Here $\mathcal{E}$ is the electric field intensity in the melt, and q_{l} and q_{p} are the components of the wavevector $\vec{q}$ along and perpendicular to $\vec{\mathcal{E}}$.

This paper is structured as follows. Section 2 discusses the segment–segment interaction and phase behavior of polymer solutions under an applied electric field. Sections 3 and 4 are devoted to a statistical mechanics based analysis of the structure factor. The results are resumed in section 5.

2. Thermodynamics of Polymeric Solutions under External Fields

We consider a blend of chains A and B, whose degrees of polymerization are N_{A} and N_{B}, respectively. Statistical segments occupy the same volume and have the same length a. The number of segments per unit volume is supposed to be a constant: At any point r the densities of A and B monomers, Φ_{A} and Φ_{B}, are related by the incompressibility condition: $1 - \Phi_{\mathrm{A}}(\vec{r}) = \Phi_{\mathrm{B}}(\vec{r})$. The average concentrations of the A and B monomers, Φ and $1 - \Phi$, are fixed.

The starting point for the understanding of the phase equilibrium of polymer solutions in the absence of applied fields is the seminal works by Flory and Huggins. The free energy (per segment) was set forth[6] as a sum of the segment–segment interaction energy E and the mixing entropy s:

$$\frac{F}{kT} = s(\Phi) + E(\Phi), \qquad E(\Phi) = \chi\Phi(1 - \Phi),$$
$$s(\Phi) = \frac{\Phi}{N_{\mathrm{A}}}\ln\Phi + \frac{1 - \Phi}{N_{\mathrm{B}}}\ln(1 - \Phi) \tag{4}$$

Here k and T have their usual meanings, the Boltzmann constant and the temperature, and χ is the Flory–Huggins[6] interaction parameter. The spinodal line and the coordinates of the critical point

$$\frac{\mathrm{d}^2F(\Phi)}{(\mathrm{d}\Phi)^2} \equiv 0 \rightarrow \frac{1}{(1 - \Phi)N_{\mathrm{B}}} + \frac{1}{\Phi N_{\mathrm{A}}} - 2\chi = 0$$

$$\frac{\mathrm{d}^3F(\Phi_{\mathrm{c}})}{(\mathrm{d}\Phi)^3} \equiv 0 \rightarrow \chi_{\mathrm{c}}^{-1} = \frac{2N_{\mathrm{A}}N_{\mathrm{B}}}{(N_{\mathrm{A}}^{1/2} + N_{\mathrm{B}}^{1/2})^2},$$
$$\Phi_{\mathrm{c}} = \frac{N_{\mathrm{B}}^{1/2}}{N_{\mathrm{A}}^{1/2} + N_{\mathrm{B}}^{1/2}} \tag{5}$$

are straightforwardly deduced from this free energy. The corresponding phase diagram is shown in Figure 1.

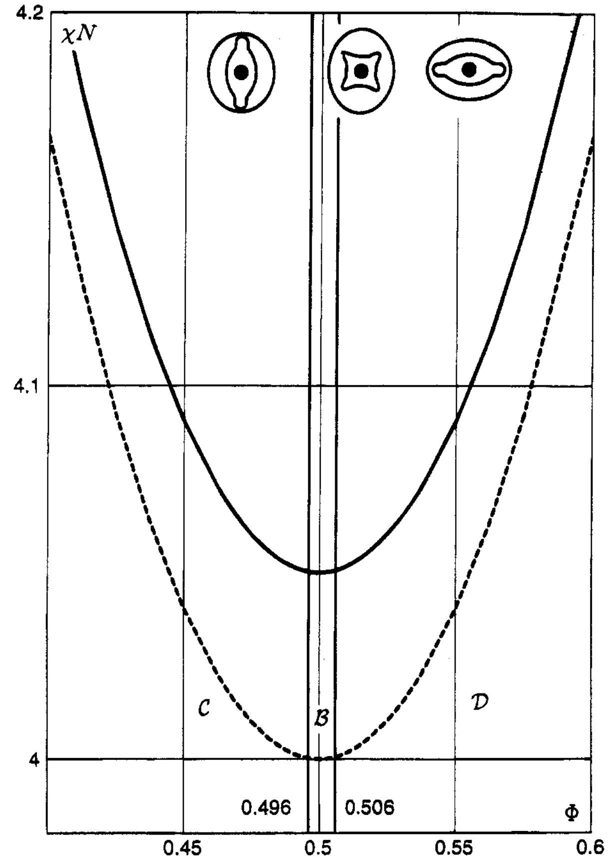

Figure 1. Spinodal lines for zero (dashed) and nonzero (solid) electric fields shown in coordinates Φ with $\chi(N_A + N_B)$ for $N_A = N_B$. The contours of isointense scattering are depicted in accordance with (9) for the example considered in section 5. Anisotropic polarizabilities for A and B segments are assumed to have different signs.

Energy of Broken-Link Systems under Electric Fields. Thermodynamics of Dielectric Fluids. In the absence of the electric field the only origin of intermolecular forces is via the dipole–dipole van der Waals interactions[1–3] between spontaneously mutually induced dipoles $\vec{\mathscr{R}}$. In fact,[9] this is the Flory–Huggins interaction χ. This interaction, which results in the effective repulsion of A and B units, is local: It acts and strongly fluctuates on molecular times and scales (as well as the molecular spontaneously fluctuating electric field $\vec{\mathscr{F}}$). Over a distance of several statistical lengths this interaction is completely screened (that is why the Flory–Huggins term in the free energy expansion is local). After the statistical averaging all correlators

$$\langle\vec{\mathscr{R}}(\vec{r}_I)\rangle,\ \langle\vec{\mathscr{R}}(\vec{r}_I)\ \vec{\mathscr{R}}(\vec{r}_J)\rangle,\ \langle\vec{\mathscr{F}}(\vec{r}_I)\ \vec{\mathscr{F}}(\vec{r}_J)\rangle,\ ...$$

equal zero if only $\vec{r}_I \neq \vec{r}_J$. For $\vec{r}_I = \vec{r}_J$, these dipole–dipole interactions $\langle\vec{\mathscr{R}}\vec{\mathscr{R}}\rangle$ are introduced phenomenologically through the Flory–Huggins parameter χ.

An external electric field brings two other contributions to the energy of local interactions—the interaction of induced dipoles with the applied field, $\vec{E}\vec{P}$, and the interaction between induced dipoles themselves, $\vec{P}\vec{P}$. The first term, $\vec{E}\vec{P}$, not being composition dependent, leads to a trivial shift of the zero free energy level and can be discarded. (Stress, nevertheless, that this term makes chains birefringent, changes the Gaussian statistics and influences on the configurational entropy.) As to the dipole–dipole interaction, $\vec{P}\vec{P}$, its influence is more complicated.[12] From the one side, it results in the fact that the internal electric field $\mathscr{E}$ in melts differs from the external applied electric field E. From the other side, the dipole–dipole interaction is very sensitive to the space arrangement of A and B segments.

An important physical point is that the two dipole–dipole interactions $\vec{P}\vec{P}$ and $\vec{\mathscr{R}}\vec{\mathscr{R}}$ do not interfere. Indeed, experimentally available electric fields are too weak ($\mathscr{E} < 10^7$ V m^{-1}) in comparison with fluctuating molecular electric fields ($|\vec{\mathscr{F}}| \sim 10^8 \div 10^{10}$ V m^{-1}) to change molecular polarizability α; i.e., the Flory–Huggins interaction parameter χ is insensitive to an applied field. On the other hand, a spontaneous dipole moment $\vec{\mathscr{R}}$, which fluctuates on molecular times, does not contribute to the induced "permanent" dipole moment $\vec{P}$ of a link. The thermodynamically averaged energy of the dipole–dipole interaction between the Ith and the Jth units at positions $\vec{r}_I$ and $\vec{r}_J = \vec{r} + \vec{r}_I$ is split into two independent parts:

$$\langle(\vec{P}_I + \vec{\mathscr{R}}_I)(\vec{P}_J + \vec{\mathscr{R}}_I)\rangle = \vec{P}_I\vec{P}_J + \langle\vec{\mathscr{R}}_I\vec{\mathscr{R}}_J\rangle$$

It is straightforward to see that while the van der Waals attractive $-\vec{\mathscr{R}}\vec{\mathscr{R}}$ interactions (caused by spontaneously fluctuating molecular electric fields $\vec{\mathscr{F}}$) lead to the effective repulsion χ of A and B segments

$$-(\mathscr{R}^{(A)})^2 - (\mathscr{R}^{(B)})^2 + 2\mathscr{R}^{(A)}\mathscr{R}^{(B)} \rightarrow -\langle\mathscr{F}^2\rangle(\alpha^{(A)} - \alpha^{(B)})^2 \rightarrow -\chi,$$

the repulsive interactions $\vec{P}\vec{P}$ between dipoles induced by an applied field result in effective attraction of A and B segments

$$(P^{(A)})^2 + (P^{(B)})^2 - 2P^{(A)}P^{(B)} \rightarrow \mathscr{E}^2(\alpha^{(A)} - \alpha^{(B)})^2 \rightarrow \chi\mathscr{E}^2/\langle\mathscr{F}^2\rangle$$

The total energy term E contains both contributions

$$\frac{E(\Phi,\mathscr{E})}{kT} = \tilde{\chi}\Phi(1 - \Phi),\ \ \tilde{\chi} = \chi(1 - \mathscr{E}^2/\langle\mathscr{F}^2\rangle)$$

The above argumentation (in the spirit of the textbook[10]) shows (i) why an applied field disfavors the separation, (ii) why the shift of the spinodal and coexistence curves is proportional to the square of the electric field intensity and (iii) why it is proportional to the square of the first derivative and dielectric susceptibility with respect to the composition, $(\alpha^{(A)} - \alpha^{(B)})^2$ (see ref 11). Since experimentally accessible fields are $10-10^2$ times weaker than the molecular fields of van der Waals attractions, this shift of the phase diagram is relatively small:

$$\frac{\delta\chi}{\chi} = \frac{\mathscr{E}^2}{\langle\mathscr{F}^2\rangle} \sim 10^{-3}$$

(Figure 1).

3. Critical Fluctuations in Polymer–Polymer Solutions under Electric Field

Though the free energy (4) was first supported only by an analogy with the thermodynamics of monomeric solutions and by oversimplified lattice models, the predicted phase diagram (Figure 1) turned out to be in a good quantitative agreement with experiments. The reason for this (a consequent thermodynamic theory based on statistical mechanics) dates back to the works of Edwards[7] and Jannink and de Gennes.[8] First, it was shown[7] that in the absence of the specific repulsion between the A and B segments chains are Gaussian. This Flory theorem ensures that, for solutions with $\chi \equiv$

0, the partition function of the chain end-to-end vector $\vec{r}$ reads

$$e^{-(r/2R)^2}$$

(R is the gyration radius). The second suggested idea[7,8] was to consider monomer–monomer inteactions in dense melts through a self-consistent field. The third principal point in the development was to treat χ as a small parameter. This last point is directly related to the polymeric nature of the material. Indeed, the demixing is entropically penalized by kT per macromolecule, whereas the profit of the Flory–Huggins energy per macromolecule is on the order of $kT\chi N$ (N is the degree of polymerization). A balance between the repulsive energy and the entropy defines the condition for the separation of A and B polymers: $\chi_c \sim N^{-1}$. The more the degree of polymerization N is, the less is the χ_c value at the spinodal line. The small parameter $\chi \sim N^{-1}$ permits a detailed description of separation, since for large N the Flory–Huggins parameter χ near the spinodal line is so small that the entropy of chains can be calculated for $\chi \equiv 0$. Such a situation is unique for statistical mechanics, and no analogues exist for low molecular weight systems.

The above three ideas led to a rather sophisticated but constructive method[7–9] known as the random-phase approximation. Applied to the problem of demixing in a polymer–polymer solution,[10] this method not only reproduced the phase diagram shown in Figure 1 (i.e., gave comprehensive statistical mechanics based explanation for the Flory–Huggins form (4) of the free energy) but also allowed the calculation of the scattering intensity $S(q)$

$$S^{-1}(q) = -2\chi + \frac{1}{\Phi G_{AA}(q)} + \frac{1}{(1-\Phi)G_{BB}(q)} \qquad (6)$$

where G are the Debye functions

$$G(\vec{q}) = \frac{2N}{x^2}(x + e^{-x} - 1), \qquad x = (\vec{q}\vec{R})^2$$

of A and B chains, respectively, and R is the corresponding gyration radius. For $q = 0$, this expression defines the spinodal line (5), the line at which the concentration fluctuations diverge. The contours of the isointense scattering are described in Fourier space by spheres of constant $|q|$.

The derivation[7–9] of the structure factor (6) is formally based on the assumptions of the Gaussian statistics for chains. But under an applied electric (or deformation) field chains are no longer Gaussian. The gyration spheres are deformed in the gyration ellipsoids. Substituting the radius vectors of the gyration ellipsoids for radii of the gyration spheres

$$\vec{R}_A \rightarrow [R_l^{(A)}(\vec{\mathcal{E}}), R_p^{(A)}(\vec{\mathcal{E}})], \qquad \vec{R}_B \rightarrow [R_l^{(B)}(\vec{\mathcal{E}}), R_p^{(B)}(\vec{\mathcal{E}})]$$

into the Debye correlators G, we get[12] the structure factor for birefringent polymer solutions.

$$S^{-1}(\vec{q},\vec{\mathcal{E}}) = \frac{1}{\Phi G_{AA}(\vec{q},\vec{\mathcal{E}})} + \frac{1}{(1-\Phi)G_{BB}(\vec{q},\vec{\mathcal{E}})} - 2\chi(\mathcal{E}) \qquad (7)$$

The size of the gyration radii R_l and R_p vs $\mathcal{E}$ is defined by (1).

Let us now examine the structure factor (7) in detail. When the gyration ellipsoids of both A and B chains are elongated by an electric field in the same direction (i.e., when $S^{(A)}, S^{(B)} > 1$), one expects contours of isointense scattering to be oblate along $\vec{E}$. When the anisotropic polarizabilities of A and B segments are negative, $S^{(A)}$ $S^{(B)} < 1$, given $|q|$, the minimum of the intensity lies at the wavevectors forming a ring perpendicular to $\vec{E}$. In this case isointensity lines resemble diamonds prolate along $\vec{E}$. For large and small wavevectors, the contours of isointensity have the form of ellipsoids: The ratio of the polar and equatorial diameters of the contour of isointensity

$$\frac{1}{2}\,\frac{(1-\Phi)(3-S^{(A)}) + \Phi(3-S^{(B)})}{(1-\Phi)S^{(A)} + \Phi S^{(B)}} \qquad (8)$$

measures the degree of induced anisotropy. An essential deviation from this "trivial" ellipsoidal form becomes apparent for

$$q \sim 1/(R^{(A)}R^{(B)})^{1/2}$$

When $S^{(A)} > 1$ but $S^{(B)} < 1$, the extremum of the scattering intensity does not necessarily correspond to the wavevectors strictly parallel or perpendicular to $\vec{E}$ but may lie in any direction. As a result, the scattering patterns can exhibit ($\mathcal{D}$) "prolate diamonds", ($\mathcal{O}$) "oblate diamonds", and even ($\mathcal{B}$) "four-wing butterflies" or "pillows" (in a one-to-one correspondence with "two-wing normal", "two-wing abnormal" and "four-wing butterfly" observed in birefringent diblock melts and deformed polymer networks[12]). Following ref 12, we will classify birefringent polymer solutions by the type of its structure factor. An analysis shows that the following three inequalities

$$\mathcal{J}^*(f_e) \overset{(<)}{>} \mathcal{J}^*(f_p) \overset{(<)}{>} \frac{\Phi(1-S^{(B)}(\mathcal{E}))}{(1-\Phi)(S^{(A)}(\mathcal{E})-1)}$$

$$\mathcal{J}^*(f_p) \overset{(<)}{>} \mathcal{J}^*(f_e) \overset{(<)}{>} \frac{\Phi(1-S^{(B)})}{(1-\Phi)(S^{(A)}-1)} \qquad (9)$$

$$\mathcal{J}^*(f_p) \overset{(<)}{>} \frac{\Phi(1-S^{(B)})}{(1-\Phi)(S^{(A)}-1)} \overset{(<)}{>} \mathcal{J}^*(f_e)$$

where

$$\frac{f_e}{1-f_e} = \frac{S^{(A)}N_A}{S^{(B)}N_B}, \quad \frac{f_p}{1-f_p} = \frac{(3-S^{(A)})N_A}{(3-S^{(B)})N_B}$$

divide the composition axis $\Phi \in [0,1]$ into three domain corresponding to classes $\mathcal{O}$, $\mathcal{D}$, $\mathcal{B}$, respectively (Figures 1 and 2). The composition regions of classes are defined merely by the universal curve $\mathcal{J}^*(f)$ shown in Figure 2.

Since experimentally available fields compress or elongate the gyration ellipsoids of chains rather weakly, in the first nonzero order in $\mathcal{E}$ the structure factor (7) is given by (2).

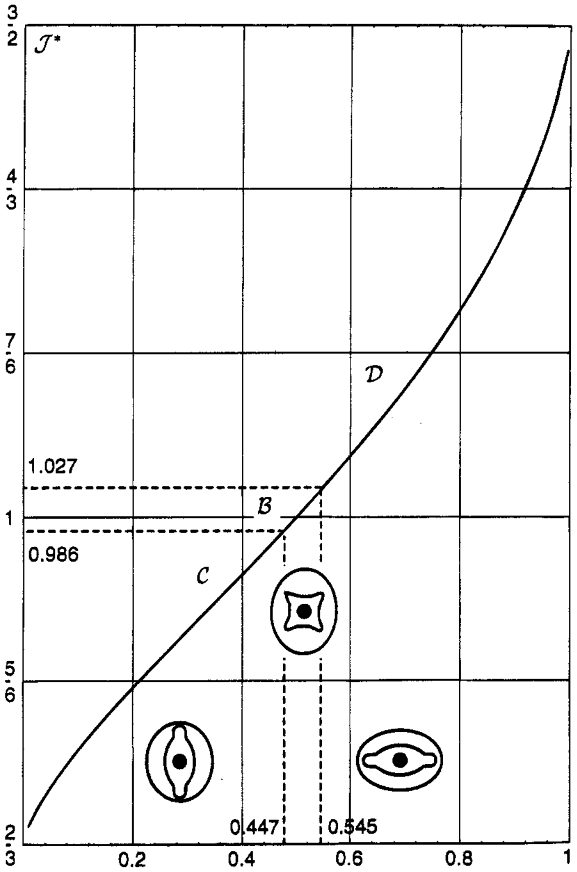

Figure 2. Universal curve $\mathcal{J}^*(f)$ determining classes of birefringent polymer solutions.

4. Critical Fluctuations in Polymer–Monomer Solutions under Electric Field

In the same approximation (6), the limit $N_B \rightarrow 1$ yields for the intensity of the light scattering:

$$S^{-1}(\vec{q},\epsilon) = \frac{1}{\Phi G_{AA}(\vec{q}\bar{R}_A)} - 2\tilde{\chi} \qquad (10)$$

Though the mean-field theory is expected[9] not to approximate well the critical point for polymer–monomer solutions, expression (10) clarifies the microscopic nature and the physical origin of the phenomenological parameters used in ref 5. Moreover, since only ellipsoidal correlation holes of A chains are involved in the structure factor, the contours of isointensity for birefringent polymer–monomer solutions are ellipsoidal.[5]

5. Concluding Remarks. Broken Affinity

In summary, we have studied birefringent binary polymeric solutions: the anisotropy of the concentration fluctuations and the field-induced shift of the spinodal and coexistence curves.

The basic result of this consideration is that an external field, though it deforms chains ("makes chains birefringent"), affects the phase behavior of polymer solutions only through the local dipole–dipole interactions. Putting this in other words, the field-induced shift of the phase diagram is insensitive to the polymeric nature of the material, and, as a result, the shift must be the same as that for a binary mixture of nonlinked segments.[5] The latter problem, behavior of monomeric solutions under an electric field, is elaborated[1,2] in detail. Explained by Landau and Lifshitz and observed later by Debye and Kleboth for low-molecular-weight mixtures, the field-induced shift of the spinodal line

$$\chi \rightarrow \chi(1 - \mathcal{E}^2/\langle \mathcal{P}^2 \rangle)$$

is proven to be negative and proportional to the square of the electric field intensity $\vec{\mathcal{E}}$. The predicted suppression of the separation of A and B segments by an electric field is in accordance with experimental results in refs 1 and 2.

On the contrary, the fluctuations of the concentration are directly related to the polymeric nature of materials. Based on a statistical mechanics description, the present theory explains the form of the structure factor, allows the assignment of an explicit physical meaning to parameters used in phenomenological models, and answers a set of rather delicate questions.

On the question of how, for instance, the anisotropy (10) of the light scattering scales in the critical point (5) for a polymer A–monomer B solution, the present picture yields

$$N_A^{1/2} \nu_A \mathcal{E}^2$$

That is, the degree of the anisotropy and its direction, along or perpendicular to $\vec{\mathcal{E}}$, are given by the degree of the A chain polymerization and the dielectric anisotropy of A segments.

Another curious question concerns polymer–polymer mixtures in which A segments are oriented along whereas B segments are perpendicular to the field, $\nu_A > 0$, $\nu_B < 0$: In which direction, along or perpendicular to $\vec{\mathcal{E}}$, are the isointensity lines stretched? Expressions (2) and (7) show that in the critical point the anisotropy of the concentration fluctuations at large and small q depends on the sign of the following combination:

$$\frac{\nu_A}{N_A^{1/2}} + \frac{\nu_B}{N_B^{1/2}}$$

(Figures 1 and 2). When this sum is positive, the corresponding scattering patterns resemble diamonds oblate along $\vec{\mathcal{E}}$. When it is negative, the diamonds are prolate along $\vec{\mathcal{E}}$.

One of the most unexpected predictions of the current analysis is that in between diamonds prolate and diamonds oblate one may detect pillowlike forms of the isointensity contours (Figures 1 and 2). These four types of isointensity lines, $\mathcal{C}$, $\mathcal{D}$, $\mathcal{B}$, and $\mathcal{A}$, diamonds prolate, diamonds oblate, pillows, and circles (for unstrained Gaussian chains) respectively, present four classes of birefringent polymer solutions.

For an illustration, consider a solution of A and B polymers with $N_A = N_B$. The anisotropic parts of the dielectric polarizabilities of segments are assumed to be $\nu_A = 10^{-38}$ C^2 m^2 J^{-1} and $\nu^{(B)} = -10^{-38}$ C^2 m^2 J^{-1}.[16] In an electric field 10^8 J C^{-1} m^{-1}, which is at the limit of the dielectric strength of polymeric liquids, at 25 °C (i.e., for $kT = 4 \times 10^{-21}$ J) the parameters $S^{(A)}$ and $S^{(B)}$ are 1.09 and 0.91, respectively [see (1)]. By definitions (2) and (9), $f_e = 0.545$, $f_p = 0.477$, and the two corresponding values of $\mathcal{J}^*$ are equal to 1.027 and 0.986 (Figure 2). As a result, the pillows of isointensity may be observed if only $\Phi \in [0.496, 0.506]$. For smaller and larger compositions Φ, the isointensity contours resemble ellipsoids oblate or prolate along $\vec{E}$, respectively. For Φ equal to 0.3 and 0.9 the ratios (8) of the polar and equatorial diameters of the contour of isointensity are 0.94 and 1.11. Let us note that even for very strong electric fields class $\mathscr{B}$ covers an extremely narrow region of the compositions Φ, about 1%.

Finally, I would like to comment on the underlying physics of the present results. This can be resumed as follows: Under an applied field A and B monomers are not randomly oriented, and the thermodynamics of polymers constructed for Gaussian chains must be essentially modified to take into account a new statistics:

$$e^{-(r_l/2R_l)^2} e^{-(r_p/2R_p)^2}$$

If the average distance between segments I and J of some chain has been specified by a vector $[r_l, r_p]$, under an applied field this vector is transformed into $[(S^{(A)})^{1/2} r_l, (3 - S^{(A)})^{1/2} r_p]$ or $[S^{(B)})^{1/2} r_l, (3 - S^{(B)})^{1/2} r_p]$ for A and B chains, respectively. If only $S^{(A)} \neq S^{(B)}$, the affinity of blend deformation is broken. Two different types of ellipsoidal correlation holes,[9] for A and B chains, respectively, compete with each other in forming the structure factor. As we have tried to show here and in ref 12, for the broken affinity, the consequences of this competition are rather surprising.

As to extensions of the present work, the picture is directly applicable to the problem of liquid cystalline polymeric solutions or solutions under magnetic or stress[15] fields.

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References and Notes

(1) Debye, P. J.; Kleboth, K. *J. Chem. Phys.* **1965**, *42*, 3155.

(2) Landau, L. D.; Lifshitz, E. M. *Electrodynamics of Continuous Media* (in Russian, 1958); Pergamon Press: Oxford, U.K., 1984; sections 11 and 17, Vol. 8. The shift of the chemical potential due to the dipole–dipole interaction was taken into account through the composition-dependent dielectric constant (for similar representations, see ref 3).

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(4) In analyzing experiments, it is sometimes convenient to introduce in the free energy "the electrostatic term" proportional to $(\vec{E}\vec{q})^2\Phi^2(\vec{q})$. (Onuki, A.; Doi, M. *Europhys. Lett.* **1992**, *17*, 63. Amundson, K.; Helfand, E.; Quan, X.; Hudson, S. D.; Smith, S. D. *Macromolecules* **1992**, *25*, 1935.) However, the standard[1,2] electrostatic energy describing the interaction of induced dipoles with an applied (constant) electric field $\vec{E}$ and the dipole–dipole interactions in an inhomogeneous fluid dielectric medium, $\langle \mathcal{E}(\vec{r})\vec{P}(\vec{r})\rangle \equiv \langle(\vec{E} + \vec{P}(\vec{r}))\vec{P}(\vec{r})\rangle \propto \text{const} + \langle \vec{P}(\vec{r})^2\rangle = \text{const} + \langle(\alpha_A\Phi_A(\vec{r}) + \alpha_B\Phi_B(\vec{r}))^2E^2\rangle$, contributes to the free energy of incompressible liquids only as $(\alpha_B - \alpha_A)^2E^2\delta^2\Phi$. Here $\vec{P}(\vec{r})$ is the dipole moment at the point $\vec{r}$, $\mathcal{E}(\vec{r}) \equiv \vec{P}(\vec{r}) + \vec{E}$ is an internal electric field in the sample, and α are dielectric polarizabilities of segments. (See for instance: de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979; eqs 3.2–3.5, section 4.4.) The electrostatic term $(\vec{E}\vec{q})^2\Phi^2(\vec{q})$ does not appear also in microscopic quantum theories,[3] and the present theoretical approach does not use it. In this work nontrivial corrections to the free energy at finite $\vec{q}$ emerge only from the configurational entropy of birefringent chains (as any nontrivial segment–segment correlations in polymer systems over distances larger than the size of the statistical segment). But we note that terms $(\vec{E}\vec{q}^{2,4,6...})^2\delta^2\Phi(\vec{q})$ may appear at wavevectors $\vec{q}$ which are on the order of or less than the inverse statistical segment length. At these scales, the classical electrodynamics of continuous media[1,2] is not applicable, and even the Flory–Huggins parameter χ itself is not a constant but a $\vec{q}$-dependent function.

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(11) This behavior directly follows from eqs 9.5 and 14.1 of the textbook in ref 2. The effective dielectric permittivity for a weakly fluctuating medium was first calculated by Landau and Lifshitz in section 9 of ref 2. (See: Onuki, A.; Doi, M. *J. Chem. Phys.* **1986**, *85*, 1190.) The influence of an electric field on dielectric fluids is rather universal. An electric field always tends to mix dielectric substances (opposite to van der Waals forces). Let us also stress that the second derivation of dielectric permittivity over the local composition does not appear in the expression for the correction to the free energy. (See 9.5 section in ref 2.)

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