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Theory of Microphase Separation in Block Copolymers

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ABSTRACT: A microscopic statistical theory of phase equilibria in noncrystalline block copolymers of type A–B is developed. In particular, the onset of an ordered mesophase from a homogeneous melt is studied and a criterion of the microphase separation is found. The only relevant parameters of the theory turn out to be the product χN (χ is the Flory parameter characterizing A–B interactions; N is the polymerization index) and f, the fraction of monomers A in a chain. It is shown that under certain critical conditions a specific unstable mode appears in the homogeneous copolymer melt; this announces the microphase separation transition (MST). After the MST a mesophase with the periodicity equal to the wavelength of the unstable mode and with the symmetry of a body-centered-cubic (bcc) lattice should appear. For a large range of compositions a bcc mesophase is expected to be a metastable phase. Only two other ordered phases, a hexagonal mesophase and a lamellar mesophase, may be stable near the MST. The regions of stability are calculated and the phase diagram of the system is provided. First-order transitions are predicted between different ordered phases. A new method of measuring of the parameter χ, crucial for verification of the theory, is proposed.

I. Introduction

The particular chemical structure of block copolymer materials is reflected in the most fundamental and interesting way by incompatibility effects. These effects give block copolymers a number of specific, new morphologies and original physical and mechanical properties which have led to valuable technological applications (for general references see ref 1). The purpose of the present paper is to formulate a microscopic theory which, on the basis of statistical physics, would explain how and under which conditions the incompatibility of molten copolymer constituents leads to the formation of different ordered structures (mesophases). This general theory is applied to provide a phase diagram of the simplest copolymer system—molten diblock copolymer A–B. Both sequences of monomers A and B, forming a copolymer molecule, are supposed not to be able to crystallize.

The most characteristic feature of a block copolymer is the strong repulsion between unlike *sequences* even when the repulsion between unlike *monomers* is relatively weak. As a result sequences tend to segregate, but as they are chemically bonded even the complete segregation cannot lead to a macroscopic phase separation as in mixtures of two homopolymers. However, in the case of a sufficiently strong incompatibility, microphase separation occurs: microdomains rich in A (in B) are formed.

Such an effect was first observed in concentrated solutions of block copolymers and afterward in many other copolymer systems, particularly in molten block copolymers (see, e.g., review articles 3–8 and references given therein). When microphase separation occurs, the microdomains are not located at random but they may form a regular arrangement giving rise to a periodic structure (macrolattice). Several techniques (e.g., annealing, ex-

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trusion) enable samples to be obtained which exhibit a very regular, oriented macrolattice extended over large volume.[9,7,10-13]

Mesophases with three types of lattice have been observed: cubic lattice of spheres, two-dimensional hexagonal lattice of cylinders, and one-dimensional lamellar structures.

Various experimental techniques such as small-angle X-ray scattering (SAXS), electron microscopy, and electron diffraction have given relatively rich data about molten block copolymer mesophases. Symmetries, periodicities, and microdomain dimensions and their dependencies on molecular parameters such as molecular mass, fraction of monomers A in the chain (composition), and chemical nature of copolymer monomers have been studied in detail. There is relatively less information about the conditions of microphase separation. Nevertheless the existence of the disordered (homogeneous) phase has been established for copolymers with a low polymerization index by several experimental methods (microcalorimetry,[14-18] SAXS,[14,15,19] electron microscopy[20]) and the microphase separation transition (MST) from the disordered phase to a mesophase has been directly observed.[14,15,19]

In the last decade a considerable effort has been made to develop a microscopic theory of the molten block copolymer (see, e.g., ref 9 and ref 21–29). The approaches hitherto adopted considered a specified mesophase (i.e., with a specified symmetry and shape of the microdomain pattern) and evaluated and minimized the free energy of the system in this mesophase in order to obtain the periodicity and microdomain dimensions. The calculation of the free energy of molten block copolymer encountered essential difficulties—it required very restrictive assumptions about the microdomain interfaces and also the introduction of phenomenological parameters not directly available from experiments (compare, e.g., review articles 30–32). Recently, Helfand has proposed a self-consistent-field method to obtain the free energy of the molten block copolymer solely in terms of molecular parameters characterizing copolymer chains (molecular mass, composition, monomer lengths, and monomer interaction energy).[27] The application of the method even to the simplest possible lamellar phase requires complicated numerical computations. The assumption that the interphase between domains is narrow compared with domain size simplifies the theory and permits valuable predictions to be made of domain periodicity and size for the lamellar and spherical (close-packed cubic) mesophase.[28,29,31,32] In the present paper we shall be concerned with a very different regime, namely, the onset of a microphase from a homogeneous melt. The narrow interphase approximation completely breaks down in this regime: here even the notion of an interphase disappears since the concentration of monomers A (B) does not change abruptly over a small distance but, on the contrary, varies smoothly over the whole period of the microphase structure (see section II; compare ref 29, 30, and 33). Therefore, the Helfand approximation cannot be used and another approach is needed.

A complete understanding of the microphase separation transition (MST) in molten block copolymers requires not only a statistical study of microdomain structures (mesophases) appearing after the transition but also a study of the homogeneous (disordered) phase. In particular one should find a quantity which may be used to introduce an order parameter (see section II). Here we study the monomer A density correlation functions in a disordered phase, using a generalization of the "random-phase approximation" (RPA) method of de Gennes,[34] which is known to work well in other molten polymer systems.[35,36] We find that under certain specific critical conditions an unstable mode with a nonvanishing wave vector appears in the system; i.e., a certain Fourier component of the monomer density fluctuations diverges. This instability announces the microphase separation transition. It is interesting to note that the microphase separation transition is in many respects analogous to the crystallization of a liquid. The latter has generated a renewal of interest recently (e.g., ref 37 and 38).

Once correlation functions have been found, we make use of general statistical physics relations which provide the free energy of the block copolymer in terms of the order parameter of the microphase separation transition. The applied approach has the advantage of taking into account the connectedness of the blocks in a block copolymer molecule in a very simple and natural way. Only two quantities turn out to be relevant parameters for the characterization of phase equilibria in molten diblock copolymers: the composition f (the fraction of monomers A in a chain) and the product χN (where N is the polymerization index and χ is the Flory parameter characterizing the effective interaction of monomers A–B; for the definition of χ see eq II-2). Hence, the determination of the phase diagram of the system consists of calculating the regions of stability of different phases (disordered phase, mesophases) in a plane with coordinates χN and f. Our analysis of the free energy leads to predictions concerning (i) both the symmetry and the periodicity of phases appearing just after the microphase separation transition, (ii) the criterion for the microphase separation transition (χN as a function of f for which microdomain structures occur in the system), (iii) the phase diagram in the vicinity of the microphase separation transition line, and (iv) existence of transitions between mesophases with different symmetry. Detailed comparisons of the theory with experiments will depend on our knowledge of the interaction parameter χ, which is difficult to measure experimentally (compare, e.g., ref 39). We show that the small-angle X-ray scattering by block copolymers is strongly dependent on monomer–monomer interactions and may provide a new method of determining χ.

In the next section we present a qualitative description of the microphase separation transition which follows from the present theory and which indicates the guidelines along which this theory is constructed.

II. Thermodynamic Description of Microphase Separation

In this paper, we will consider a molten diblock copolymer where all chains have the same index of polymerization N and the same composition $f = N_A/N$ ($N_A \gg 1$ and $N_B \gg 1$ denote the number of monomers of type A and B, respectively; $N = N_A + N_B$); i.e., we neglect the polydispersity of the chains. For the sake of simplicity we will assume that both blocks have the same Kuhn statistical segment length a. We will limit our analysis to the situations where thermal equilibrium is achieved.

Molten polymers have very low compressibilities. This means that any local compression of the system will lead to a huge increase of the free energy which can be compensated neither by the decrease of monomer interactions nor by entropy changes (cf. ref 27). Thus it is justified to consider the limit of zero compressibility and to assume that at any point in the copolymer liquid

$$\rho_A(\vec{r}) + \rho_B(\vec{r}) = 1 \tag{II-1}$$

where $\rho_A(\vec{r})$ and $\rho_B(\vec{r})$ denote the reduced density of monomers A and B, respectively. $\rho_A(\vec{r})$ is defined as the ratio of the local density of monomers A at the point $\vec{r}$ to the overall monomer density averaged over the sample.

Although the overall density of monomers is constant (eq II-1), ρ_A and ρ_B themselves may exhibit local fluctuations and it is these fluctuations which will be at the very root of the microphase separation. The species A and B tend to realize an equilibrium density profile $\rho_A(\vec{r})$ and $\rho_B(\vec{r})$ which minimizes the free energy of the system. The energy of interaction of different chemical species (per monomer) may be written as (see, e.g., ref 35 and 40)

$$\alpha\rho_A\rho_B \equiv kT\chi\rho_A\rho_B \tag{II-2}$$

In the lattice model, the effective interaction parameter α may be related to the energy of interactions between two monomers A–A (ϵ_{AA}), B–B (ϵ_{BB}), and A–B (ϵ_{AB}): $\alpha = \epsilon_{AB} - {}^1/_2(\epsilon_{AA} + \epsilon_{BB})$. Experiments show that χ is positive[41] (of the order of 10^{-3}–10^{-1}); monomers A and B effectively repel each other. In fact, since χ is positive there is a *tendency* to decrease the number of contacts between monomers A and B in order to lower the contribution of the interaction energy contribution to the free energy (eq II-2). However, a decrease in the number of contacts A–B diminishes the entropy of the system and consequently increases the free energy. Hence, $\rho_A(\vec{r})$ and $\rho_B(\vec{r})$ profiles are the result of a "competition" between these two opposite trends.

For $\chi = 0$ or χ finite but sufficiently small, the entropy effects are dominant, and they favor mixing: the system exhibits an isotropic phase with sequences A and B of the chains interpenetrating each other so that for all points

$$\langle\rho_A(\vec{r})\rangle = f \qquad \langle\rho_B(\vec{r})\rangle = 1 - f \tag{II-3}$$

($\langle\ \rangle$ denotes the thermal average). Such a phase will be called the disordered phase. On the other hand, when the system is cooled (or composed of longer chains) so that χN is larger than a certain value $(\chi N)_t$ (to be computed in section V), the enthalpic term (eq II-2) in the free energy dominates and the system exhibits a microphase separation; i.e., $\langle\rho_A\rangle$ and $\langle\rho_B\rangle$ are not uniform: there are domains (A rich) where $\langle\rho_B\rangle$ is smaller than $1 - f$ and others (B rich) where $\langle\rho_A\rangle$ is smaller than f. Then at all points the product $\rho_A\rho_B$ is small and the enthalpic term is low. A phase of the system in which a microdomain structure occurs will be called an ordered phase (or mesophase). As it has been already mentioned, depending on the value of composition f and on the interaction parameter χ (temperature T), several different mesophases may be observed.

In order to characterize the different phases of a liquid copolymer as well as the transitions between them, we will introduce an order parameter $\psi(\vec{r})$, defined as

$$\psi(\vec{r}) = \langle(1 - f)\rho_A(\vec{r}) - f\rho_B(\vec{r})\rangle \tag{II-4}$$

In the disordered phase $\psi(\vec{r})$ is uniform and vanishes at all points. In different ordered phases (with different domain patterns) ψ does not vanish. In a single domain sample (macrolattice) $\psi(\vec{r})$ is a periodic function. As incompressibility of the system (eq II-1) has been assumed, $\psi(\vec{r})$ fully describes its thermodynamic state. It should be noted that (from eq II-1)

$$\psi(\vec{r}) = \langle\delta\rho_A(\vec{r})\rangle \equiv \langle\rho_A(\vec{r}) - f\rangle \tag{II-5}$$

i.e., ψ describes the average deviation from the uniform distribution of monomers A and B.

Let us consider the system where χN is so small that the disordered phase occurs: the average value of $\delta\rho_A = \rho_A - f$ vanishes at all points. However, when χ becomes larger (as a result of cooling the system) so that χN approaches the value $(\chi N)_t$ (for which the microphase separation transition occurs) the local values of $\delta\rho_A$ have large fluctuations. These fluctuations may be characterized by a density–density correlation function

$$\tilde{S}(\vec{r} - \vec{r}\,') = \frac{1}{kT}\langle\delta\rho_A(\vec{r})\delta\rho_A(\vec{r}\,')\rangle \tag{II-6}$$

The Fourier transform $\tilde{S}(\vec{q})$ of the correlation function (eq II-6) can be studied by elastic radiation scattering experiments: light, X-ray, or neutron scattering ($\vec{q}$ deontes the scattering vector with length $4\pi[\sin(\theta/2)]/\lambda$, where λ is the wavelength and θ the scattering angle). The scattering power $\tilde{S}(\vec{q})$ can be calculated with the help of the RPA method.[34] This method assumes that the chains are nearly ideal.[35] This is a good approximation for homopolymer melts, where RPA predictions have been compared with neutron experiments using partially deuterated chains with particularly small effective interactions between marked and unmarked monomers ($\chi \lesssim 10^{-3}$) and polymerization indices not too high ($N \lesssim 10^3$). When segregation effects become important the RPA must be modified to take into account the monomer interactions (compare studies of correlations in the problem of homopolymer mixtures[42,36]). The scattering power $\tilde{S}(\vec{q})$ is calculated and discussed in section IV.

From a thermodynamic standpoint, this calculation leads to the important conclusion that only certain fluctuations become anomalously large when the interaction parameter χ tends toward the transition point value χ_t: $\tilde{S}(\vec{q})$ has a very narrow maximum for a certain value of $|\vec{q}| = q^* \neq 0$. (In the isotropic phase $\tilde{S}$ depends only on the length of the $\vec{q}$ vector.) A remarkable property of molten copolymers is that q^* is independent of the interaction parameter χ. As χN becomes greater than $(\chi N)_t$ and is equal to a certain value $(\chi N)_s$ the fluctuations with wave vector $|\vec{q}| = q^*$ diverge: $\tilde{S}(q^*) \rightarrow \infty$. This is the spinodal point. The spinodal point determines the limit of metastability of the system. When the system is quenched to the metastability region ($(\chi N)_t < \chi N < (\chi N)_s$) the microphase separation can take place by the nucleation of droplets of mesophases inside the disorder phase. The interface energy is positive and the droplets are formed by a slow thermoactivated process. On the contrary, when $N = (\chi N)_s$ the interface energy vanishes: the system becomes unstable.

The simplest way to analyze qualitatively the MST is to examine the expansion of the free-energy density F of an ordered phase (occurring below the transition: $\chi N > (\chi N)_t$) in powers of the order parameter ψ. The quadratic term has the form (see sections III and V)

$$F_2 = \mathcal{V}^{-1}\sum_{\vec{q}}\tilde{S}^{-1}(\vec{q})\psi(\vec{q})\psi(-\vec{q}) \tag{II-7}$$

where $\psi(\vec{q})$ denotes the Fourier transform of $\psi(\vec{r})$ and $\mathcal{V}$ the volume of the system. As we have pointed out, near the phase transition $\tilde{S}^{-1}(\vec{q})$ has a deep minimum for the wave vectors $\vec{q}$ with $|\vec{q}| = q^*$, but the higher order terms F_3, F_4, ... have no singular behavior for q^*. As a consequence the only Fourier components of ψ which are important (near the transition) are those with $|\vec{q}| = q^*$. For $\chi N > (\chi N)_t$ the free energy is lowered by the presence of a finite $\psi(\vec{q})$ ($|\vec{q}| = q^*$): a periodic ordered mesophase appears. The periodicity of the ordered phase is equal to $2\pi/q^*$ and is of the order of the radius of gyration of copolymer molecules. The detailed structure and magnitude of the coefficients $\psi(\vec{q})$ ($|\vec{q}| = q^*$) for various orientations of $\vec{q}$ will depend crucially on the higher order terms F_3, F_4, ... It is important to note that for $f \neq 0.5$ the third-order term F_3 in the expansion of F does not vanish. As pointed out long ago by Landau,[47] this implies that the transition should be of the first order: at $(\chi N)_t$

$\psi(q^*)$ has a jump. Hence, the microphase separation transition is analogous to the solidification of the liquid, but q^* for the MST is much smaller; i.e., the periodicity of molten block copolymer mesophases is much larger than the periodicity of a crystal lattice.

General symmetry considerations show that the existence of the third-order term in the expansion of the free-energy density F allows for $\chi N = (\chi N)_t$ the onset of only two periodic microdomain structures: one with the symmetry of the planar triangular lattice and another with that of the body-centered-cubic lattice. In order to decide which of these two structures will actually appear as well as to calculate $(\chi N)_t$, i.e., to predict a criterion of the microphase separation, it is necessary to find the coefficients of the third and the fourth order in the expansion of F. The calculation of these coefficients also permits examination of the stability of different mesophases for χN close to $(\chi N)_t$ and prediction of phase transitions between them (see sections V and VI).

In section III we will formulate a theory leading to the free-energy expansion in powers of ψ.

III. Free Energy of Molten Block Copolymers

The microphase separation transition in molten block copolymer A–B essentially differs from demixing in the mixture of two homopolymers A and B. The latter is a gas–liquid-type phase transition (with instability for $\vec{q} = 0$), whereas, as we have pointed out in section II, MST is a liquid–solid-type transition (with instability for a finite wave vector $|\vec{q}| = q^*$). Moreover, in block copolymers the low-temperature ordered phase is a mesophase with nonhomogeneities occurring at distances of the order of molecular dimensions (radius of gyration). For these reasons the simple lattice-type Flory–Huggins theory developed for homopolymer mixtures is inadaptable to study MST in copolymers. In fact, such a theory would require the calculation of the number of configurations available for copolymer chains (disorientation entropy[40]). The inclusion of constraints which prevent separation of copolymer chain sequences gives rise to enormous difficulties.

We propose here a quite different approach based on the RPA. This approach avoids the problem of calculating separately the entropy of disorientation and leads directly to the free-energy density F of the molten copolymer as a function of the order parameter $\psi(\vec{r})$. The essential point of the method is a theorem which relates the coefficients of the expansion of the free energy of the system in powers of $\psi(\vec{r})$ to the response functions (section III.1). To get equations for response functions of the copolymer melt we make use of the random-phase approximation (section III.2). Then RPA equations are solved and the free-energy density F is obtained in terms of response functions of ideal (Gaussian) chains (calculated in Appendix B).

1. Free-Energy Expansion and Response Functions. In the theory of magnetic phase transitions general relations between response functions (connected Green functions) and coefficients in the expansion of a free-energy functional in powers of an order parameter are often used (e.g., ref 43–45). In this section we establish similar relations between monomer density correlation functions and the free energy of the molten copolymer. Since the method of derivation of such relations is analogous to that in the magnetic problem, we only sketch here the essential points and recall some definitions which will be of use later (section III.2).

Let us consider the liquid copolymer under the constraint of the existence of a long-range order. The average value of $\delta\rho_A(\vec{r}) = \rho_A(\vec{r}) - f$ does not vanish ($\psi(\vec{r}) = \langle\delta\rho_A(\vec{r})\rangle \neq 0$). The total free-energy density of the system F may be divided into two parts. The first one, F_0, the free energy of the copolymer liquid in the absence of the constraint of $\psi(\vec{r}) \neq 0$, includes the naturally occurring correlations of the liquid state. The second one, F, is due to the constraint $\psi(\vec{r}) \neq 0$ and it vanishes when $\psi = 0$. When the system is below the MST, i.e., $\chi N > (\chi N)_t$, the microphase separation appears spontaneously, F is negative, and the system occurs in a stable ordered phase. Its $\psi(\vec{r})$ minimizes F. On the contrary, for $\chi N < (\chi N)_t$ for any $\psi(\vec{r}) \neq 0$, F is positive and the disordered phase with $\psi = 0$ is the stable one. Thus it is sufficient to find F as a function of $\psi(\vec{r})$ to determine the conditions for the microphase separation as well as to investigate the stability of different ordered phases.

We are looking for the coefficients of expansion of F in powers of $\psi(\vec{r})$. We consider the system in the disordered phase and we suppose, quite formally, that external potentials $U_A(\vec{r})$ and $U_B(\vec{r})$ act on monomers A and B, respectively, so that the energy of interaction reads

$$\int U_A(\vec{r})\delta\rho_A(\vec{r})\,d^3r + \int U_B(\vec{r})\delta\rho_B(\vec{r})\,d^3r = \int U(\vec{r})\delta\rho_A(\vec{r})\,d^3r \quad \text{(III-1)}$$

where $U(\vec{r}) = U_A(\vec{r}) - U_B(\vec{r})$ is the external field conjugated to the order parameter $\psi(\vec{r})$. (The incompressibility condition II-1 has been used.) As a result a nonvanishing, nonuniform $\psi(\vec{r})$ appears in the system. The free energy of such a system (with $\psi(\vec{r}) \neq 0$) is the function $F'(U)$ of the external field U. We shall see below that the coefficients of expansion of F' in powers of U are easy to derive: they are related directly to the correlation functions of the unperturbed system. However, from the physical point of view, a description in which ψ rather than U plays the role of independent variable is more important. Actually, the external field U was introduced only formally in order to impose the constraint of concrete $\psi(\vec{r})$. The Legendre transformation

$$F(\psi) = F'(U) - \int U(\vec{r})\psi(\vec{r})\,d^3r \quad \text{(III-2)}$$

permits the free energy of the system to be obtained in terms of ψ instead of U. In practice, it is sufficient to obtain the external field U as a function of ψ and then to integrate the equation

$$U(\vec{r}) = -\delta F/\delta\psi(\vec{r}) \quad \text{(III-3)}$$

which follows from (III-2).

The free-energy density $F'([U])$ equals

$$F' = -kT \ln Z([U(\vec{r})]) \quad \text{(III-4)}$$

where $Z([U])$ is the partition functional of the system when the external field U is applied

$$Z = \mathrm{Tr}\exp\left[-\beta\left(H_0 + \int U\delta\rho_A\,d^3r\right)\right] = Z_0\left\langle \exp\left(-\beta\int U\delta\rho_A\,d^3r\right)\right\rangle \quad \text{(III-5)}$$

H_0, Z_0, and $\langle\ \rangle$ denote the Hamiltonian, the partition function, and the thermal average in the absence of external fields ($U = 0$). The free-energy functional F' (III-4) may be developed in powers of U

$$F' = F_1 + \sum_{n=1}^{\infty} \frac{(-\beta)^{n-1}}{n!} \int \tilde{G}^{(n)}(\vec{r}_1, ..., \vec{r}_n)U(\vec{r}_1) \ldots U(\vec{r}_n)\,d^3r_1 \ldots d^3r_n \quad \text{(III-6)}$$

where $\beta = 1/kT$.

The coefficients of expansion are the monomer density correlation functions defined as

$$\tilde{G}^{(n)}(\vec{r}_1, ..., \vec{r}_n) = \left.\frac{(-kT)^n \delta^n \ln (Z/Z_0)}{\delta U(\vec{r}_1) \ldots \delta U(\vec{r}_n)}\right|_{U=0} \quad \text{(III-7)}$$

It is easy to check (from eq III-5) that this definition gives the well-known formulas for correlation functions (cf. ref 46)

$$\langle \delta\rho_{\mathrm{A}} \ldots \delta\rho_{\mathrm{A}}(\vec{r}_n)\rangle = \sum_{\{I_\alpha\}}\prod_{\alpha} \tilde{G}^{(|I_\alpha|)}(\vec{r}_1, ..., \vec{r}_{|I_\alpha|}) \quad \text{(III-8)}$$

where for the sake of simplicity we have denoted by I the set $\{1, ..., n\}$, by $\{I_\alpha\}$ any partition of I, and by $|I|$ the cardinal of the set I. As an example we use (III-8) to write down the lowest order correlation functions which we will need later

$$\tilde{G}^{(1)}(\vec{r}_1) = \langle \delta\rho_{\mathrm{A}}(\vec{r}_1)\rangle = 0 \quad \text{(III-9a)}$$

$$\tilde{G}^{(2)}(\vec{r}_1, \vec{r}_2) = \langle \delta\rho_{\mathrm{A}}(\vec{r}_1)\delta\rho_{\mathrm{A}}(\vec{r}_2)\rangle \quad \text{(III-9b)}$$

$$\tilde{G}^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \langle \delta\rho_{\mathrm{A}}(\vec{r}_1)\delta\rho_{\mathrm{A}}(\vec{r}_2)\delta\rho_{\mathrm{A}}(\vec{r}_3)\rangle \quad \text{(III-9c)}$$

$$\begin{aligned}\tilde{G}^{(4)}(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4) = \langle \delta\rho_{\mathrm{A}}(\vec{r}_1)\delta\rho_{\mathrm{A}}(\vec{r}_2)\delta\rho_{\mathrm{A}}(\vec{r}_3)\delta\rho_{\mathrm{A}}(\vec{r}_4)\rangle - \\ \tilde{G}^{(2)}(\vec{r}_1, \vec{r}_2)\tilde{G}^{(2)}(\vec{r}_3, \vec{r}_4) - \tilde{G}^{(2)}(\vec{r}_1, \vec{r}_3)\tilde{G}^{(2)}(\vec{r}_2, \vec{r}_4) - \\ \tilde{G}^{(2)}(\vec{r}_1, \vec{r}_4)\tilde{G}^{(2)}(\vec{r}_2, \vec{r}_3) \quad \text{(III-9d)}\end{aligned}$$

(In (III-9) the fact that the system is disordered when $U = 0$ (i.e., $\langle \delta\rho_{\mathrm{A}}\rangle = 0$) has been used.)

It should be noted that the average of $\delta\rho_{\mathrm{A}}$ in the presence of the field U, which we call ψ, is equal to

$$\begin{aligned}\psi(\vec{r}) &= Z^{-1}\,\mathrm{Tr}\left\{\delta\rho_{\mathrm{A}}(\vec{r}) \exp\left[-\beta\left(H_0 + \int U\delta\rho_{\mathrm{A}}\, \mathrm{d}^3r\right)\right]\right\} \\ &= \delta F/\delta U(\vec{r})\end{aligned} \quad \text{(III-10)}$$

Hence, $(-\beta)^{n-1}\tilde{G}^{(n)}(\vec{r}_1, ..., \vec{r}_n)/(n-1)!$ may be interpreted as the response function of the nth order. Actually, from (III-6), the response ψ of the system to the external potential U reads

$$\psi(\vec{r}) = \sum_{n=0}^{\infty}\frac{(-\beta)^n}{n!}\int \tilde{G}^{(n+1)}(\vec{r}, \vec{r}_1, ..., \vec{r}_n)U(\vec{r}_1) \ldots U(\vec{r}_n)\, \mathrm{d}^3r_1 \ldots \mathrm{d}^3r_n \quad \text{(III-11)}$$

(Yvon's theorem). It will be convenient in the following to use the Fourier transform of (III-11)

$$\psi(\vec{q}_1) = \sum_{n=1}^{\infty}\frac{(-\beta)^{n-1}}{(n-1)!}\mathcal{V}^{-n}\sum_{\vec{q}_2,...,\vec{q}_n}\delta(\vec{q}_1 + ... + \vec{q}_n) \times \tilde{G}^{(n)}(\vec{q}_1, ..., \vec{q}_n)U(\vec{q}_1) \ldots U(\vec{q}_n) \quad \text{(III-12)}$$

where $O(\vec{q}) = \int O(\vec{r})e^{i\vec{q}\vec{r}}\, \mathrm{d}^3r$ denotes the Fourier transform of a function O and the use of the translational invariance of the system has been made.

In order to get $F(\psi)$ we need U as a function of ψ, so we should invert (III-12). This may be done by the iteration method. Then, by integrating (III-10) we get the expansion of F as a power series of ψ

$$F = F_0 + kT\sum_{n=2}^{\infty}\mathcal{V}^{-n}\frac{1}{n!}\sum_{\vec{q}_1,...,\vec{q}_n}\Gamma_n(\vec{q}_1, ..., \vec{q}_n)\psi(\vec{q}_1) \ldots \psi(\vec{q}_n) \quad \text{(III-13)}$$

The coefficients Γ_n in expansion III-13 are related to the correlation functions $\tilde{G}^{(n)}, \tilde{G}^{(n-1)}, ..., \tilde{G}^{(2)}$. As we will confine our interest to the temperature region near the transition, it is justified to drop out in expansion III-13 all terms containing higher powers of ψ than the fourth power. The coefficients of interest are given by

$$\Gamma_2(\vec{q}_1, \vec{q}_2) = 1/\tilde{G}^{(2)}(\vec{q}_1, \vec{q}_2) \quad \text{(III-14)}$$

$$\Gamma_3(\vec{q}_1, \vec{q}_2, \vec{q}_3) = -\tilde{G}^{(3)}(\vec{q}_1, \vec{q}_2, \vec{q}_3)/\prod_{i=1}^{3}\tilde{G}^{(2)}(\vec{q}_i, -\vec{q}_i) \quad \text{(III-15)}$$

$$\begin{aligned}\Gamma_4(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) = \{\tilde{G}^{(4)}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) - \\ \mathcal{V}^{-1}\sum_{\vec{q}\,'}\tilde{G}^{(2)-1}(\vec{q}\,', -\vec{q}\,')[\tilde{G}^{(3)}(\vec{q}_1, \vec{q}_2, \vec{q}_4{}')\tilde{G}^{(3)}(-\vec{q}\,', \vec{q}_3, \vec{q}_4) + \\ \tilde{G}^{(3)}(\vec{q}_1, \vec{q}_3, \vec{q}\,')\tilde{G}^{(3)}(-\vec{q}\,', \vec{q}_2, \vec{q}_4) + \\ \tilde{G}^{(3)}(\vec{q}_1, \vec{q}_4, \vec{q}\,')\tilde{G}^{(3)}(-\vec{q}\,', \vec{q}_2, \vec{q}_3)]\}/\prod_{i=1}^{4}\tilde{G}^{(2)-1}(\vec{q}_i, -\vec{q}_i)\end{aligned} \quad \text{(III-16)}$$

It is very important to note that, from the definition of ψ, it turns out that

$$\psi(\vec{q} = 0) = \int \mathrm{d}^3r\, \psi(\vec{r}) = \int \mathrm{d}^3r\, \langle \rho_{\mathrm{A}} - f\rangle = 0 \quad \text{(III-17)}$$

This implies that $\tilde{G}^{(2)}(0, 0) = 0$ as well as $\tilde{G}^{(3)}(\vec{q}_1, \vec{q}_2, 0) = 0$ for $\vec{q}_1 + \vec{q}_2 = 0$. In turn, when $|\vec{q}_1 + \vec{q}_2| = |\vec{q}_3 + \vec{q}_4| = 0$, from (III-17) it follows that on the right-hand side of (III-16) the second term does not appear.

In the following we use the RPA to calculate the correlation functions $\tilde{G}^{(n)}(\vec{q}_1, ..., \vec{q}_n)$ $(n = 1, ..., 4)$. Then, the relations (III-14) to (III-16) permit calculation of the free-energy density of the system, F, and an investigation of the transition region.

2. Random-Phase Approximation for Block Copolymers. Free Energy near the MST. In this section we generalize a standard RPA method[34] in order to calculate both linear and nonlinear response functions of block copolymers and the free-energy expansion in powers of the order parameter.

We denote by ψ_i the average value of $\delta\rho_i$, where $i = 1$, 2 correspond to the species A and B, respectively. If we suppose that two different fields U_i act on the monomers, then the response of the system (i.e., the average change of $\delta\rho_i$) is equal to (see eq III-12)

$$\begin{aligned}\psi_i(\vec{q}_1) = -\beta\tilde{S}_{ij}(\vec{q}_1)U_j(\vec{q}_1) + \\ \frac{1}{2}\beta^2\mathcal{V}^{-2}\sum_{\vec{q}_2,\vec{q}_3}\tilde{G}^{(3)}_{ijk}(\vec{q}_1, \vec{q}_2, \vec{q}_3)U_j(\vec{q}_2)U_k(\vec{q}_3) - \\ \frac{1}{3!}\beta^3\mathcal{V}^{-3}\sum_{\vec{q}_2,\vec{q}_3,\vec{q}_4}\tilde{G}^{(4)}_{ijkl}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4)U_j(\vec{q}_2)U_k(\vec{q}_3)U_l(\vec{q}_4) \\ \equiv \psi_i{}^{(1)} + \psi_i{}^{(2)} + \psi_i{}^{(3)}\end{aligned} \quad \text{(III-18)}$$

where $\tilde{G}^{(n)}_{i_1,...,i_n}(\vec{q}_1, ..., \vec{q}_n)$ denote the correlation functions of monomer densities $\delta\rho_{i_1}(\vec{r}_1), ..., \delta\rho_{i_n}(\vec{r})$ (see eq III-9) and $\tilde{S}_{ij}(\vec{q}) = \mathcal{V}^{-1}\tilde{G}^{(2)}_{ij}(\vec{q}, -\vec{q})$. $\psi^{(1)}$, $\psi^{(2)}$, and $\psi^{(3)}$ denote, respectively, the contribution to ψ of the first, second, and third order in external potentials U_i. In (III-18) and in the following the summation convention over the repeated indices is used. It should be stressed that from the incompressibility condition $\sum_{i=1}{}^2\psi_i = 0$, it turns out that there is only one independent correlation function of the nth order, e.g., $\tilde{S}_{11} = \tilde{S}$, $\tilde{G}^{(3)}_{111} = \tilde{G}^{(3)}$ and $\tilde{G}^{(4)}_{1111} = \tilde{G}^{(4)}$ (cf. eq III-12).

The basic point of the RPA method is the fact that in polymer melts chains are nearly ideal on the scale of one coil (e.g., ref 35 and 40). It may be supposed that when the interactions between monomers are switched off the monomer density correlation functions are equal to those of the ideal (Gaussian) independent copolymer chains (which will be denoted by S_{ij}, $G^{(3)}_{ijk}$, $G^{(4)}_{ijkl}$). In the RPA one calculates the response of the system to the external potentials U_i as if the response functions were those of the ideal chains, but the potentials acting on monomers U_i^{eff} (different from the external potentials U_i) were corrected to take into account monomer interactions. These corrections are of two different types (cf. ref 42). First of all, to ensure the constant overall monomer density (incompressibility) a self-consistent potential V acting on all monomers (both A and B) is present. Secondly, to express the fact that external potentials change the average monomer densities and, consequently, change also the effective monomer interaction by the quantity $kT\chi\psi_1\psi_2$ (see eq II-2), the internal potentials $kT\chi\psi_2$ acting on monomers A and $kT\chi\psi_1$ acting on B are introduced. Hence

$$\psi_i(\vec{q}) = -\beta S_{ij}(\vec{q})U_j^{\text{eff}}(\vec{q}) + \frac{1}{2}\beta^2\mathcal{V}^{-2}\sum_{\vec{q}_1,\vec{q}_2} G^{(3)}_{ijk}(\vec{q}, \vec{q}_1, \vec{q}_2)U_j^{\text{eff}}(\vec{q}_1)U_k^{\text{eff}}(\vec{q}_2) - \frac{1}{3!}\beta^3\mathcal{V}^{-3}\sum_{\vec{q}_1,\vec{q}_2,\vec{q}_3} G^{(4)}_{ijkl}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4)U_j^{\text{eff}}(\vec{q}_1)U_k^{\text{eff}}(\vec{q}_2)U_l^{\text{eff}}(\vec{q}_3) \quad \text{(III-19)}$$

where

$$U_i^{\text{eff}}(\vec{q}) = U_i(\vec{q}) + V_{im}\psi_m(\vec{q}) + V(\vec{q}) \quad \text{(III-20)}$$

with $V_{11} = V_{22} = 0$ and $V_{12} = V_{21} = kT\chi$. Equations III-19 together with the condition

$$\sum_{i=1}^{2}\psi_i = 0 \quad \text{(III-21)}$$

form the RPA equation set. A simple procedure to solve this set is presented in Appendix A. The procedure provides the correlation functions of the system $\tilde{S}$, $\tilde{G}^{(3)}$, and $\tilde{G}^{(4)}$ in terms of the correlation functions of the noninteracting ideal copolymer chains S_{ij}, $G^{(3)}_{ijk}$, and $G^{(4)}_{ijkl}$.

The coefficients of the free-energy density expansion in powers of ψ (eq III-13) may be obtained by putting the solutions of the RPA equations (cf. Appendix A) (eq III-19 to III-21) into eq III-14 to III-16. The result reads

$$\Gamma_2(\vec{q}_1, \vec{q}_2)\mathcal{V}^{-1}\delta(\vec{q}_1 + \vec{q}_2) = \tilde{S}^{-1}(\vec{q}_1) = S(\vec{q}_1)/W(\vec{q}_1) - 2\chi \quad \text{(III-22)}$$

$$\Gamma_3(\vec{q}_1, \vec{q}_2, \vec{q}_3) = -G^{(3)}_{ijk}(\vec{q}_1, \vec{q}_2, \vec{q}_3)[S_{i1}^{-1}(\vec{q}_1) - S_{i2}^{-1}(\vec{q}_1)] \times [S_{j1}^{-1}(\vec{q}_2) - S_{j2}^{-1}(\vec{q}_2)][S_{k1}^{-1}(\vec{q}_3) - S_{k2}^{-1}(\vec{q}_3)] \quad \text{(III-23)}$$

$$\Gamma_4(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) = \gamma_{ijkl}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4)[S_{i1}^{-1}(\vec{q}_1) - S_{i2}^{-1}(\vec{q}_1)][S_{j1}^{-1}(\vec{q}_2) - S_{j2}^{-1}(\vec{q}_2)][S_{k1}^{-1}(\vec{q}_3) - S_{k2}^{-1}(\vec{q}_3)][S_{l1}^{-1}(\vec{q}_4) - S_{l2}^{-1}(\vec{q}_4)] \quad \text{(III-24)}$$

with

$$\gamma_{ijkl}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) = \mathcal{V}^{-1}\sum_{\vec{q}'} S_{mn}^{-1}(\vec{q}')[G^{(3)}_{ijm}(\vec{q}_1, \vec{q}_2, \vec{q}') \times G^{(3)}_{nkl}(-\vec{q}', \vec{q}_3, \vec{q}_4) + G^{(3)}_{ikm}(\vec{q}_1, \vec{q}_3, \vec{q}')G^{(3)}_{njl}(-\vec{q}', \vec{q}_2, \vec{q}_4) + G^{(3)}_{ilm}(\vec{q}_1, \vec{q}_4, \vec{q}')G^{(3)}_{nkj}(-\vec{q}', \vec{q}_3, \vec{q}_2)] - G^{(4)}_{ijkl}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) \quad \text{(III-25)}$$

For the case of $\vec{q}_1 + \vec{q}_2 = 0$ (or any other $\vec{q}_i + \vec{q}_j = 0$) formula III-25 is to be modified (compare the comment below eq III-17). The first term on the right-hand side of (III-25) takes the form

$$\sum_{mn} S^{-1}(0)G^{(3)}_{ijm}(\vec{q}_1, \vec{q}_2, 0)G^{(3)}_{nkl}(0, \vec{q}_3, \vec{q}_4) \quad \text{(III-26)}$$

In eq III-22 to III-26 the following notations has been used: $S_{ij}^{-1}(\vec{q})$ denotes the (i, j)th element of the matrix $\|S^{-1}(\vec{q})\|$—the inverse of the matrix $\|S(\vec{q})\|$ composed of the correlation functions of the ideal independent copolymer chain $S_{ij}(\vec{q})$; $S(\vec{q})$ denotes the sum of all elements of the matrix $\|S\|$ (i.e., $S = \sum_{ij}S_{ij}$); and $W(\vec{q})$ is the determinant of $\|S\|$ (i.e., $W = S_{11}S_{22} - S_{12}^2$).

A very remarkable property of the coefficients Γ_3 and Γ_4 in the expansion of the free energy in powers of the order parameter is their independence of the interaction constant χ. Actually eq III-23 to III-26 reveal that these coefficients depend solely on correlation functions of ideal copolymer chains, i.e., only on the composition f and the polymerization index N. This means that the terms of higher order than the second in the expansion of F in powers of ψ are of entropic origin and have no singular behavior at the transition point. It should be also noted that for $f = 0.5$, $S_{11} = S_{22}$ (for ideal chains) and $\Gamma_3 = 0$ as might be expected from the symmetry considerations.

Contrary to the coefficients Γ_3 and Γ_4 the coefficient of the second-order Γ_2 (eq III-22) depends on the interaction constant χ. The dependence on χ is particularly simple. This will facilitate the calculation of the spinodal line (see section V).

Equations III-22 to III-26 will be used to study the phase diagram of the block copolymer melt (sections V and VI). These equations are very general; they apply for any polymeric melt composed of two monomers (in particular they are valid also for a mixture of two homopolymers). Their application to a block copolymer melt requires preliminary knowledge of correlation functions of ideal copolymer chains. In Appendix B a general method of calculating these functions is described.

IV. Radiation Scattering by Liquid Copolymers

Radiation scattering experiments provide a very attractive method for studying the various aspects of the microphase separation. The scattering techniques of particular interest are those which give monomer correlation functions, i.e., which involve scattering vectors smaller than a^{-1} and even $N^{-1/2}a^{-1}$ (e.g., light, X-ray (SAXS), and neutron (SANS) small-angle scattering).

Below the MST, the scattering by the periodic microdomain structure gives the characteristic diffraction spectrum. The detailed structure of the Bragg peaks reflects the symmetry and the periodicity of the system (e.g., ref 5 and 8). Above the transition, in the disordered phase, the scattering spectrum is completely different from that observed below the MST as well as from that of a liquid composed from small molecules. The discussion of the scattering by the disordered phase is the subject of the present section. Particular emphasis will be laid on the role of monomer interactions. In this respect the choice of an appropriate experimental technique should be carefully considered. SAXS is very suitable when the chemical species of the copolymer chain have significantly different electron densities (e.g., copoly(styrene–isoprene)), which usually implies a high degree of incompatibility, i.e., a rather large χ. Consequently, the studied structure will exhibit a microdomain architecture (unless chains are sufficiently short) and a diffraction pattern will be observed. On the other hand, neutron scattering experiments may permit study of copolymers formed from two very similar species (e.g., copoly(styrene–α-dimethylstyrene) if only one of them is deuterated. It is even possible to deal with partially deuterated chains composed of the same monomers (e.g., polystyrene), in which a case the interaction constant is very small ($\chi \sim 10^{-4}$–10^{-3}). Therefore, the SANS technique offers a possibility for studying the copolymers in both cases when a microphase separation occurs or not, even for long chains.

The scattering intensity for the disordered phase of the block copolymer is proportional to the correlation function $\tilde{S}(\vec{q})$. Within the RPA this function is given by (see Appendix A, eq A-7)

$$\tilde{S}(\vec{q}) = W(\vec{q})/[S(\vec{q}) - 2\chi W(\vec{q})] \quad \text{(IV-1)}$$

where S is the sum of all elements and W the determinant of the matrix composed of the correlation functions of the ideal independent copolymer chains $\|S_{ij}\|$. The calculation of $S_{ij}(\vec{q})$ functions with the help of the method exposed in Appendix B is straightforward. For $fN \gg 1$ and $N(1-f) \gg 1$ one gets (see B-18)

$$S_{11}(\vec{q}) = Ng_1(f, x)$$
$$S_{22}(\vec{q}) = Ng_1(1-f, x) \qquad \text{(IV-2)}$$
$$S_{12}(\vec{q}) = S_{21}(\vec{q}) = \tfrac{1}{2}N[g_1(1, x) - g_1(f, x) - g_1(1-f, x)]$$

where $g_1(f, x)$, the Debye function, is defined as

$$g_1(f, x) = 2[fx + \exp(-fx) - 1]/x^2 \qquad \text{(IV-3)}$$

and

$$x = q^2Na^2/6 = q^2R^2 \qquad \text{(IV-4)}$$

with R denoting the radius of gyration of an ideal chain with N monomers. The final formula for $\tilde{S}$ reads

$$\tilde{S}(\vec{q}) = N/[F(x) - 2\chi N] \qquad \text{(IV-5)}$$

where

$$F(x) = g_1(1, x)/\{g_1(f, x)g_1(1-f, x) - \tfrac{1}{4}[g_1(1, x) - g_1(f, x) - g_1(1-f, x)]^2\} \qquad \text{(IV-6)}$$

Equation IV-5 for the scattering function $\tilde{S}(\vec{q})$ shows that for large $\vec{q}$ vectors ($qR \gg 1$), $\tilde{S}(\vec{q})$ tends to zero like $1/q^2$

$$\tilde{S}(\vec{q}) \approx 2Nf(1-f)/q^2R^2 \qquad \text{(IV-7)}$$

This means that on the scale of a coil the monomer density fluctuations are like those of a Gaussian chain and are independent of the effective repulsion between monomers A and B. Also for very small $\vec{q}$ vectors ($qR \ll 1$) the correlation function does not depend on the interaction parameter χ

$$\tilde{S}(\vec{q}) \simeq 2Nf^2(1-f)^2q^2R^2/3 \qquad \text{(IV-8)}$$

At small angles ($q = 0$) the scattering power vanishes. This is due to the incompressibility of the system. The increase of $\tilde{S}$ with q (eq IV-8) is related to the correlation hole effect:[34] the probability of finding in the vicinity of an A monomer another A monomer belonging to a different chain is slightly decreased as the result of the repulsion of the polymer coils (this repulsion ensures the incompressibility of the system). This particular asymptotic behavior (for $qR \ll 1$ and $qR \gg 1$) requires that the A monomers' correlation function $\tilde{S}$ has a maximum in the intermediate range $qR \sim 1$. It should be stressed, however, that the existence of this maximum does not result from the segregation effects. Actually, as the asymptotic behavior is independent of χ, even when there is no effective repulsion between monomers A and B ($\chi = 0$), $\tilde{S}(\vec{q})$ has a maximum for scattering vectors $\vec{q}$ with the length $|\vec{q}| = q^*$ (see Figure 3). Recently, a peak (bump) in scattering intensity has been observed in SANS by a liquid polystyrene with partially deuterated chains (triblock chains).[46] Good agreement with the RPA theory with $\chi = 0$ has been found (N of the chains was $\sim$400 so it is reasonable to neglect segregation effects and put $\chi N = 0$).

Although the presence of the peak in $\tilde{S}(\vec{q})$ is independent of the segregation effects, its shape strongly depends on the interaction parameter χ. Equation IV-5 shows that the relevant parameter is the product χN rather than χ. Figure 1 gives the plot of $\tilde{S}(\vec{q})$ as a function of $x = q^2R^2$ for different values of χN. First of all we observe that the peak becomes more narrow and its maximum higher when χN is increased. There is a certain critical value of χN, $(\chi N)_s$, for which the correlation function $\tilde{S}(\vec{q})$ diverges at $|\vec{q}| = q^*$; this is the spinodal point (cf. section V). However, the instability is masked by the earlier appearance of a first-order transition to a mesophase for $(\chi N)_t < (\chi N)_s$; see section V). It is very important to stress that for χN close to $(\chi N)_s$ the peak is so narrow that $\tilde{S}(\vec{q})$ may be neglected for all $\vec{q}$ vectors which do not lay on the sphere of the radius q^*.

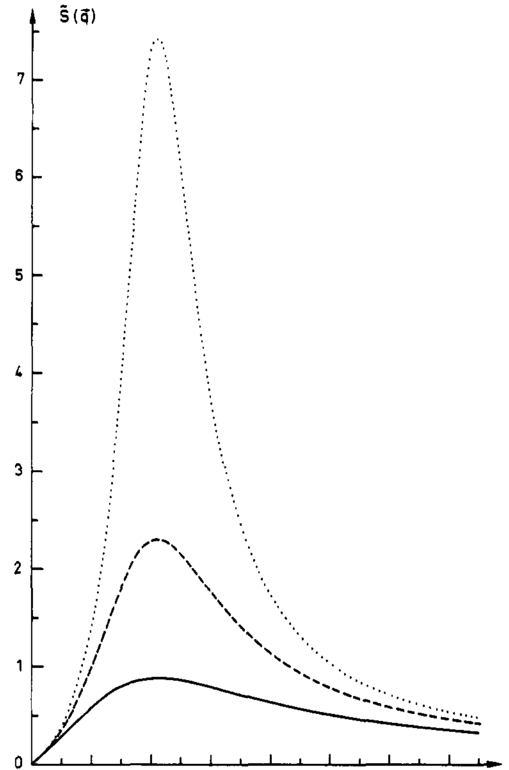

Figure 1. Scattering intensity (in arbitrary units) of the molten diblock copolymer with composition $f = 0.25$ as a function of $x = (qR)^2$ ($q = 4\pi[\sin(\theta/2)]/\lambda$) for three values of interaction parameter: (···) $\chi N = 17.5$; (---) $\chi N = 16.0$; (—) $\chi N = 12.5$. The interaction parameter for which $\tilde{S}(q^*)$ diverges (spinodal point) is given by $\chi N = 18.2$. The MST is expected to occur for $\chi N = 17.6$.

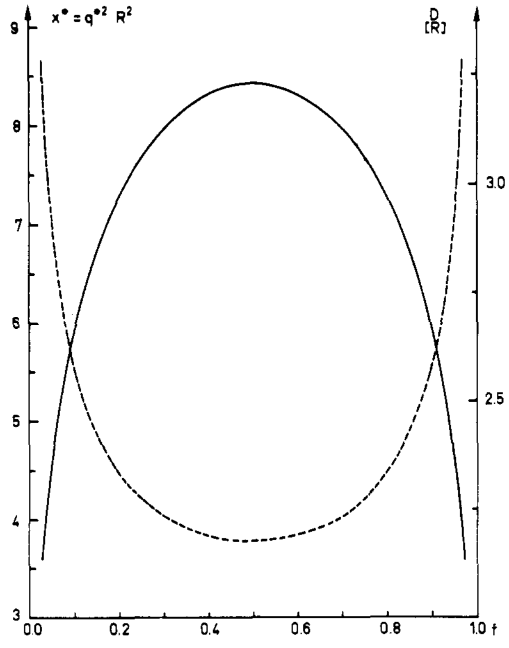

Figure 2. Plot of $x^* = q^{*2}R^2$ vs. composition f (—) and of the periodicity D (the unit is R) of the mesophase just after the MST (---).

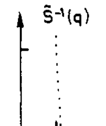

Figure 3. Plot of $\tilde{S}^{-1}(\vec{q})$ as a function of $x = q^2R^2$ for the sample with $f = 0.4$ and for three values of χN: (···) $\chi N = 0.0$; (---) $\chi N = 2.0$; (—) $\chi N = 5.0$. The curves for the different χN are parallel.

Figure 1 shows that the position of the maximum q^* does not depend on the monomer interactions. In fact, expression IV-5 has a maximum for $x^* = q^{*2}R^2$ for which the function $F(x^*)$ (independent of χ) has a minimum. This is due to the fact that the monomer interactions are local and would not be the case if they had a finite range. The shape of the peak and the position of its maximum depend on the chains' composition f. Figure 2 shows a plot of x^* vs. f. The dependence is weak for $0.2 < f < 0.8$ for which q^* is of the order of $2/R$. For f small (large) q^* increases rapidly.

The fact that the correlation function $\tilde{S}(\vec{q})$ is sensitive to the interactions provides a direct method of measuring the interaction parameter χ. Actually by measuring the scattering intensity by a molten block copolymer with chains with different molecular mass (but the same composition f) and by plotting the extracted $\tilde{S}^{-1}(\vec{q})$ vs. q^2R^2, one should obtain a series of parallel curves (Figure 3). The relative distance between the curves even for small χN is rather large, so the method seems to be promising.

The value of spinodal point $(\chi N)_s$ at which the instability occurs depends on the composition f of the chain. This dependence is illustrated in Figure 4.

V. Stability of Ordered Phases

In this section we predict the symmetry and the periodicity of the microdomain structure appearing just after the microphase separation transition (section V.1). Then we study the stability of various microdomain patterns and determine conditions of their equilibria (section V.2). These considerations lead to a phase diagram of the diblock copolymer melt which will be discussed in section VI.

1. Criterion of the Microphase Separation. A. Landau Theory of the MST.

We shall use a Landau-type analysis[47] to describe the MST. In this approach the free-energy density functional obtained in section III should be minimized with respect to the order parameter $\psi(\vec{r})$ for different values of the interaction parameter χ (temperature T). This rather formidable task is much simplified when one considers the copolymer liquid near its spinodal point, i.e., when χN is close to the value $(\chi N)_s$ for which $\tilde{S}(q^*)$ diverges. Actually, in such a case the correlation function has a very pronounced maximum for $|\vec{q}| = q^*$ (cf. section IV and Figure 1). The contribution to the quadratic term in the free-energy expansion (eq III-13, -14, -22)

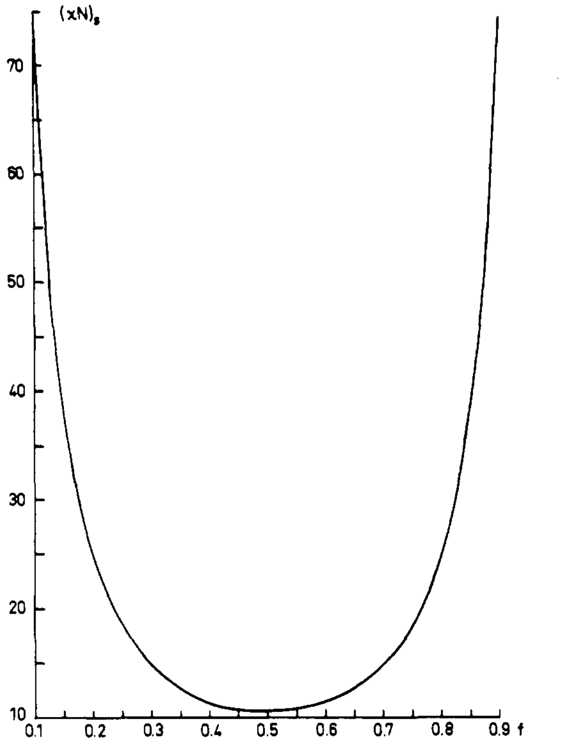

Figure 4. The spinodal point $(\chi N)_s$ as a function of composition f. For $\chi N = (\chi N)_s$, $\tilde{S}(q^*)$ diverges.

$$F_2 = \tfrac{1}{2}\mathcal{V}^{-1}\sum_{\vec{q}}\tilde{S}^{-1}(\vec{q})\psi(\vec{q})\psi(-\vec{q}) \qquad \text{(V-1)}$$

from the Fourier components of ψ with $|\vec{q}| \neq q^*$ is very large. The terms of higher order in ψ (F_3, F_4, ...) have no singularity for $\chi N = (\chi N)_s$ so that the contributions of $\psi(\vec{q})$ to F_3, F_4, ... with different $\vec{q}$ are roughly equivalent. This implies that near the spinodal the important fluctuations should be those with wave vectors $|\vec{q}| = q^*$ and that $\psi(\vec{r})$ may be approximated by

$$\psi(\vec{r}) = \sum_{\vec{q}\in\{\pm\vec{Q}_i\}}\psi(\vec{q})e^{i\vec{q}\vec{r}} \qquad \text{(V-2)}$$

$$|\vec{Q}_i| = q^*$$

$$i = 1, ..., n$$

with $\psi^*(\vec{q}) = \psi(-\vec{q})$. From eq IV-1 and from the definition of the spinodal point

$$F_2 = \tilde{S}^{-1}(q^*)\sum_{\vec{q}\in\{\pm\vec{Q}_i\}}\psi(\vec{q})\psi(-\vec{q}) = 2N(\chi_s - \chi)\sum_{\vec{q}\in\{\pm\vec{Q}_i\}}|\psi(\vec{q})|^2 \qquad \text{(V-3)}$$

The coefficient of this term is independent of the specific set $\{\vec{Q}_i\}$. Therefore, to study the stability of different ordered phases the free energy density should be minimized at fixed $\sum_{\vec{q}\in\{\pm\vec{Q}_i\}}|\psi(\vec{q})]^2$. Making use of the symmetry properties of the coefficients $\Gamma_3(\vec{q}_1, \vec{q}_2, \vec{q}_3)$ and $\Gamma_4(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4)$, one can argue that at equilibrium the magnitude $|\psi(\vec{q})|$ for all $\vec{q} \in \{\pm\vec{Q}_i\}$ should be equal. However, the relative phase of different components $\psi(\vec{q})$ may be important. Thus, the order parameter $\psi(\vec{r})$ takes the form

$$\psi(\vec{r}) = \frac{1}{\sqrt{n}}\psi_n \sum_{k=1}^{n} \{\exp[i(\vec{Q}_k\vec{r} + \varphi_k)] + \mathrm{cc}\} \qquad \text{(V-4)}$$

The equilibrium value of the amplitude ψ_n, $\bar{\psi}_n$, for an ordered phase characterized by the set $\{\vec{Q}_i\}$ $(i = 1, ..., n)$ is to be determined by minimizing the free-energy density F with respect to ψ_n and $\{\varphi_n\}$. For a given χN the stable phase is that corresponding to the smallest free energy $F(\bar{\psi}_n)$. As far as the MST is concerned, one can calculate χN at which the transition to different possible ordered phases may occur. In principle, the mesophase actually appearing is that corresponding to the smallest χN (the highest temperature T). The calculus shows that this value $(\chi N)_t$ is close to the spinodal $(\chi N)_s$ for a large range of compositions f. This justifies the adopted approach (see section VI).

It should be pointed out that the third- and the fourth-order terms F_3 and F_4 depend crucially on the set $\{\vec{Q}_i\}$. For this reason, a prediction of the conditions of the MST requires a detailed analysis of F_3 and F_4. As we have already mentioned, for $f \neq 0.5$ the third-order term F_3 does not vanish identically and the MST is, in general, a first-order phase transition occurring for $(\chi N)_t < (\chi N)_s$. From eq III-13, III-23, A-11, and V-2

$$F_3 = \frac{1}{3!}\mathcal{V}^{-3} \sum_{\vec{q}_1,\vec{q}_2,\vec{q}_3 \in \{\pm\vec{Q}_i\}} \Gamma_3(\vec{q}_1, \vec{q}_2, \vec{q}_3)\psi(\vec{q}_1)\psi(\vec{q}_2)\psi(\vec{q}_3) \qquad \text{(V-5)}$$

Since $\Gamma_3(\vec{q}_1, \vec{q}_2, \vec{q}_3)$ vanishes unless $\vec{q}_1 + \vec{q}_2 + \vec{q}_3 = 0$ (cf. eq III-12 and III-23) and $|\pm\vec{Q}_i| = q^*$, the vectors $\vec{q}_1$, $\vec{q}_2$, and $\vec{q}_3$ are constrained to form an equilateral triangle, which means that at least three $\vec{Q}_i$ $(n \geq 3)$ occur in the expression for the order parameter $\psi(\vec{r})$ (eq V-4). It is important to note that $F_3 \sim \psi_n^3 n^{-1/2}$, so that only structures with small n are to be analyzed (since they give the smallest χN for the transition). The following simplest cases are allowed (cf., e.g., ref 38): $n = 3$, 6, and 15; for other $n < 15$ any set $\{\vec{Q}_i\}$ gives a contribution to F_3 identically equal to zero.

The case $n = 3$ corresponds to a two-dimensional triangular (honeycomb) lattice. The $\{\vec{Q}_i\}$ set may be chosen as follows:

$$\vec{Q}_{t1} = q^*[1, 0, 0] \qquad \vec{Q}_{t2} = \tfrac{1}{2}q^*[-1, \sqrt{3}, 0] \qquad \vec{Q}_{t3} = \tfrac{1}{2}q^*[-1, -\sqrt{3}, 0] \qquad \text{(V-6)}$$

Such a symmetry has, for instance, a rodlike mesophase with A-monomer-rich cylinders forming a planar triangular lattice in a B-monomer-rich matrix $(f < 0.5)$.

When $n = 6$ the $\vec{Q}_i$ vectors may be chosen to form an octahedron

$$\begin{aligned} \vec{Q}_{b1} &= 2^{-1/2}q^*(1, 1, 0) & \vec{Q}_{b2} &= 2^{-1/2}q^*(-1, 1, 0) \\ \vec{Q}_{b3} &= 2^{-1/2}q^*(0, 1, 1) & \vec{Q}_{b4} &= 2^{-1/2}q^*(0, 1, -1) \\ \vec{Q}_{b5} &= 2^{-1/2}q^*(1, 0, 1) & \vec{Q}_{b6} &= 2^{-1/2}q^*(1, 0, -1) \end{aligned} \qquad \text{(V-7)}$$

The reciprocal lattice spanned by $\pm\vec{Q}_i$ is a face-centered-cubic (fcc) lattice and a corresponding lattice in $\vec{r}$ space is a body-centered-cubic (bcc) lattice. Such a symmetry would have, for instance, a spherical mesophase with A-monomer-rich spheres located in a B-monomer-rich matrix at the sites of a bcc lattice $(f < 0.5)$.

The case $n = 15$ corresponds to $\vec{Q}_i$ parallel to the edges of a regular icosahedron. However, the regular icosahedron has the fivefold axis so that $\vec{Q}_i$ vectors cannot span a periodic lattice (cf., e.g., ref 49).

Therefore, we conclude that there are two microdomain structures that may appear after the MST: the hexagonal and bcc mesophases. In order to decide which mesophase will actually appear, it is necessary to analyze the free energy of these phases in more detail.

B. Free Energy of Hexagonal and bcc Mesophases. Let us consider a mesophase characterized by the set of vectors $\{\vec{Q}_i\}$ $(i = 1, 2, ..., n)$. Its free-energy density may be written in the form

$$FN/kT = 2N(\chi_s - \chi)\psi_n^2 - \alpha_n\psi_n^3 + \beta_n\psi_n^4 \qquad \text{(V-8)}$$

The determination of the coefficients α_n and β_n requires rather tedious calculations of the correlation functions of Gaussian chains by the method explained in Appendix B. For the sake of simplicity it is important to use some symmetry properties of coefficients Γ_3 and Γ_4 and to contract the notation.

First of all we note that $\Gamma_3(\vec{q}_1, \vec{q}_2, \vec{q}_3)$ vanishes unless $\vec{q}_1 + \vec{q}_2 + \vec{q}_3 = 0$ and all nonvanishing $\Gamma_3(\vec{q}_1, \vec{q}_2, \vec{q}_3)$ are equal (since $|\vec{q}_1| = q^*$) and will be denoted by Γ_3. The coefficient $\Gamma_4(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) \neq 0$ only if $\sum_{i=1}^{4}\vec{q}_i = 0$, so that Γ_4 depends only on the two independent angles, e.g., between vectors $\vec{q}_1$ and $\vec{q}_2$ and between vectors $\vec{q}_1$ and $\vec{q}_4$ (since $|\vec{q}_i| = q^*$). When these angles are equal for two different sets $\{\vec{q}_i\}$ the coefficients are also equal, e.g., $\Gamma_4(\vec{Q}_{t1}, -\vec{Q}_{t1}, \vec{Q}_{t2}, -\vec{Q}_{t2}) = \Gamma_4(\vec{Q}_{b1}, -\vec{Q}_{b1}, \vec{Q}_{b3}, -\vec{Q}_{b3})$. Therefore, it is convenient to adopt the following notation: $\Gamma_4(\{\vec{q}_i\}) = \Gamma_4(h_1, h_2)$, where $|\vec{q}_1 + \vec{q}_2|^2 = h_1 q^{*2}$ and $|\vec{q}_1 + \vec{q}_4|^2 = h_2 q^{*2}$. It should be noted that $\Gamma_4(h_1, h_2) = \Gamma_4(h_1, 4 - h_1 - h_2) = \Gamma_4(h_2, 4 - h_1 - h_2)$ since $|\vec{q}_1 + \vec{q}_2|^2 = |\vec{q}_3 + \vec{q}_4|^2$, $|\vec{q}_1 + \vec{q}_4|^2 = |\vec{q}_2 + \vec{q}_3|^2$, and $|\vec{q}_1 + \vec{q}_3|^2 = |\vec{q}_2 + \vec{q}_4|^2 = (4 - h_1 - h_2)q^{*2}$. All vectors $\vec{q}_1$ lie in the same plane if h_1 or h_2 is equal to 0 or $h_1 + h_2 = 4$.

Making use of this notation and of eq V-4, we get the following formulas for the coefficients α_3 and β_3 in expression V-8 for the free-energy density of the triangular mesophase:

$$\alpha_3 = -(2/3\sqrt{3})N\Gamma_3 \cos(\varphi_{t1} + \varphi_{t2} + \varphi_{t3}) \qquad \text{(V-9)}$$

$$\beta_3 = N[\Gamma_4(0, 0) + 4\Gamma_4(0, 1)]/12 \qquad \text{(V-10)}$$

In order to determine the relative phase φ_{t1}, φ_{t2}, and φ_{t3} of Fourier components $\psi(\vec{q}_{ti})$ $(i = 1, 2, 3)$, one should minimize F with respect to φ_{ti} $(i = 1, 2, 3)$. This gives the condition $\cos(\varphi_{t1} + \varphi_{t2} + \varphi_{t3}) = 1$ (as $-\Gamma_3$ turns out to be positive) and, then

$$\alpha_3 = -(2/3\sqrt{3})N\Gamma_3 \qquad \text{(V-11)}$$

Within the approximation adopted here (dropping out terms F_5, F_6, ...) it is not possible to determine the relative phases of $\psi(\vec{Q}_{ti})$ with more precision. However, this ambiguity in the detailed form of $\psi(\vec{r})$ is not important for calculation of the microphase separation criterion.

The coefficients α_6 and β_6 for the bcc mesophase are equal to

$$\alpha_6 = -(1/3\sqrt{6})N\Gamma_3\{\cos\alpha + \cos\beta + \cos\gamma + \cos(\alpha - \beta + \gamma)\} \qquad \text{(V-12)}$$

$$\beta_6 = N\{\Gamma_4(0, 0) + 8\Gamma_4(0, 1) + 2\Gamma_4(0, 2) + 2\Gamma_4(1, 2) \times [\cos(\alpha + \gamma) + \cos(\beta - \gamma)]\}/24 \qquad \text{(V-13)}$$

where $\alpha = \varphi_1 - \varphi_3 - \varphi_6$, $\beta = \varphi_1 - \varphi_4 - \varphi_5$, and $\gamma = \varphi_2 - \varphi_4 + \varphi_6$. The free-energy density takes the minimal value for $\alpha = \beta = \gamma = 0$. (Also for the bcc mesophase the minimization procedure does not permit a determination of all of the relative phases φ_i $(i = 1, 2, ..., 6)$). Thus

$$\alpha_6 = -(4/3\sqrt{6})N\Gamma_3 \qquad \text{(V-14)}$$

$$\beta_6 = N\{\Gamma_4(0, 0) + 8\Gamma_4(0, 1) + 2\Gamma_4(0, 2) + 4\Gamma_4(1, 2)\}/24 \qquad \text{(V-15)}$$

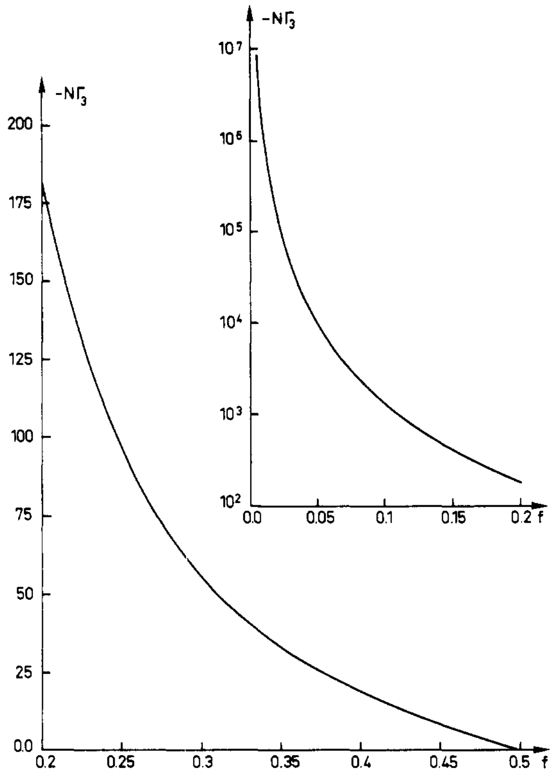

Figure 5. ($-N\Gamma_3$) as a function of composition f.

The coefficients Γ_3 and $\Gamma_4(h_1, h_2)$ occurring in the formulas for α_3, β_3, α_6, and β_6 may be calculated with the help of eq III-22 to III-26. One gets

$$\Gamma_3 = -G_{ijk}(1)[S_{i1}^{-1} - S_{i2}^{-1}][S_{j1}^{-1} - S_{j2}^{-1}][S_{k1}^{-1} - S_{k2}^{-1}] \tag{V-16}$$

$$\Gamma_4(h_1, h_2) = \gamma_{ijkl}(h_1, h_2)[S_{i1}^{-1} - S_{i2}^{-1}][S_{j1}^{-1} - S_{j2}^{-1}][S_{k1}^{-1} - S_{k2}^{-1}] \tag{V-17}$$

with

$$\begin{aligned}\gamma_{ijkl}(h_1, h_2) = {} & G_{ijm}(h_1)S_{mn}^{-1}(h_1x^*)G_{klm}(h_1) + \\ & G_{ilm}(h_2)S_{mn}^{-1}(h_2x^*)G_{jkn}(h_2) + G_{ikm}(4 - h_1 - h_2) \times \\ & S_{mn}^{-1}((4 - h_1 - h_2)x^*)G_{jln}(4 - h_1 - h_2) - G_{ijkl}(h_1, h_2)\end{aligned} \tag{V-18}$$

$S_{ij}^{-1} = S_{ij}^{-1}(x^*)$ and $S_{ij}^{-1}(0) = 1/N$. In writing the correlation functions of the ideal copolymer chain, we have introduced a notation similar to that used for coefficients Γ_3 and Γ_4. Therefore $G^{(4)}_{ijkl}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4)$ is denoted by $G_{ijkl}(h_1, h_2)$ and $G^{(3)}_{ijk}(\vec{q}_1, \vec{q}_2, \vec{q}_3)$ by $G_{ijk}(h)$, where $|\vec{q}_1 + \vec{q}_2|^2 = |q_3|^2 = hq^{*2}$ ($\vec{q}_1 + \vec{q}_2 + \vec{q}_3 = 0$). The formulas for $G_{ijk}(h)$ and $G_{ijkl}(h_1, h_2)$ are given in Appendix C. Putting eq C-1 to C-14 into eq V-16 to V-18 and setting $x = x^*$, one can calculate Γ_3, $\Gamma_4(0, 0)$, $\Gamma_4(0, 1)$, $\Gamma_4(0, 2)$, and $\Gamma_4(1, 2)$. In Figure 5 we have plotted $-N\Gamma_3$ as a function of the composition f. Figure 6 shows plots of $N\Gamma_4(0, 0)$, $N\Gamma_4(0, 2)$, and $N\Gamma_4(1, 2)$ vs. the composition f. In the scale of Figure 6 it is not possible to distinguish between $\Gamma_4(0, 1)$ and $\Gamma_4(0, 2)$. It is important to stress that for all f, $\Gamma_4(0, 2) > \Gamma_4(0, 1)$.

C. Conditions for the MST. Periodicity of the Ordered Phase. The conditions for the transition from the disordered phase to the mesophase (characterized by $n = 3$ or $n = 6$) may be written as

$$\left.\frac{\partial F}{\partial \psi_n}\right|_{\psi_n=\bar{\psi}_n} = 0 \qquad \left.\frac{\partial^2 F}{\partial {\psi_n}^2}\right|_{\psi_n=\bar{\psi}_n} > 0 \qquad F(\bar{\psi}_n, \chi_n) = 0 \tag{V-19}$$

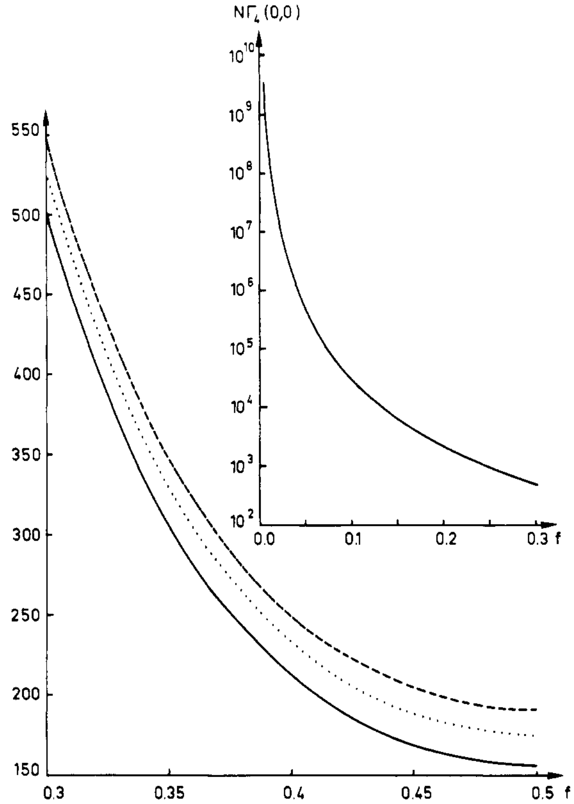

Figure 6. $N\Gamma_4(0, 0)$ (—), $N\Gamma_4(0, 1)$ (···), and $N\Gamma_4(1, 2)$ (---) vs. f. The difference between $N\Gamma_4(0, 1)$ and $N\Gamma_4(0, 2)$ cannot be illustrated in the scale of the picture. For $f < 0.3$ in the scale of the figure there is no difference between $N\Gamma_4(0, 0)$, $N\Gamma_4(0, 1)$, $N\Gamma_4(0, 2)$, and $N\Gamma_4(1, 2)$.

The first two conditions express the fact that at equilibrium the order parameters $\bar{\psi}_n$ take the value which minimizes the free energy F. The last condition says that at the transition point ($\chi = \chi_n$), F vanishes (as it vanishes in the disordered phase). From (V-9) and (V-19)

$$\bar{\psi}_n = 3\alpha_n(1 + \gamma_n)/8\beta_n \tag{V-20}$$

with

$$\gamma_n = [1 - 64\beta_n(\chi_s - \chi)N/9{\alpha_n}^2]^{1/2} \tag{V-21}$$

$F(\bar{\psi}_n) = 0$ requires $\psi_n = {}^1/_3$ and consequently

$$\chi_n N = \chi_s N - {\alpha_n}^2/8\beta_n \tag{V-22}$$

Equations V-10, V-11, and V-16 to V-18 and eq C-1 to C-3 and C-7 to C-11 show both coefficients α_n and β_n do not depend directly on N (only through x^*), which means that the relevant parameter is the product χN and not χ itself. In order to predict the phase which appears after the MST ${\alpha_3}^2/\beta_3$ and ${\alpha_6}^2/\beta_6$ should be compared. From (V-12 to V-15) and (V-22) it follows that a bcc mesophase appears first if

$$k = \frac{4[\Gamma_4(0, 0) + 4\Gamma_4(0, 1)]}{\Gamma_4(0, 0) + 8\Gamma_4(0, 1) + 2\Gamma_4(0, 2) + 4\Gamma_4(1, 2)} > 1 \tag{V-23}$$

Otherwise the triangular structure will appear. It is important to note that ${\alpha_3}^2 < {\alpha_6}^2$; i.e., the bcc phase is favored by the third-order term. However, $\beta_3 < \beta_6$ (as is shown by our calculation in section V.1B) and it is not obvious that the bcc mesophase appears first. For this reason inequality V-21 must be carefully examined. The detailed numerical calculations employing formulas of Appendix C show that for all compositions (V-21) is fulfilled and that

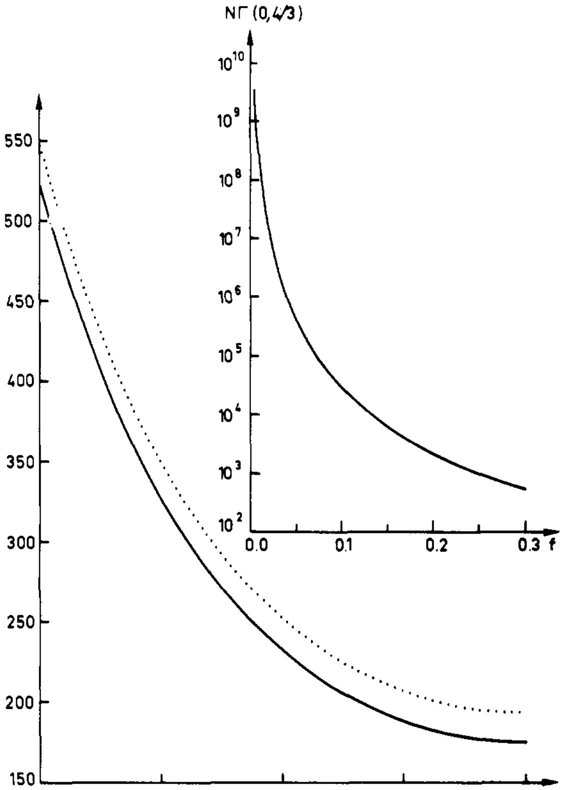

Figure 7. Plot of $N\Gamma_4(0, {}^4/_3)$ (—) and $N\Gamma_4({}^4/_3, {}^4/_3)$ (···) vs. f.

the bcc mesophase is expected to appear just after the MST. Actually, it turns out (cf. Figures 5 and 6) that for any f $\Gamma_4(0, 0) < \Gamma_4(0, 1) < \Gamma_4(0, 2) < \Gamma_4(1, 2)$ and therefore $k > 4\Gamma_4(0, 0)/3\Gamma_4(1, 2)$. The ratio $\Gamma_4(0, 0)/\Gamma_4(1, 2)$ has a minimum for $f = 0.5$ and increases as f tends to 0 or 1. For $f = 0.5$, $\Gamma_4(0, 0)/\Gamma_4(1, 2) \simeq 0.82$, which means that $k > 1$ and that (V-23) is fulfilled for any $f \neq 0.5$.

Hence, the structure which appears first is the mesophase with the body-centered-cubic lattice symmetry. The condition for the microphase separation transition reads

$$(\chi N)_t = \chi_6 N = (\chi N)_s - 8N\Gamma_3{}^2/9[\Gamma_4(0, 0) + 8\Gamma_4(0, 1) + 2\Gamma_4(0, 2) + 4\Gamma_4(1, 2)] \tag{V-24}$$

For $\chi N < (\chi N)_t$ the system exhibits the disordered phase. The calculated $(\chi N)_t$ is plotted vs. f in Figure 8. The periodicity of the system just after the transition is $D = 2\pi/q^*$ (see Figure 2).

Let us remark that the above considerations do not apply to $f = 0.5$. For this composition the free-energy density F must be invariant with respect to the change of $\psi = \langle \delta\rho_A \rangle$ into $-\psi = \langle \delta\rho_A \rangle$. Thus, the third-order term in F, F_3, vanishes identically and the Landau theory predicts the second-order phase transition. We will return to this point in the next section.

2. Transitions between Different Ordered Phases. In this section we will study various ordered phases near the spinodal point, $\chi N > (\chi N)_s$. We are interested in regions where these different phases are stable and in conditions for phase transitions. We assume that $|\chi N - (\chi N)_s| \ll (\chi N)_s$, so that the ordered parameter may be still written in the form (V-2) and that all fluctuations with wave vectors $|\vec{q}| \neq q^*$ are negligible. It should be noted that, as $\chi N > (\chi N)_s > (\chi N)_t$, the second-order term in the free-energy expansion (V-3) is negative, which implies that even a phase with the vanishing third-order term (V-5) may be the stable one. It is the stability of phases with $F_3 = 0$ we analyze first. Consider a phase characterized by the set of vectors $\{\vec{Q}_i\}$ ($i = 1, ..., n$) for which $\alpha_n = 0$; the free energy (V-8) is equal to

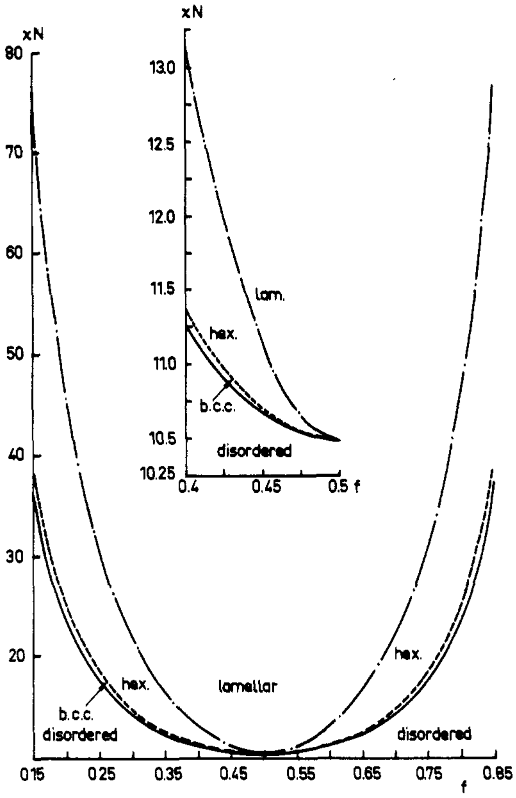

Figure 8. Phase diagram for the diblock copolymer: (—) transition line from the disordered to the bcc phase ($(\chi N)_t$ vs. f); (---) transition line from the bcc phase to the hexagonal mesophase ($(\chi N)_1$ vs. f); (–·–) transition line from the hexagonal to the lamellar mesophase $(\chi N)_3$ vs. f.

$$FN/kT = -N^2(\chi - \chi_s)^2/\beta_n \tag{V-25}$$

since at equilibrium $\bar{\psi}_n{}^2 = N(\chi - \chi_s)/\beta_n$. Thus, for all χN (close to $(\chi N)_s$) the stable phase is that with the smallest coefficient β_n (of course, this phase may be less stable than a phase for which $\alpha_n \neq 0$; this problem will be discussed later). We calculate β_n for different microdomain structures.

One-Dimensional Structure. Lamellar Mesophase. The one-dimensional structure, the lamellar mesophase, corresponds to the case $n = 1$ with $\vec{Q} = q^*[1, 0, 0]$. In such a phase the monomer-A density is constant in the plane yz but varies along the x axis. From (V-11) we get

$$\beta_1 = N\Gamma_4(0, 0)/4 \tag{V-26}$$

The coefficient $\Gamma_4(0, 0)$ has been calculated in section V.1.

Two-Dimensional Structures. There are two types of two-dimensional structures. The first, the triangular mesophase, already discussed, has the symmetry of a planar triangular (honeycomb) lattice ($n = 3$). The second corresponds to $n = 2$ and has the symmetry of a rhombic lattice ($\vec{Q}_1$ and $\vec{Q}_2$ form the angle ν, $h = |\vec{Q}_1 + \vec{Q}_2|/q^{*2} = 4\cos^2(\nu/2)$). The coefficient β_2 is equal to (cf. eq V-11)

$$\beta_2 = N[\Gamma_4(0, 0) + 2\Gamma_4(0, h)]/8 \tag{V-27}$$

Three-Dimensional Structures. Simple Cubic Mesophase. This mesophase corresponds to $\psi(\vec{r})$ which has the symmetry of a simple cubic lattice. The $\vec{Q}$ vectors may be chosen to be $\vec{Q}_1 = q^*[1, 0, 0]$, $\vec{Q}_2 = q^*[0, 1, 0]$, and $\vec{Q}_3 = q^*[0, 0, 1]$ ($n = 3$). The coefficient β_c is equal to

$$\beta_c = N[\Gamma_4(0, 0) + 4\Gamma_4(0, 2)]/12 \tag{V-28}$$

Rhombohedric Mesophase. This mesophase would be characterized by $\psi(\vec{r})$ that has the symmetry of a rhombohedric lattice spanned by the following $\vec{Q}$ vectors: $\vec{Q}_1 = q^*[1, 0, 0]$, $\vec{Q}_2 = q^*[\cos\alpha, \sin\alpha, 0]$, and $\vec{Q}_3 = q^*[\cos\alpha, \cos\alpha \tan(\alpha/2), 1 - \cos^2\alpha\{1 + \tan^2(\alpha/2)\}]$ ($n = 3$). The coefficient β_r equals

$$\beta_r = N[\Gamma_4(0, 0) + 4\Gamma_4(0, 4\tan^2(\alpha/2))]/12 \qquad \text{(V-29)}$$

Face-Centered-Cubic (fcc) Mesophase (Close-Packed Hexagonal). This mesophase is characterized by $\psi(\vec{r})$ which has the symmetry of a fcc lattice (or a hexagonal-close-packed lattice). The corresponding $\vec{Q}$ vectors are $\vec{Q}_1 = q^*[1, 1, 1]/\sqrt{3}$, $\vec{Q}_2 = q^*[-1, 1, 1]/\sqrt{3}$, $\vec{Q}_3 = q^*[-1, -1, 1]/\sqrt{3}$, and $\vec{Q}_4 = q^*[1, 1]/\sqrt{3}$ ($n = 4$). The coefficient β_4 equals

$$\beta_4 = N[\Gamma_4(0, 0) + 6\Gamma_4(0, 4/3) + 2\Gamma_4(4/3, 4/3) \times \cos(\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4)]/16$$

and F takes a minimal value for $\cos(\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4) = -1$ so that

$$\beta_4 = N[\Gamma_4(0, 0) + 6\Gamma_4(0, 4/3) - 2\Gamma_4(4/3, 4/3)]/16 \qquad \text{(V-30)}$$

The coefficients $N\Gamma_4(0, {}^4/_3)$ and $N\Gamma_4({}^4/_3, {}^4/_3)$ are plotted vs. f in Figure 7.

It should be noted that the coefficient $\Gamma_4(0, h)$ has a minimum for $h = 0$, increases with an increase in h, and takes a maximum value for $h = 2$. Then for $h \rightarrow 4$, $\Gamma_4(0, h)$ tends to $\Gamma_4(0, 0)$ (cf. Figure 6). It should also be stressed that $\Gamma_4({}^4/_3, {}^4/_3) > \Gamma_4(0, 0)$. Hence $\beta_2 > 3N\Gamma_4(0, 0)/8$, β_c and $\beta_r > 5N\Gamma_4(0, 0)/12$, and $\beta_4 > N[7\Gamma_4(0, 0) - 2\Gamma_4({}^4/_3, {}^4/_3)]/16$; we see that the most stable phase is the lamellar phase for which $\beta_1 = N\Gamma_4(0, 0)/4$ (cf. eq V-25) and the free energy F has the smallest value.

To establish the phase diagram of the liquid block copolymer near the spinodal point, we should consider the phase equilibria of three mesophases: bcc, triangular, and lamellar. We note that $\beta_1 < \beta_3 < \beta_6$, which means that for large χN (low temperatures) the most stable phase is the lamellar mesophase. In fact for such χN the third-order term in the expansion of F is less important than the fourth-order term. To give a precise argument one reasons as follows. We denote by $(\chi N)_1$ the value of χN for which the free energy of the bcc phase, F_b, equals that of the triangular phase, F_t (for $\chi N < (\chi N)_1$ $F_b < F_t$), by $(\chi N)_6$ the value of χN for which F_b equals F_l, the free energy of the lamellar mesophase, and by $(\chi N)_3$ the value of χN for which $F_t = F_l$. By putting (V-20) to (V-9) we get the free energy of the triangular (or bcc phase)

$$F = 27\alpha_n^4(1 + \gamma_n)^3(3\gamma_n - 1)/4096\beta_n^3 \qquad \text{(V-31)}$$

with γ_n given by (V-21). When $\chi N = (\chi N)_3$ (or $(\chi N)_6$) $F_t = F_l$ (or $F_b = F_l$). F_l is given by (V-25) or in terms of γ_n

$$F_l = -81(\gamma_n^2 - 1)^2\alpha_n^4/4096\beta_n^2\beta_1 \qquad \text{(V-32)}$$

From (V-32) and (V-33) we determine the values of γ_3 and γ_6 for which the transition should take place

$$\gamma_n = [3a_n + 1 + (3a_n + 1)^{1/2}]/3(a_n - 1) \qquad \text{(V-33)}$$

where $a_n = \beta_n/\beta_1$ ($\gamma > 1$ since $(\chi N)_n > (\chi N)_s$). By putting β_3 and β_6 into eq V-34 one obtains $\gamma_3 > \gamma_6$ and consequently $(\chi N)_3 > (\chi N)_6$. It is thus obvious that $(\chi N)_1$ cannot be greater than $(\chi N)_6$ since for χN such that $(\chi N)_6 < \chi N < (\chi N)_3$ we have $F_t < F_l < F_b$ and at $(\chi N)_1$ $F_t = F_b$. This means that $(\chi N)_1 < (\chi N)_6 < (\chi N)_3$ and that the most stable phase for high χN is the lamellar phase (for $\chi N > (\chi N)_3$ F_l is the smallest).

To sum up we may state that for χN above $(\chi N)_s$ a bcc → triangular phase transition is expected (for $\chi N = (\chi N)_1$) and then, for $\chi N = (\chi N)_3$, a transition from the triangular to the lamellar phase.

We have already determined $(\chi N)_3$. In fact it is sufficient to use (V-21) and (V-33) with $n = 3$

$$(\chi N)_3 = (\chi N)_s + 9(\gamma_3^2 - 1)\alpha_3^2/64\beta_3 \qquad \text{(V-34)}$$

Figure 8 shows $(\chi N)_3$ vs. composition f, calculated with the help of (V-34). In order to determine the value of $\chi N = (\chi N)_1$ for which the transition from a bcc to triangular phase takes place, it is necessary to find χN for which F_t and F_b, given by (V-32) with $n = 3$ and $n = 6$, respectively, are equal. The comparison of F_t and F_b leads to eq V-35 for $x = (\chi N)_1 - (\chi N)_s$. Solving this equation we find $(\chi N)_1$, which is plotted for different compositions f in Figure 8.

$$\beta_6^3[-1 + 3(1 + 48x\beta_3/\Gamma_3^2N^2)^{1/2}] \times [1 + (1 + 48x\beta_3/N^2\Gamma_3^2)^{1/2}]^3 - 4\beta_3^3[-1 + 3(1 + 24x\beta_6/N^2\Gamma_3^2)^{1/2}][1 + (1 + 24x\beta_6/\Gamma_3^2N^2)^{1/2}]^3 = 0 \qquad \text{(V-35)}$$

Thus we have determined the phase diagram of a liquid block copolymer near the spinodal point. It will be discussed in section VI.

It should be noted that for $f = 0.5$, $\alpha_3 = \alpha_6 = 0$ and the Landau-type analysis predicts the second-order phase transition from the disordered to the lamellar phase at $\chi N = (\chi N)_s$. For $\chi N > (\chi N)_s$ the lamellar phase is the stable one.

VI. Discussion of the Phase Diagram

In section V we have studied the possible phase transitions in the amorphous diblock copolymer melt. The essential conclusion is that, at equilibrium, the state of the system is determined by only two relevant parameters: the copolymer chain composition f and the product χN. Therefore, the results of section V can be summarized on a universal phase diagram (Figure 8) which presents the regions of stability of different phases in the plane with coordinated χN and f.

When χN is smaller than $(\chi N)_t$, calculated with the help of eq V-24, the system exhibits the disordered phase. This phase is characterized by the uniform (homogeneous) average distribution of monomers A (B) in the sample. As it has been discussed in detail in section IV radiation scattering experiments provide a good method of studying this phase: the monomer density fluctuations have a very specific spectrum with a maximum for the scattering vector $|\vec{q}| = q^*$ (cf. Figure 1); q^*R is the universal quantity independent of the species A and B. In copolymer melts the segregation effects are strong: for $0.3 < f < 0.7$ $(\chi N)_t$ is of the order of 10–15. For many monomer pairs the Flory interaction parameter χ is about 0.1, so the microphase separation should not occur for chains with $N < 100$, i.e., for relatively low molecular mass. These results are to be compared with those obtained for mixtures of two homopolymers. The critical point of demixing is given by $\chi N = 2$ (e.g., ref 34–36 and 40). Thus, for some temperatures, a copolymer melt would exhibit a homogeneous disordered phase, whereas the corresponding mixture of homopolymers would separate into two phases. This is confirmed qualitatively by experimental observations (e.g., ref 18 and 49).

The most interesting prediction of our analysis is that the microphase separation transition is the first-order phase transition from the disordered phase to the mesophase with the symmetry of a body-centered-cubic lattice. A bcc lattice is not a close-packed structure. Till now it was assumed that the phase which occurs after the MST had the symmetry of a face-centered-cubic lattice (e.g., ref

29). We have shown in section V that the fcc mesophase cannot be an equilibrium phase near the MST. Actually, the result of the present theory is not surprising. We have already stressed that the MST is analogous to the solidification of a liquid (cf. sections II and III). For the latter transition a bcc structure is also favored.[38] The periodicity of the mesophase occurring just below the MST is expected to be equal to $D = 2\pi/q^*$ (Figure 2), i.e., of the order of the radius of gyration of the copolymer chains. There is no sharp interface between the A- and B-monomer-rich domains but the monomer density varies smoothly over the whole period (see eq V-4).

In section V we have shown that near the spinodal of the copolymer melt, apart from the bcc mesophase, two other phases may be stable, namely, the triangular and lamellar microdomain structures. We predict the conditions of the first-order transitions between these different phases. The transition from the bcc to the triangular phase is expected to occur for $\chi N = (\chi N)_1$ (see eq V-35 and Figure 8). It is of crucial importance to note that $(\chi N)_1$ is greater than $(\chi N)_s$; however, for a large composition range ($0.2 < f < 0.8$) $(\chi N)_s$ is very close to $(\chi N)_1$. (The difference between $(\chi N)_s$ and $(\chi N)_1$ cannot be clearly illustrated on the scale of Figure 8; $(\chi N)_s$ as a function of f is given in Figure 4.) Therefore, the bcc mesophase should be essentially a metastable phase, as for $(\chi N)_t < \chi N < (\chi N)_s$ the formation of a microphase structure is a very slow process. This may explain why there is no direct observation of the onset of the bcc mesophase just below the MST in copolymer melts. Some X-ray data on concentrated copolymer solutions suggest that a bcc (or eventually a simple cubic) but not a fcc mesophase exists.[50] It may be expected that it would be easier to detect a bcc phase for small compositions ($f < 0.2$ or $f > 0.8$). For these compositions the difference $(\chi N)_1 - (\chi N)_s$ is important and the temperature range of stability of the bcc phase may be sufficiently large.

The transition from the triangular to the lamellar mesophase should occur at $\chi N = (\chi N)_3$ (cf. eq V-34 and Figure 8).

There is no observation of this transition for amorphous block copolymer melts. A transition from the lamellar to the hexagonal mesophase was observed for PS–POE block copolymer.[14,15] However, at the transition point POE blocks were in a crystalline state for which our theory is not applicable. Some experimental argument for existence of phase transitions in amorphous block copolymer can be extracted from the data on PS–BP copolymers.[49] It turned out that in some PS–PB samples two types of mesophases were observed and/or coexisted (hexagonal and lamellar structures). In the case of one sample even the existence of three mesophases has been reported.

Another qualitative argument for the predicted phase diagram is given by a discussion of its predictions for fixed χN. The diagram shows that by increasing f one should observe, respectively, a cubic, a triangular, a lamellar, an inverted triangular, and an inverted cubic mesophase. This is in agreement with all available data and the well-established empirical rule.[1]

Our theory indicates that the lamellar phase is the most stable phase for high χN. This result is confirmed by many experiments, in particular by those of Terrisse,[11] who studied PS–PI copolymers with $f = 0.5$ and various, high molecular masses.

Unfortunately, till now, systematic studies of the MST or of the stability of the mesophases were not available, so the quantitative verification of the theory is not possible. The main difficulty is the lack of data concerning the interaction parameter χ and its temperature dependence. We hope that the method of determining χN from X-ray scattering measurements proposed in section IV will be helpful and enable the detailed study of the phase diagram. It is to be stressed, however, that the first-order character of phase transitions makes them more difficult to study, as it may lead to hysteresis phenomena. Moreover, χ does not vary strongly with the temperature (cf. ref 29). Thus the scanning of the phase diagram would require a careful choice of sample composition and of polymerization index.

It is important to point out some limitations of the present theory. A Landau-type analysis has been used to describe phase transitions. This is justified in many macromolecular phase transitions. In polymer melts fluctuation effects are strongly reduced as a result of screening, due to interactions of chains with a large number of other chains.[35] In the case of the MST the instability is very special: the order parameter has diverging fluctuations on a whole sphere $|\vec{q}| = q^*$ and not, as is usual, at the single point $\vec{q} = 0$. For $f \neq 0.5$, $(\chi N)_t$ is close to the spinodal point $(\chi N)_s$ and it is justified to take into account solely the fluctuations with $|\vec{q}| = q^*$. For $f = 0.5$ the Landau analysis predicts a second-order continuous phase transition at $\chi N = (\chi N)_s$. However, for $f = 0.5$, the fluctuations with $|\vec{q}| \neq q^*$ would play an important role. They would restore a first-order character of the phase transition.[37] The consideration of fluctuations with wave vectors $|\vec{q}| \neq q^*$, important only for $f \simeq 0.5$, would require a rather refined and complicated analysis. In view of experimental difficulties which arise in experimental studies of copolymer melts and especially in view of imprecise data concerning the parameter χ, a very refined analysis seems to be unnecessary. Much more important than fluctuation effects are those effects resulting from the polydispersity of the copolymer blocks. Figure 8 shows that even a small change of f changes strongly $(\chi N)_t$, $(\chi N)_1$, and $(\chi N)_3$. Thus it seems that even a small polydispersity of the sample may be crucial. Experimental studies of polydispersity effects confirm this conclusion.[11,49] Our next project is to include these effects in the theoretical formalism.

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Appendix A. Solution of RPA Equations

The solution of the RPA equation set (III-19) consists in determination of the expansion of ψ_i in powers of the external potentials. The coefficients of this expansion provide the correlation functions of the molten copolymer in terms of those of ideal, noninteracting chains. The most convenient method of dealing with (III-19) is an iteration procedure: let $\psi_i^{(k)}$ and $V^{(k)}$ denote the contribution of the kth order in external potentials U_i to ψ_i and V, respectively; one puts into (III-19) $\psi_i = \psi_i^{(1)} + \psi_i^{(2)} + \psi_i^{(3)}$ and $V = V^{(1)} + V^{(2)} + V^{(3)}$ and separates contributions of different order in U_i. This gives three sets of equations for $\psi_i^{(k)}$ ($k = 1, 2, 3$): a linear set

$$\psi^{(1)}(\vec{q}) = -\beta \tilde{S}_{ij}(\vec{q}) U_j(\vec{q}) = -\beta \mathrm{S}_{ij}(\vec{q}) U_j^{\mathrm{eff}(1)}(\vec{q})$$

$$\psi_1^{(1)} + \psi_2^{(1)} = 0 \qquad \text{(A-1)}$$

where

$$U_i^{\mathrm{eff}(1)} = U_i + V_{im}\psi_m^{(1)} + V^{(1)} \qquad \text{(A-2)}$$

A second-order set

$$\psi_i^{(2)}(\vec{q}_1) = \tfrac{1}{2}\beta^2\mathcal{V}^{-2}\sum_{\vec{q}_2,\vec{q}_3}\tilde{G}^{(3)}_{ijk}(\vec{q}_1, \vec{q}_2, \vec{q}_3)U_j(\vec{q}_2)U_k(\vec{q}_3)$$
$$= -\beta S_{ij}(\vec{q}_1)U_j^{\mathrm{eff}(2)}(\vec{q}_1) + \tfrac{1}{2}\beta^2\mathcal{V}^{-2}\sum_{\vec{q}_2,\vec{q}_3}G^{(3)}_{ijk}(\vec{q}_1, \vec{q}_2, \vec{q}_3)U_j^{\mathrm{eff}(1)}(\vec{q}_2)U_k^{\mathrm{eff}(1)}(\vec{q}_3) \qquad \text{(A-3)}$$

$$\psi_1^{(2)} + \psi_2^{(2)} = 0$$

where

$$U_i^{\mathrm{eff}(2)} = V_{im}\psi_m^{(2)} + V^{(2)} \qquad \text{(A-4)}$$

A third-order set

$$\psi_i^{(3)}(\vec{q}_1) = -\frac{1}{3!}\beta^3\mathcal{V}^{-3}\sum_{\vec{q}_2,\vec{q}_3,\vec{q}_4}\tilde{G}^{(4)}_{ijkl}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) \times U_j(\vec{q}_2)U_k(\vec{q}_3)U_l(\vec{q}_4) = -\beta S_{ij}(\vec{q}_1)U_j^{\mathrm{eff}(3)}(\vec{q}_1) +$$
$$\beta^2\mathcal{V}^{-2}\sum_{\vec{q}_2,\vec{q}_3}G^{(3)}_{ijk}(\vec{q}_1, \vec{q}_2, \vec{q}_3)U_j^{\mathrm{eff}(1)}(\vec{q}_2)U_k^{\mathrm{eff}(2)}(\vec{q}_3) - \frac{1}{3!}\beta^3\mathcal{V}^{-3}\sum_{\vec{q}_2,\vec{q}_3,\vec{q}_4}G^{(4)}_{ijkl}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) \times U_j^{\mathrm{eff}(1)}(\vec{q}_2)U_k^{\mathrm{eff}(1)}(\vec{q}_3)U_1^{\mathrm{eff}(1)}(\vec{q}_4)$$

$$\psi_1^{(3)} + \psi_2^{(3)} = 0 \qquad \text{(A-5)}$$

where

$$U_i^{\mathrm{eff}(3)} = V_{im}\psi_m^{(3)} + V^{(3)} \qquad \text{(A-6)}$$

It is straightforward to find the solution of the linear set (A-1) and to obtain the correlation function $\tilde{S}(\vec{q})$

$$\tilde{S}(\vec{q}) = \tilde{S}_{11}(\vec{q}) = W(\vec{q})/[S(\vec{q}) - 2\chi W(\vec{q})] \qquad \text{(A-7)}$$

where

$$W(\vec{q}) = S_{11}(\vec{q})S_{22}(\vec{q}) - S_{12}^2(\vec{q}) \qquad \text{(A-8)}$$

$$S(\vec{q}) = S_{11}(\vec{q}) + 2S_{12}(\vec{q}) + S_{22}(\vec{q}) \qquad \text{(A-9)}$$

W denotes the determinant of the matrix $\|S\|$ whose elements S_{ij} are the correlation functions of the ideal, noninteracting copolymer chains. The expression for $\tilde{S}$ is discussed in detail in section IV.

Making use of the above result and expressing $U_i^{\mathrm{eff}(1)}$ in the form (cf. (A-1) and (A-2))

$$U_i^{\mathrm{eff}(1)}(\vec{q}) = S_{im}^{-1}(\vec{q})\tilde{S}_{mn}(\vec{q})U_n(\vec{q}) \qquad \text{(A-10)}$$

one can solve the second-order set (A-3) and get the $\tilde{G}^{(3)}$ correlation function

$$\tilde{G}^{(3)}(\vec{q}_1, \vec{q}_2, \vec{q}_3)\mathcal{V}^{-1}\delta(\vec{q}_1 + \vec{q}_2 + \vec{q}_3) = \tilde{S}(\vec{q}_1)\tilde{S}(\vec{q}_2)\tilde{S}(\vec{q}_3)G^{(3)}_{ijk}(\vec{q}_1, \vec{q}_2, \vec{q}_3)[S_{i1}^{-1}(\vec{q}_1) - S_{i2}^{-1}(\vec{q}_1)][S_{j1}^{-1}(\vec{q}_2) - S_{j2}^{-1}(\vec{q}_2)][S_{k1}^{-1}(\vec{q}_3) - S_{k2}^{-1}(\vec{q}_3)] \qquad \text{(A-11)}$$

The same approach as for the second-order set may be used to solve the third-order set (A-5). One expresses $U_i^{\mathrm{eff}(2)}$ in terms of external potential U_i (cf. (A-3) and (A-4), puts the result into (A-5), and then finds $\psi_i^{(3)}$ as a function of U_i. The resulting expression for $\tilde{G}^{(4)}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4)$ is rather complicated. However, relative to the simplest response function $\tilde{S}$ directly measurable in scattering experiments the nonlinear response functions $\tilde{G}^{(3)}$ and $\tilde{G}^{(4)}$ are of less interest and so we do not give here an explicit expression for $\tilde{G}^{(4)}$. More important is expression for the coefficient Γ_4 in the expansion of F in powers of ψ (cf. eq III-16). It turns out that the second term in (III-16) (containing $\tilde{G}^{(3)}$) cancels exactly with a term in $\tilde{G}^{(4)}$ and as a result one gets a compact expression for Γ_4, eq III-24.

Appendix B. Correlation Functions of Gaussian, Noninteracting Copolymer Chains

In this appendix we show how to calculate the correlation functions of Gaussian, noninteracting copolymer chains. The method presented here is applicable not only to block copolymers but also to systems composed of chains with an arbitrary distribution of monomers A and B along the chain.

Let us denote by I ($I = 1, 2, ..., N$) the Ith monomer in each chain and by $\rho_I(\vec{r})$ the density of monomers I at point $\vec{r}$; i.e., $\rho_I(\vec{r}) = 1$ if there is such a chain that its Ith monomer lies at point $\vec{r}$ and $\rho_I(\vec{r}) = 0$ otherwise. The quantity $\delta\rho_I = \rho_I(\vec{r}) - 1/N$ characterizes the deviation from the average, uniform distribution in the disordered phase. Making use of the fact that $\langle\delta\rho_I\rangle = 0$, we may write the expressions for the monomer density correlation functions as follows (cf. eq III-9)

$$G^{(2)}_{IJ}(\vec{r}_1, \vec{r}_2) = \langle\delta\rho_I(\vec{r}_1)\delta\rho_J(\vec{r}_2)\rangle \qquad \text{(B-1)}$$

$$G^{(3)}_{IJK}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \langle\delta\rho_I(\vec{r}_1)\delta\rho_J(\vec{r}_2)\delta\rho_K(\vec{r}_3)\rangle \qquad \text{(B-2)}$$

$$G^{(4)}_{IJKL}(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4) = \langle\delta\rho_I(\vec{r}_1)\delta\rho_J(\vec{r}_2)\delta\rho_K(\vec{r}_3)\delta\rho_L(\vec{r}_4)\rangle - G^{(2)}_{IJ}(\vec{r}_1, \vec{r}_2)G^{(2)}_{KL}(\vec{r}_3, \vec{r}_4) - G^{(2)}_{IK}(\vec{r}_1, \vec{r}_3)G^{(2)}_{JL}(\vec{r}_2, \vec{r}_4) - G^{(2)}_{IL}(\vec{r}_1, \vec{r}_4)G^{(2)}_{JK}(\vec{r}_2, \vec{r}_3) \qquad \text{(B-3)}$$

In order to calculate $G^{(2)}_{IJ}$ we observe that

$$G^{(2)}_{IJ}(\vec{r}_1, \vec{r}_2) = \langle\rho_I(\vec{r}_1)\rho_J(\vec{r}_2)\rangle - 1/N^2 \qquad \text{(B-4)}$$

There are two different ways to have $\rho_I(\vec{r}_1)\rho_J(\vec{r}_2) = 1$.

First, there is the Ith monomer of a chain at point $\vec{r}_1$ and the Jth monomer of the same chain at point $\vec{r}_2$. Secondly, there is the Ith monomer at $\vec{r}_1$ and the Jth at $\vec{r}_2$ but they belong to different chains. Thus

$$\langle\rho_I(\vec{r}_1)\rho_J(\vec{r}_2)\rangle = \frac{1}{N}P_{IJ}(\vec{r}_1, \vec{r}_2) + 1/N^2 \qquad \text{(B-5)}$$

where $P_{IJ}(\vec{r}_1, \vec{r}_2)$ denotes the probability that the chain with the Ith monomer at point $\vec{r}_1$ has the Jth monomer at point $\vec{r}_2$. For Gaussian chains P_{IJ} is a function of $|\vec{r}_1 - \vec{r}_2|$ with the Fourier transform equal to

$$P_{IJ}(\vec{q}) = \int \mathrm{d}^3r\, e^{i\vec{q}\vec{r}}P_{IJ}(\vec{r}) = \exp(-y|I - J|) \qquad \text{(B-6)}$$

where $y = q^2a^2/6$. From eq B-4 and B-5 we get

$$G^{(2)}_{IJ}(\vec{r}_1, \vec{r}_2) = P_{IJ}(\vec{r}_1, \vec{r}_2)/N \qquad \text{(B-7)}$$

and its Fourier transform equal to

$$G^{(2)}_{IJ}(\vec{q}_1, \vec{q}_2) = P_{IJ}(\vec{q}_1)\mathcal{V}^{-1}\delta(\vec{q}_1 + \vec{q}_2)/N \qquad \text{(B-8)}$$

For $G^{(3)}_{IJK}$ we get the result

$$G^{(3)}_{IJK}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \langle\rho_I(\vec{r}_1)\rho_J(\vec{r}_2)\rho_K(\vec{r}_3)\rangle + 2/N^3 - (\langle\rho_I(\vec{r}_1)\rho_J(\vec{r}_2)\rangle + \langle\rho_J(\vec{r}_2)\rho_K(\vec{r}_3)\rangle + \langle\rho_I(\vec{r}_1)\rho_K(\vec{r}_3)\rangle)/N = P_{IJK}(\vec{r}_1, \vec{r}_2, \vec{r}_3)/N \qquad \text{(B-9)}$$

where $P_{IJK}(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ is the probability that the same chain has the monomer I, J, and K at points $\vec{r}_1$, $\vec{r}_2$, and $\vec{r}_3$, respectively. In writing (B-9), eq B-5 has been used. The function P_{IJK} may be expressed in terms of pair correlation functions P_{IJ}

$$P_{IJK}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = P_{IJ}(\vec{r}_1, \vec{r}_2)P_{JK}(\vec{r}_2, \vec{r}_3) \qquad \text{(B-10)}$$
$$\text{for } I < J < K \text{ or } K < J < I$$

For other cases, I, J, K and $\vec{r}_1$, $\vec{r}_2$, $\vec{r}_3$ in (B-10) should be permuted appropriately; e.g., for $J < I < K$, $P_{IJK}(\vec{r}_1, \vec{r}_2, \vec{r}_3)$

$= P_{JI}(\vec{r}_2, \vec{r}_1)P_{IK}(\vec{r}_1, \vec{r}_3)$. Fourier transform of $G^{(3)}_{IJK}$ reads

$$G^{(3)}_{IJK}(\vec{q}_1, \vec{q}_2, \vec{q}_3) = \mathcal{V}^{-1}\delta(\vec{q}_1 + \vec{q}_2 + \vec{q}_3)P_{IJ}(\vec{q}_1)P_{JK}(\vec{q}_3)/N \tag{B-11}$$

$$\text{for } I < J < K$$

Very similar considerations can be made for the fourth-order response functions. One finds easily that

$$G^{(4)}_{IJKL}(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4) = P_{IJKL}(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4)/N \tag{B-12}$$

where $P_{IJKL}(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4)$ denotes the probability that the chain has the Ith monomer at point $\vec{r}_1$, Jth at $\vec{r}_2$, Kth at $\vec{r}_3$, and Lth at $\vec{r}_4$. In $\vec{q}$ space we get

$$G^{(4)}_{IJKL}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) = \mathcal{V}^{-1}\delta(\vec{q}_1 + \vec{q}_2 + \vec{q}_3 + \vec{q}_4)P_{IJ}(\vec{q}_1)P_{JK}(\vec{q}_1 + \vec{q}_2)P_{KL}(\vec{q}_4)/N \tag{B-13}$$

$$\text{for } I < J < K < L \text{ or } L < K < J < I$$

For other ordering of I, J, K, and L, the formula is the same but with appropriate permutation of I, J, K, L and $\vec{q}_1$, $\vec{q}_2$, $\vec{q}_3$, $\vec{q}_4$; e.g., for $I < K < L < J$

$$G^{(4)}_{IJKL}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) = \mathcal{V}^{-1}\delta(\vec{q}_1 + \vec{q}_2 + \vec{q}_3 + \vec{q}_4)P_{IK}(\vec{q}_1)P_{KL}(\vec{q}_1 + \vec{q}_3)P_{IJ}(\vec{q}_2)/N$$

From correlation functions for monomer densities (eq B-8, -11, -13) it is straightforward to determine the response functions $G^{(2)}_{ij,}$ $G^{(3)}_{ijk}$ and $G^{(4)}_{ijkl}$ ($i, j, k, l = 1, 2$; A, B) for copolymers. Let $\theta_I^{(i)}$ denote the function which characterizes the distribution of monomers A and B in the copolymer chain: when $i = 1$ (which corresponds to A monomers) $\theta_I^{(1)} = 1$ when Ith monomer is of the type A and $\theta_I^{(1)} = 0$ when it is of type B; similarly, when $i = 2$, $\theta_I^{(2)} = 0$ when the Ith monomer is of the type A and $\theta_I^{(2)} = 1$ otherwise. With the help of this notation and the definitions of $\delta\rho_A$ and $\delta\rho_B$ we obtain the following expressions for correlation functions of noninteracting, Gaussian copolymer chains:

$$G^{(2)}_{ij}(\vec{q}_1, \vec{q}_2) = \sum_{I=1}^{N}\sum_{J=1}^{N}\theta_I^{(i)}\theta_J^{(j)}G^{(2)}_{IJ}(\vec{q}_1, \vec{q}_2) \tag{B-14}$$

$$G^{(3)}_{ijk}(\vec{q}_1, \vec{q}_2, \vec{q}_3) = \sum_{I=1}^{N}\sum_{J=1}^{N}\sum_{K=1}^{N}\theta_I^{(i)}\theta_J^{(j)}\theta_K^{(k)}G^{(3)}_{IJK}(\vec{q}_1, \vec{q}_2, \vec{q}_3) \tag{B-15}$$

$$G^{(4)}_{ijkl}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) = \sum_{I=1}^{N}\sum_{J=1}^{N}\sum_{K=1}^{N}\sum_{L=1}^{N}\theta_I^{(i)}\theta_J^{(j)}\theta_K^{(k)}\theta_L^{(l)}G^{(4)}_{IJKL}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) \tag{B-16}$$

For the given sequence of monomers in the copolymer chain eq B-14 to B-16 permit calculation of the response functions of the Gaussian copolymer chains. For diblock copolymers summations are particularly simple, although they require rather formidable algebra. As explained in section V we do not need $G^{(n)}_{i_1,\ldots,i_n}$ for arbitrary $\{\vec{q}_i\}$, but only for some very special sets depending on the symmetry of the microdomain structure. Therefore, we do not present here the general expressions for arbitrary $\{\vec{q}_i\}$. The explicit formula for correlation functions which we need in section V are calculated with the help of eq B-14 to B-16 and B-6 and are given in Appendix C. Here, we show an example of such a calculation: the calculus of linear response function $G^{(2)}_{AA}$ (denoted by S_{11})

$$S_{11}(q) = \frac{1}{N}\sum_{I=1}^{N}\sum_{J=1}^{N}\theta_I^{(1)}P_{IJ}(q)\theta_J^{(1)} = \frac{1}{N}\sum_{I=1}^{fN}\sum_{J=1}^{fN}\exp[-y|I - J|] \tag{B-17}$$

We consider the $\vec{q}$ vectors such that $y = q^2a^2/6 \ll 1$, and we suppose that $fN \gg 1$ and $(1 - f)N \gg 1$. In such a case it is justified to replace the summation in (B-17) by an integration

$$S_{11}(q) = \frac{2}{N}\int_0^{fN}\mathrm{d}i\int_0^{i}\mathrm{d}j\,\exp[-y(i - j)] = Ng_1(x, f) \tag{B-18}$$

where

$$x = Ny = Nq^2a^2/6 = q^2R^2 \tag{B-19}$$

with R equal to the radius of gyration of an ideal, Gaussian chain with N links and $g_1(x, f)$ denotes the Debye function

$$g_1(x, f) = 2[fx + \exp(-fx) - 1]/x^2 \tag{B-20}$$

Appendix C. Formulas for Nonlinear Response Functions of Gaussian Copolymer Chains

In order to calculate the correlation functions $G_{ijk}(h)$ and $G_{ijkl}(h_1, h_2)$ of Gaussian independent copolymer chains we will use eq B-15 and B-16. Making the same assumptions as in (B-17) and (B-18) we get

$$G_{111}(h) = 2\int_0^{fN}\mathrm{d}i\int_0^{i}\mathrm{d}j\int_0^{j}\mathrm{d}k\,[2P_{ij}(q)P_{jk}(h^{1/2}q) + P_{ij}(q)P_{jk}(q)]/N = 2N^2[2g_2(f, h) + g_2(f, 1)] \tag{C-1}$$

$$G_{112}(h) = 2\int_{fN}^{N}\mathrm{d}i\int_0^{fN}\mathrm{d}j\int_0^{j}\mathrm{d}k\,P_{ij}(h^{1/2}q)P_{jk}(q)/N = 2N^2g_3(f, h) \tag{C-2}$$

$$G_{121}(h) = G_{211}(h) = \int_{fN}^{N}\mathrm{d}i\int_0^{fN}\mathrm{d}j\int_0^{j}\mathrm{d}k\,[P_{ij}(q)P_{jk}(h^{1/2}q) + P_{ij}(q)P_{jk}(q)]/N = N^2[g_4(f, h) + g_3(f, 1)] \tag{C-3}$$

To obtain $G_{222}(h)$, $G_{221}(h)$, and $G_{212}(h)$ one should change f to $1 - f$ in formulas C-1, C-2, and C-3, respectively. The functions g_2, g_3, and g_4 are defined as

$$g_2(f, h) = \{fx - 1 - 1/h + h\exp(-fx)/(h - 1) - \exp(-hfx)/h(h - 1)\}/hx^3 \tag{C-4}$$

$$\text{for } h \neq 0, 1, 3, 4$$

$$g_2(f, 0) = g_2(f, 4) = \{f^2x^2/2 - fx + 1 - \exp(-fx)\}/x^3 \tag{C-4a}$$

$$g_2(f, 1) = g_2(f, 3) = \{fx\exp(-fx) + fx - 2 + 2\exp(-fx)\}/x^3 \tag{C-4b}$$

$$g_3(f, h) = \{1 - \exp[-h(1 - f)x]\} \times \{1/h - \exp(-fx)/(h - 1) + \exp(-hfx)/h(h - 1)\}/hx^3 \tag{C-5}$$

$$\text{for } h \neq 0, 1, 3, 4$$

$$g_3(f, 0) = (1 - f)\{fx + \exp(-fx) - 1\}/x^2 \tag{C-5a}$$

$$g_3(f, 1) = \{1 - \exp[-(1 - f)x]\}\{1 - fx\exp(-fx) - \exp(-fx)\}/x^3 \tag{C-5b}$$

$$g_4(f, h) = \{1 - \exp[-(1 - f)x]\} \times \{1 + \exp(-hfx)/(h - 1) + h\exp(-fx)/(h - 1)^2\}/hx^3 \tag{C-6}$$

$$\text{for } h \neq 0, 1, 3, 4$$

$$g_4(f, 0) = \{1 - \exp[-(1 - f)x]\}\{fx - 1 + \exp(-fx)\}/x^3 \quad \text{(C-6a)}$$

$$g_4(f, 1) = g_4(f, 3) = g_3(f, 1) \quad \text{(C-6b)}$$

For third-order response functions $G_{ijkl}(h_1, h_2)$ we get

$$\begin{aligned} G_{1111}(h_1, h_2) = {} & \frac{8}{N}\int_0^{fN}\mathrm{d}i \int_0^{i}\mathrm{d}j \int_0^{j}\mathrm{d}k \int_0^{k}\mathrm{d}l\ [P_{ij}(q)P_{jk}(h_1^{1/2}q)P_{kl}(q) + \\ & P_{ij}(q)P_{jk}[(4 - h_1 - h_2)^{1/2}q]P_{kl}(q) + \\ & P_{ij}(q)P_{jk}(h_2^{1/2}q)P_{ki}(q)] = \\ & 8N^3[f_1(f, h_1) + f_1(f, 4 - h_1 - h_2) + f_1(f, h_2)] \quad \text{(C-7)} \end{aligned}$$

$$G_{1112}(h_1, h_2) = G_{1121}(h_1, h_2) = G_{1211}(h_1, h_2) = G_{2111}(h_1, h_2) = 2N^3[f_2(f, h_1) + f_2(f, 4 - h_1 - h_2) + f_2(f, h_2)] \quad \text{(C-8)}$$

$$G_{1122}(h_1, h_2) = G_{2211}(h_1, h_2) = 4N^3 f_3(f, h_1)f_3(1 - f, h_1) \quad \text{(C-9)}$$

$$G_{1221}(h_1, h_2) = G_{2112}(h_1, h_2) = 4N^3 f_3(f, 4 - h_1 - h_2)f_3(1 - f, 4 - h_1 - h_2) \quad \text{(C-10)}$$

$$G_{1212}(h_1, h_2) = G_{2121}(h_1, h_2) = 4N^3 f_3(f, h_2)f_3(1 - f, h_2) \quad \text{(C-11)}$$

where

$$\begin{aligned} f_1(f, h) = {} & \{fx/h + fx\exp(-fx)/(h - 1) + (2h - 3)\exp(-fx)/(h - 1)^2 + \exp(-fhx)/h^2(h - 1)^2 - \\ & (2h + 1)/h^2\}/x^4 \quad \text{(C-12)} \end{aligned}$$

for $h \neq 0, 1, 3, 4$

$$f_1(f, 0) = f_1(f, 4) = \{f^2x^2/2 - fx\exp(-fx) - 3\exp(-fx) - 2fx + 3\}/x^4 \quad \text{(C-12a)}$$

$$f_1(f, 1) = f_1(f, 3) = \{f^2x^2\exp(-fx)/2 + fx + 2fx\exp(-fx) + 3\exp(-fx) - 3\}/x^4 \quad \text{(C-12b)}$$

$$f_2(f, h) = \{1 - \exp[-(1 - f)x]\}\{1/h - (h - 2)\exp(-fx)/(h - 1)^2 - \exp(-fhx)/h(h - 1)^2 - fx\exp(-fx)/(h - 1)\}/x^4 \quad \text{(C-13)}$$

for $h \neq 0, 1, 3, 4$

$$f_2(f, 0) = \{1 - \exp[-(1 - f)x]\} \times \{2\exp(-fx) + fx\exp(-fx) - 2 + fx\}/x^4 \quad \text{(C-13a)}$$

$$f_2(f, 1) = \{1 - \exp[-(1 - f)x]\} \times \{1 - \exp(-fx) - f^2x^2\exp(-fx)/2 - fx\exp(-fx)\}/x^4 \quad \text{(C-13b)}$$

$$f_3(f, h) = \{h - 1 - h\exp(-fx) + \exp(-hfx)\}/h(h - 1)x^2 \quad \text{(C-14)}$$

for $h = 0, 1, 3, 4$

$$f_3(f, 0) = g_1(f, x)/2 \quad \text{(C-14a)}$$

$$f_3(f, 1) = \{1 - \exp(-fx) - fx\exp(-fx)\}/x^2 \quad \text{(C-14b)}$$

In order to obtain $G_{2221}(h_1, h_2) = G_{2212}(h_1, h_2) = G_{2122}(h_1, h_2) = G_{1222}(h_1, h_2)$ and G_{2222} one should change f to $1 - f$ in eq C-8 and C-7, respectively.

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