PHYSICAL REVIEW E **73**, 041803 (2006)

# Micelle formation in statistical copolymers

A. N. Semenov
*Institut Charles Sadron, 6 rue Boussingault, 67083 Strasbourg Cedex, France*

(Received 13 May 2005; revised manuscript received 11 August 2005; published 20 April 2006)

Formation of microdomain structures in concentrated systems of irregular (stochastic) copolymers with weak composition asymmetry ($\epsilon \ll 1$) is considered theoretically. The study is focused on the weak segregation regime for infinitely long copolymer chains near the disorder-to-order transition. It is shown that the transition occurs below the spinodal (at $\chi_0 < \chi^*$) and that it results in the formation of micelles rather than in a superposition pattern of a few harmonic composition waves. The micelle size is inversely proportional to $\Delta\chi = \chi - \chi_0$. For small $\Delta\chi$ the micelles are like large nearly uniform droplets with "reflected" composition, $-\epsilon$. As $\Delta\chi$ increases the micelle composition profile develops oscillations. A first-order transition from spherical-wave micelles to micelles with internal bcc structure is predicted at $\chi/\chi^* - 1 \propto \epsilon^2$. Interaction of micelles is also considered. It is shown that micelles always tend to form a fcc superlattice. The micellization in the weak segregation regime is controlled by the so-called nonlocal free energy. The classical fourth order (in composition parameter $A$) approximation for this energy is significantly generalized in the regime of low volume fraction of micelles. It is shown that the nonlocal energy strongly (exponentially) increases with $A$ near and above a certain critical value $A \simeq A^*$.

DOI: 10.1103/PhysRevE.73.041803 PACS number(s): 36.20.−r

## I. INTRODUCTION

Microdomain structures in irregular (AB) multiblock copolymers have attracted much attention recently [1–17]. These structures are normally described in terms of the "order parameter" field $\eta(\boldsymbol{r})$, the local composition excess. An incompatibility of A and B blocks (quantified by the Flory interaction parameter $\chi$) serves as the driving force for domain formation.

An irregular (statistical) copolymer involves a lot of different chemical sequences, i.e., a mixture of a huge number of components. This multicomponent nature of the system is reflected in the so-called nonlocal contribution to its free energy if its macroscopic state is defined by just one field $\eta(\boldsymbol{r})$ and the sequence disorder is quenched. On the theoretical side the crucial point was made in 1989 by Shakhnovich and Gutin [1] who calculated the nonlocal free energy by perturbations for small $\eta$

$$F_{\text{nloc}} \simeq C \int_{q,q'} \frac{|\eta_q|^2 |\eta_{q'}|^2}{q^2 + q'^2} \tag{1}$$

where $\eta_q = \int \eta(\boldsymbol{r}) e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} d^3 r, \int_{q,q'} \equiv \int \frac{d^3q}{(2\pi)^3} \frac{d^3q'}{(2\pi)^3}$, and $C$ is a constant. Equation (1) is valid for very long copolymer chains: Their Gaussian size must be much larger than $1/q$. Microdomain superstructure formation in melts of nearly symmetric random (block) copolymers was originally predicted [1,7,11] as a continuous disorder-to-order transition (DOT) at some $\chi = \chi^*$. These theories were hinged on the fourth-order approximation for the nonlocal free energy, Eq. (1). Just above $\chi^*$ the structure was characterized by a superposition of a number of weak harmonic waves $\eta \sim A \Sigma_s e^{i\boldsymbol{q}_s \cdot \boldsymbol{r}}, |q_s| = q^*$. The amplitude $A$ is vanishing and $1/q^*$ is formally diverging at the transition point. Later on it was shown [9,12,13] that a phase separation (disordered/ordered phases) is more favorable than homogeneous domain formation. Hence a discontinuous disorder-to-order transition was predicted.

These predictions have been further challenged recently. It was shown that a regular array of ordered regions (i.e., a secondary domain superstructure) is more favorable than two macroscopic coexisting phases (disordered and ordered) [10,14,15]. It was argued that Eq. (1) is not accurate enough, so that the secondary superstructure cannot be established using this expression for the nonlocal free energy: It is necessary to take into account higher-order terms (up to $\eta^8$). Hence an alternative approach (involving two order parameters) was developed in Refs. [14,15].

Unfortunately the two-parameter approach also becomes insufficient very close to the DOT where the sizes of primary and secondary domains are comparable. It is this regime that is studied in the present paper. In the next section we describe the model, underline the importance of the nonlocal free energy, and show that micelle formation should be anticipated near the DOT. Equation (1) is generalized in Sec. III. An asymptotically exact expression for the nonlocal energy valid for small concentration of micelles is obtained there. In Sec. IV the non-local energy is further generalized to the strongly non-linear regimes where the inhomogeneous composition field induces a significant "fractionation" of copolymer sequences. The results are applied to investigate micelle/superstructure formation in random copolymers near DOT (Sec. V).

## II. MODEL

Let us consider a melt or a concentrated solution of AB copolymers. We assume that the polymer system is incompressible, i.e., that the total concentration of A and B units is constant$=c_0$[1]

$$c_{\mathrm{A}}(\boldsymbol{r}) + c_{\mathrm{B}}(\boldsymbol{r}) = c_0. \tag{2}$$

Here $c_{\mathrm{A}}(\boldsymbol{r})$ is local number concentration of A units at position $\boldsymbol{r}$. For simplicity we assume that A and B monomer volumes are equal: $v_{\mathrm{A}}=v_{\mathrm{B}}$. The gross mean fraction of A units is $1/2+\epsilon$. An inhomogeneous state of the system can be characterized by the composition field

$$\eta(\boldsymbol{r}) = [(1/2-\epsilon)c_{\mathrm{A}}(\boldsymbol{r}) - (1/2+\epsilon)c_{\mathrm{B}}(\boldsymbol{r})]/c_0. \tag{3}$$

Obviously $\eta$ can vary between $-1/2-\epsilon$ and $1/2-\epsilon$. In the uniform system $\eta=0$.

Each copolymer is a long chain or A and B units. The chemical sequence of each chain is quenched; it can be represented by a sequence of "spins" $\{\sigma_n\}$, $n=1,2,\ldots,N$, where $\sigma_n=1/2-\epsilon$ if $n$th unit of the chain is A, and $\sigma_n=-1/2-\epsilon$ otherwise. We consider the case of uniformly stochastic sequences with local correlations: It is assumed that sequences of different chains are independent and that the same is true for distant enough fragments of the same chain (locality). All copolymer fragments of a given length are characterized by the same sequence distribution (uniformity). The correlation function of spins on the same chain

$$\langle \sigma_n \sigma_{n'} \rangle = C_\sigma(n-n') \tag{4}$$

depends only on the number of units between $n$ and $n'$. Obviously $C_\sigma(0)=1/4-\epsilon^2$. The results considered in this paper are rather universal, they are not sensitive to the details of spin correlations. The essential parameter is

$$\int_{-\infty}^{\infty} C_\sigma(n)dn \equiv K_0 = (1/4-\epsilon^2)m.$$

The parameter $m$ defines the range of spin correlations. We assume that $m \gg 1$, i.e., random multi-*block* copolymer sequences; the typical block length is $m$. For the correlated random copolymers which have been studied in some detail theoretically [11,15] the spin correlation function is $C_\sigma(n) = (1/4-\epsilon^2)e^{-2|n|/m}$.

Formation of positional structures in the copolymer systems is driven by incompatibility of A and B components which are necessarily mixed to some degree due to copolymer primary structure. The excess energy of mixing in the Flory-Huggins approximation is

$$F_{\mathrm{int}} = \frac{\chi}{c_0}\int c_{\mathrm{A}}(\boldsymbol{r})c_{\mathrm{B}}(\boldsymbol{r})d^3r,$$

where $\chi$ is the effective energy cost for each contact between A and B units (the thermal energy $k_{\mathrm{B}}T$ is treated as the energy unit here and below). This free energy can be rewritten as

$$F_{\mathrm{int}} = \mathrm{const} - \chi c_0 \int \eta^2(\boldsymbol{r})d^3r. \tag{5}$$

The above expression can be validated on the more general grounds: It can be obtained by expanding $F_{\mathrm{int}}$ as a series in $\eta(r)$ and truncating the expansion after the quadratic term. In addition we neglect the wavelength dependence of the vertex function in the quadratic term. The first approximation is justified if $\eta$ is small enough, the second—if the range of AB interactions is short enough as compared with the characteristic length scale of the domain structure. A further discussion of the approximation, Eq. (5), is not appropriate here for two reasons: (i) the Flory-Huggins model is standard and is largely adopted in theoretical studies; (ii) this paper is focused on the effects driven by the nonlocal free energy to which $F_{\mathrm{int}}$ does not contribute. Generally, corrections to the approximation, Eq. (5), just lead to some renormalizations of the parameters involved in the local free energy.

The Flory parameter $\chi$ depends on temperature, concentration $c_0$, solvent quality (which can be tuned, for example, by using mixed solvents), and on other physical and chemical conditions in the solution (for example, on ionic strength if charges are involved in polymer chains). The system is homogeneous (disordered) at low $\chi$'s. An inhomogeneous structure is formed above certain threshold $\chi_0$. This transition is weak (close to second order) if composition is symmetric, $\epsilon=0$, and $m \gg 1$. It is the vicinity of the critical point $\epsilon=0, \chi=\chi^*$ (the spinodal $\chi^*$ is defined below) that attracted most of the theoretical interest [2,10,12–17]. This study is also focused on the critical region which is interesting for two reasons: (i) $\eta$ is small hence $\eta$ expansions are useful there; (ii) almost all qualitatively different microdomain structures are competitive in this regime, some structural features can be even more pronounced there (for example, the difference between primary and secondary domain sizes) [15].

The free energy $F=F[\eta(\boldsymbol{r})]$ for a given order parameter field $\eta(\boldsymbol{r})$ is a sum of two terms, local and nonlocal [1,5,7,9,15] (for simplicity we set $F=0$ in the reference homogeneous state)

$$F = F_{\mathrm{loc}} + F_{\mathrm{nloc}}.$$

The local free energy $F_{\mathrm{loc}}$ can be represented as an integral of energy density

$$F_{\mathrm{loc}} = \int f_{\mathrm{loc}} d^3r.$$

$F_{\mathrm{loc}}$ is equal to the free energy of the corresponding *annealed* copolymer system which is characterized by the same sequence statistics in the disordered state (i.e., the sequence statistical properties of the *homogeneous* annealed system are identical to those of the quenched system). In the critical region (where the typical $\eta$ is small) it is enough to expand $f_{\mathrm{loc}}$ as a series in $\eta$ neglecting the terms of higher than fourth order (in $\eta, \nabla$)

---

[1] See Ref. [21] for clarifications as to why the compressibility of a concentrated (or even semidilute) copolymer solution (in a good solvent) can be neglected as long as microphase separation is concerned.

$$f_{\mathrm{loc}} \simeq \frac{\gamma_2}{2}\eta^2 + \frac{\gamma_2'}{2}(\nabla \eta)^2 + \frac{\gamma_3}{3!}\eta^3 + \frac{\gamma_4}{4!}\eta^4.$$

For symmetric blockcopolymers with A and B blocks characterized by the same statistical segments $b$, we get [5,7–9]

$$\gamma_2 = \frac{c_0}{K_0} - 2c_0\chi, \quad \gamma_2' \sim c_0 b^2, \quad \gamma_4 \sim \frac{c_0}{m}, \quad \gamma_3 \simeq \epsilon\gamma_4.$$

Thus $\gamma_2 = 2c_0(\chi^* - \chi)$, where the critical Flory parameter corresponding to the spinodal is $\chi^* = \frac{1}{2K_0} = \frac{1}{2(1/4-\epsilon^2)m}$ ; $\chi^* \simeq \frac{2}{m}$ since $\epsilon \ll 1$. The local free energy can be rewritten as

$$f_{\mathrm{loc}} \simeq \frac{c_0}{m}\{-2\tau\eta^2 + l^2(\nabla\eta)^2 + 4\epsilon\Gamma_4\eta^3 + \Gamma_4\eta^4\}, \tag{6}$$

where $\tau = \frac{\chi}{\chi^*} - 1 = \frac{\chi m}{2} - 1$, $l^2 = \frac{\gamma_2' m}{2c_0}$, $\Gamma_4 = \frac{\gamma_4 m}{24 c_0}$. Normally $l$ is $\sim$ the block Gaussian size, $l \sim m^{1/2}b$, and $\Gamma_4 \sim 1$. For example, for correlated random copolymers [11,15]

$$l^2 \simeq mb^2/6, \quad \Gamma_4 \simeq 2.$$

The nonlocal free energy can be also expanded as the order parameter series. The main term (of the fourth order) was calculated by Shakhnovich and Gutin, Eq. (1), where the constant

$$C = \frac{6c_0}{2Vb^2K_0^2} \simeq \frac{c_0}{m^2}\frac{48}{Vb^2}. \tag{7}$$

Microdomain formation in statistical block copolymers in a near-critical regime was considered in Refs. [9,12,13,15]. The system is disordered for $\tau < 0$. For $0 < \tau < 10.2\epsilon$ it shows complicated microdomain structures characterized by two significantly different length scales [15]. For example, at $\tau = 1.1\epsilon$ the predicted structure involves layers of thickness $\Lambda \sim l/\epsilon$. The layers alternatively are either homogeneous, or are characterized by an internal (primary) composition pattern of body centred cubic (bcc) symmetry. The characteristic length scale of the primary pattern $L \sim l/\epsilon^{1/2}$ is much shorter than the thickness of secondary layers $\Lambda$. Similar secondary structures are predicted for higher $\tau$'s, involving patterns with different symmetries, other than bcc (see Ref. [15] for more details).

The picture outlined above implies that at small $\tau$'s the mean-square amplitude of the composition field $\langle\eta^2\rangle \sim \tau^2$. The system is homogeneous (disordered) at $\tau = 0$. A closer analysis shows however that these features cannot be true. In fact, consider the following structure at $\tau = 0$: Droplets of size $R_d$ occupying a small fraction $p \equiv c_d V_d$ of the total volume, where $c_d$ is the concentration of droplets, $V_d = \frac{4\pi}{3}R_d^3$, the droplet volume. The typical distance between the droplets is much larger than $R_d$ since $p \ll 1$. The composition field $\eta(r) \sim -A$ inside the droplets, and $\eta = pA$ in the nearly homogeneous matrix outside.

Calculating the free energy ($f$) per unit volume of the system using Eqs. (1), (6), and (7) and neglecting numerical constants we get

$$\frac{m}{c_0}f \sim p\left(\frac{A^2 l^2}{R_d^2} - \epsilon A^3 + A^4\right) + p^2 R_d^2 A^4,$$

where the terms in brackets correspond to the last three terms in Eq. (6), and the last $p^2$ term represents the nonlocal energy. Minimization of $f$ with respect to $p$, $R_d$, $A$ results in

$$p \sim \epsilon^2, \quad R_d \sim l/\epsilon, \quad A \sim \epsilon, \quad f \sim -\frac{c_0}{m}\epsilon^6. \tag{8}$$

Thus the system is not homogeneous at $\tau = 0$: Formation of droplets of finite size (i.e., micelles) is favorable since $f < 0$.

Formation of micelles is driven by the cubic ($\eta^3$) term in the local free energy. This is an essential feature of this regime: In all the regimes theoretically considered for statistical copolymers so far the local cubic term was always subdominant, i.e., it could not possibly drive a structure formation.

On the other hand there is some analogy between the micelle formation and the classical phase separation in a binary system: The latter is also driven by the cubic term (apart from the special case at the critical point). The argument above shows that micelle formation takes place at some $\tau < 0$. This point can be associated with the binodal of a binary system, whereas $\tau = 0$ is the spinodal. I stress, however, that this analogy does not buy much, as it completely misses the main character in statistical copolymer play, namely, the nonlocal free energy that largely defines the micelle size, and the intra- and inter-micelle structure.

An important question is whether the free energy expressions considered above are valid in the regime of micelles. There is no problem regarding the local energy expansion, Eq. (6), which is valid since $|\eta| \ll 1, R_d \gg l$. The validity of the $\eta^4$ approximation for the nonlocal energy [Eq. (1)] was analyzed in Refs. [10,14]: It is applicable if the composition contrast $A$ is much smaller than the standard deviation of the mean composition of the characteristic chain fragment of size $R_d$ (i.e., copolymer blob of size $\sim$ typical length scale of the structure), i.e., if $AR_d/l \ll 1$. Using Eqs. (8) we find: $AR_d/l \sim 1$ which corresponds to the onset of the regime of significantly perturbed blobs (cf. Ref. [10]). Hence $\eta^4$ approximation for nonlocal energy is not applicable here: Higher-order terms are non-negligible for $F_{\mathrm{nloc}}$. Below we show however that the problem is still tractable: In the next section we obtain $F_{\mathrm{nloc}}$ without resorting to an $\eta$-expansion.

The effect of order parameter fluctuations on phase behavior of random copolymers was analyzed in Refs. [2,3,12,13]. The fluctuations are important near the critical point $|\epsilon| \lesssim \bar{m}^{-1/4}$, where $\bar{m} = mb^6c_0^2$. Below we neglect fluctuations and analyze the mean-field near-critical regime $1 \gg |\epsilon| \gg \bar{m}^{-1/4}$.

## III. NONLOCAL FREE ENERGY FOR LOW FRACTION OF MICELLES $p \ll 1$

### A. Formal general derivation

We first note that nonlocal free energy $F_{\mathrm{nloc}} = F_{\mathrm{nloc}}[\eta]$ has nothing to do with interactions of A and B units, therefore it is sufficient to analyze an ideal system of noninteracting copolymers: $F^{\mathrm{id}}[\eta]=F^{\mathrm{id}}_{\mathrm{loc}}[\eta]+F_{\mathrm{nloc}}[\eta]$, where "id" stands for "ideal system." The local energy $F^{\mathrm{id}}_{\mathrm{loc}}$, i.e., the free energy of the corresponding *annealed* copolymer system, can be found using the classical Lifshitz approach [18].

First, a formal external potential field is applied; the corresponding total potential energy is

$$F_U \equiv \int (c_{\mathrm{A}}(\boldsymbol{r})U_{\mathrm{A}}(\boldsymbol{r})+c_{\mathrm{B}}(\boldsymbol{r})U_{\mathrm{B}}(\boldsymbol{r}))d^3r$$

where $U_{\mathrm{A}},U_{\mathrm{B}}$ are the potential energies of A, B units, respectively. Then the total free energy in the presence of the field $\widetilde{F}_{\mathrm{loc}}[U_{\mathrm{A}},U_{\mathrm{B}}]$, is defined. The required free energy $F^{\mathrm{id}}_{\mathrm{loc}}[\eta]$ is then defined as $\widetilde{F}_{\mathrm{loc}}-F_U$ provided that $U_{\mathrm{A}},U_{\mathrm{B}}$ are appropriately chosen [the time-averaged distributions of A and B units in the presence of the fields must satisfy Eqs. (2) and (3)].

On the other hand, we note that $\widetilde{F}_{\mathrm{loc}}[U_{\mathrm{A}},U_{\mathrm{B}}]=\mathcal{N}F_{\mathrm{ann}}$, where $\mathcal{N}$ is the number of copolymer chains in the system, and $F_{\mathrm{ann}}$ is the free energy of a single annealed copolymer chain in the presence of the fields $U_{\mathrm{A,B}}$ [19]

$$F_{\mathrm{ann}}=-\ln\langle Z\rangle_{\mathrm{seq}}$$

where $Z=Z[U_{\mathrm{A}},U_{\mathrm{B}},\mathrm{seq}]$ is the corresponding single-chain partition function, $\mathrm{seq}=\{\sigma_1,\sigma_2,\ldots,\}$ stands for copolymer sequence, and $\langle\cdot\rangle_{\mathrm{seq}}=\Sigma_{\mathrm{seq}}\cdot\rho_0(\mathrm{seq})$ means averaging over the *a priori* sequence distribution $\rho_0(\mathrm{seq})$. For weak and smooth enough external fields (inducing weak order parameter $|\eta| \ll 1$ with large characteristic length $\lambda \gg l$) the sequence-averaged partition function $\langle Z\rangle_{\mathrm{seq}}$ is nearly equal to the partition function of a homopolymer chain in the potential field $U^*=U-\frac{1}{2}K_0\varphi^2$ [cf. Ref. [1]], where $U=U(\boldsymbol{r})$ and $\varphi=\varphi(\boldsymbol{r})$ are related to $U_{\mathrm{A,B}}$

$$U_{\mathrm{A}}=U+(1/2-\epsilon)\varphi, \quad U_{\mathrm{B}}=U-(1/2+\epsilon)\varphi. \tag{9}$$

The condition $c_{\mathrm{A}}+c_{\mathrm{B}}=c_0$ implies that $U^*=\mathrm{const}$ (=0 for simplicity), therefore $\langle Z\rangle_{\mathrm{seq}}=V$ ($V$ is the total volume of the system), $F_{\mathrm{ann}}=-\ln V$, and

$$F_U=c_0\int (U+\varphi\eta)d^3r=c_0\int\left(\frac{1}{2}K_0\varphi^2(\boldsymbol{r})+\varphi\eta\right)d^3r.$$

Taking also into account that $\delta F^{\mathrm{id}}_{\mathrm{loc}}/\delta\eta=-c_0\varphi$, where $\frac{\delta}{\delta\eta}$ means variational derivative, we get

$$F^{\mathrm{id}}_{\mathrm{loc}}=\widetilde{F}_{\mathrm{loc}}-F_U \simeq \frac{c_0}{2K_0}\int \eta^2 d^3r.$$

Here we omitted the trivial ideal-gas term $-\mathcal{N}\ln V$ which is negligible in the limit of very long chains. Note that higher-order terms in $\eta$ are small since $\eta \ll 1$; these terms are neglected here as well.

The same approach can be formally used to obtain the total free energy $F^{\mathrm{id}}$. The only difference is that equation $\widetilde{F}_{\mathrm{loc}}=-\mathcal{N}\ln\langle Z\rangle_{\mathrm{seq}}$ must be replaced by [1,19]

$$\widetilde{F}=-\mathcal{N}\langle\ln Z\rangle_{\mathrm{seq}}.$$

Let us consider $F_{\mathrm{nloc}}$ as a small correction. In this case we can use the theorem on small variations [20] and approximate $F_{\mathrm{nloc}}=F^{\mathrm{id}}-F^{\mathrm{id}}_{\mathrm{loc}}$ by $\widetilde{F}-\widetilde{F}_{\mathrm{loc}}$

$$F_{\mathrm{nloc}} \simeq \mathcal{N}(\ln\langle Z\rangle_{\mathrm{seq}}-\langle\ln Z\rangle_{\mathrm{seq}}), \tag{10}$$

where $Z$ in both terms must be calculated for *the same* $U_{\mathrm{A}},U_{\mathrm{B}}$ defined in Eqs. (9) with $U=U^{(0)}$ and $\varphi=\varphi^{(0)}$

$$U^{(0)}=\frac{1}{2}K_0\varphi^2, \quad \varphi^{(0)}=-\eta/K_0.$$

This approximation is valid if the differences $\delta\varphi=\varphi-\varphi^{(0)}$ and $\delta U=U-U^{(0)}$ between the actual $\varphi=\varphi[\eta],U=U[\eta]$ and the approximate potentials defined above are negligible. In effect this means that the nonlocal correction $\delta E$ to the energy of interaction between a micelle (droplet) and a copolymer chain overlapping it is small: $\delta E \ll k_{\mathrm{B}}T$. The magnitude of $\delta E$ can be estimated as $\delta E \sim g_d\delta U$, where $g_d \sim R_d^2/b^2$ is the number of units in a chain fragment (blob) overlapping the droplet. Further, inside the droplet $\delta U \sim K_0\varphi\delta\varphi \sim A\,\delta\varphi$ and $\delta\varphi=-\frac{1}{c_0}\frac{\delta F_{\mathrm{nloc}}[\eta]}{\delta\eta}$, i.e., $\delta\varphi \sim \frac{F_{\mathrm{nloc}}}{Ac_0V_d}$. Thus we arrive at the condition

$$F_{\mathrm{nloc}}/(c_0R_db^2) \ll 1. \tag{11}$$

Analytical calculation of $\langle\ln Z\rangle_{\mathrm{seq}}$ is not possible in the general case. However the problem can be solved for a structure involving localized inhomogeneities (micelles) in an otherwise nearly homogeneous matrix when the micelle *volume fraction p is small*, $p \ll 1$. In this case both fields $U$ and $\varphi$ (or $U_{\mathrm{A}},U_{\mathrm{B}}$) are localized near the micelles, and the probability that a copolymer chain "feels" these fields is proportional to $p$. Therefore we can formally write $Z=V(1+W)$, where $W$ is proportional to $p$. Thus $W$ can be formally considered as a small parameter. Expanding the r.h.s. of Eq. (10) as a series in $W$ and neglecting cubic and higher-order terms we get

$$F_{\mathrm{nloc}} \simeq \frac{\mathcal{N}}{2}\langle W^2\rangle_{\mathrm{seq}}=\frac{\mathcal{N}}{2}(V^{-2}\langle Z^2\rangle_{\mathrm{seq}}-1), \tag{12}$$

where it is taken into account that $\langle Z\rangle_{\mathrm{seq}}=V$. The partition function is

$$Z=\int P_0[r]\exp\left[-\sum_{n=1}^{N}(U(\boldsymbol{r}_n)+\varphi(\boldsymbol{r}_n)\sigma_n)\right]D[r],$$

where $P_0[r]$ is the *a priori* probability of a given copolymer chain conformation $[r]=\{\boldsymbol{r}_1,\boldsymbol{r}_2\cdots\}$, and $D[r]=d^3r_1d^3r_2\cdots$ Taking into account that $\Sigma_n\varphi(\boldsymbol{r}_n)\sigma_n$ is a random variable with nearly Gaussian distribution since it is a superposition of many independent terms involving spins $\sigma_n$ from different blocks (recall that the field $\varphi(\boldsymbol{r})$ is nearly constant on the length-scale $l$ since $l \ll R_d$), we obtain

$$F_{\mathrm{nloc}} \simeq \frac{1}{2}\frac{\mathcal{N}}{V^2}\int P_0[r]P_0[r'][e^{K_0\sum_n \varphi(\boldsymbol{r}_n)\varphi(\boldsymbol{r}'_n)}-1]\mathrm{D}[r]\mathrm{D}[r'].$$

The integral above (apart from "–1" in square brackets) is formally the partition function of a Gaussian chain in six dimensions in the presence of the external field $-u(\boldsymbol{r},\boldsymbol{r}')=$

$-K_0\varphi(\mathbf{r})\varphi(\mathbf{r}')$. Using the Lifshitz formalism [18] we simplify it as

$$F_{\mathrm{nloc}} \simeq \frac{\mathcal{N}}{2V^2}\int d^3r d^3r'[\Psi(\mathbf{r},\mathbf{r}';N)-1], \tag{13}$$

where $N$ is the number of units in one copolymer chain, and the function $\Psi(r,r';n)$ satisfies the following equations:

$$\frac{\partial\Psi}{\partial n} = a^2\nabla_6^2\Psi + u(\mathbf{r},\mathbf{r}')\Psi \tag{14}$$

$$u(\mathbf{r},\mathbf{r}') = \eta(\mathbf{r})\eta(\mathbf{r}')/K_0, \quad \Psi_0(\mathbf{r},\mathbf{r}') = 1. \tag{15}$$

Here $\nabla_6^2 \equiv (\frac{\partial}{\partial r})^2 + (\frac{\partial}{\partial r'})^2$, $a^2 \equiv b^2/6$.

Taking into account that $\frac{1}{V^2}\int \nabla_6^2\Psi d^3r d^3r' \to 0$ for $V\to\infty$ and that $\int u(\mathbf{r},\mathbf{r}')d^3r d^3r' = 0$ [the first equation follows from the Gaussian theorem, the second—from the definition of $\eta(\mathbf{r})$, Eq. (3)], we find

$$F_{\mathrm{nloc}} \simeq \frac{\mathcal{N}}{2V^2}\int_0^N dn \int d^3r d^3r' u(\mathbf{r},\mathbf{r}')\Psi(\mathbf{r},\mathbf{r}';n). \tag{16}$$

This equation is valid if all lengthscales ($\lambda$) involved in $\eta(\mathbf{r})$ are long enough: $\lambda \gg l$.

### B. Order parameter expansion of the nonlocal energy

#### *1. Fourth order*

Let us apply the obtained result Eq. (16) in the regime of weak composition inhomogeneity $\eta^2 R_d^2/l^2 \ll 1$. The potential well $u(r,r')$ is shallow in this case: $|u| \sim \frac{\eta^2}{m} \ll \frac{b^2}{R_d^2}$, so that the Laplacian term in Eq. (14) would be dominant if $|\nabla^2\Psi|$ were $\sim \Psi/R_d^2$. Therefore $\Psi = 1+\delta\Psi, |\delta\Psi| \ll 1$. Doing Fourier transformation $(\mathbf{r},\mathbf{r}') \to (\mathbf{q},\mathbf{q}') \equiv \mathbf{Q}$ in Eq. (16) we find

$$F_{\mathrm{nloc}} \simeq \frac{\mathcal{N}^2}{2V^2}\int_0^N dn \int_Q u_{-\mathbf{Q}}\delta\Psi_{\mathbf{Q}},$$

where $\delta\Psi_{\mathbf{Q}}(n), u_{\mathbf{Q}}$ are Fourier transforms of $\delta\Psi(\mathbf{r},\mathbf{r}';n)$, $u(\mathbf{r},\mathbf{r}')$, respectively, and $\int_Q = \int d^3q d^3q'/(2\pi)^6$. Considering the second term in Eq. (14), $u\Psi \simeq u$, as a perturbation, we get

$$\delta\Psi_{\mathbf{Q}}(n) \simeq \frac{u_{\mathbf{Q}}}{Q^2a^2}(1-e^{-Q^2na^2})$$

and

$$F_{\mathrm{nloc}}^{(4)} \simeq \frac{c_0N}{4V}\int_Q f_D(Q^2R_N^2)|u_{\mathbf{Q}}|^2 = \frac{c_0}{4VK_0^2}\int_{q,q'} S^h(\sqrt{q^2+q'^2}) \times |\eta_{\mathbf{q}}|^2|\eta_{\mathbf{q}'}|^2, \tag{17}$$

where $f_D(t) = \frac{2}{t^2}(t-1+e^{-t})$ is the Debye function, $R_N = N^{1/2}a$ is the Gaussian gyration radius of copolymer chains, $S^h(q) \simeq Nf_D(qR_N)$ is the form factor of the corresponding homopolymer, $\eta_q$ is Fourier transform of $\eta(r)$. This result Eq. (17) is in agreement with the nonlocal free energy obtained in Ref. [5]. For long chains $R_N \gg R_d, qR_N$ is typically large $qR_N \gg 1$, so Eq. (17) reduces to the original result of Shakhnovich and Gutin, Eq. (1).

#### *2. Eighth order*

For small $\eta$ the nonlocal energy can be expanded as a series of order parameter. Equation (17) shows the main fourth-order term. Let us calculate other terms up to the eighth order. For simplicity we consider only the most important case when $\eta_q$ is peaked near $|q| = q^*$, i.e., $\eta_q$ is negligible if $|q-q^*| > \delta q$, with $\delta q \ll q^*$. In addition we assume that $q^*R_N \gg 1$ (long enough copolymer chains). In analogy with the fourth-order calculation we write $\Psi = 1+\delta\Psi$, and solve Eq. (14) by perturbations in $\delta\Psi$. The result is (only the dominant terms for small $\frac{1}{q^{*2}R_N^2}$ and $\delta q/q^*$ are kept)

$$F_{\mathrm{nloc}} \simeq \frac{c_0}{2V}\left\{\int_Q \frac{|u_Q|^2}{Q^2a^2} + \int_{Q,Q'} \frac{u_{-Q}u_{Q-Q'}u_{Q'}}{Q^2Q'^2a^4} + k^2\int_Q \frac{|(u^2)_Q|^2}{Q^2a^2}\left[1 - \frac{1-e^{-Na^2Q^2}}{Na^2Q^2}\right]\right\}, \tag{18}$$

where $(u^2)_Q$ is Fourier transform of $u(r,r')^2$, and $k = \frac{1}{2q^{*2}a^2}$. The second term in curly brackets is of sixth order in the order parameter field $\eta(\mathbf{r})$; this term is identical (apart from notation differences) to the "additional" nonlocal term reported in Ref. [16].[2] It is noteworthy that $Q^2 \simeq Q'^2 \simeq 2q^{*2}$ in the first and second terms in curly brackets. So the last equation can be simplified as

$$F_{\mathrm{nloc}} \simeq \frac{c_0}{2K_0^2V}\left\{k\left[\int \eta(r)^2 d^3r\right]^2 + \frac{k^2}{K_0}\left[\int \eta(r)^3 d^3r\right]^2\right\} + F_{\mathrm{nloc}}^{(8)}, \tag{19}$$

$$F_{\mathrm{nloc}}^{(8)} \simeq \frac{k^2}{2K_0^2}\int_{q,q'} S^h(\sqrt{q^2+q'^2})|(\eta^2)_q|^2|(\eta^2)_{q'}|^2, \tag{20}$$

where $(\eta^2)_q$ is Fourier transform of $\eta(r)^2$. The $\eta^8$ term Eq. (20) generalizes the nonlocal free energy of secondary structures calculated in Ref. [15] using a different approach. The latter result was restricted to the regime $\delta qR_N \gg 1$; in this regime the $\eta^8$ term Eq. (20) becomes

$$F_{\mathrm{nloc}}^{(8)} \simeq \frac{c_0}{2K_0^2a^2V}\int_{q,q'} \frac{1}{q^2+q'^2}|\tilde{\varphi}_q|^2|\tilde{\varphi}_{q'}|^2, \tag{21}$$

where $\tilde{\varphi}(r) = \frac{1}{\sqrt{2}q^*aK_0^{1/2}}\eta(r)^2$ is the second order parameter. Equation (21) agrees with the right-hand side (r.h.s.) of Eq. (27) in Ref. [15] for $K_0 = m/4$ corresponding to the correlated random copolymers considered there (note a different prefactor in the definition of the second-order parameter in Ref. [15]).

---

[2] Note that Ref. [16] was submitted one half-year later than the present paper.

Thus the general nonlocal energy Eq. (16) includes in a natural way the $\eta^4$ and $\eta^8$ nonlocal terms considered earlier: The two terms $F^{(4)}_{\rm nloc}$ and $F^{(8)}_{\rm nloc}$ may be viewed as nonlocal free energies of the primary and secondary structures, respectively. This point of view is clarified and generalized in Appendix A.

The general expression Eq. (16) of course includes other orders of $\eta$: In a sense it solves the problem of summation of the infinite series in $\eta$. The behavior of $F_{\rm nloc}$ with increasing $\eta$ is analyzed in the next section.

### C. Long chain limit

Let us consider the most important case of periodically arranged droplets (the nonlocal free energy primarily depends on the droplet concentration $c_d$; for $p \ll 1$ only a small correction term is affected by their arrangement, see Appendix B). Then the system can be split in equivalent cells of volume $V=1/c_d$, and we may consider just one cell with periodic boundary conditions. The cell size is $R \sim R_d/p^{1/3}$. We assume that the chains are long enough: $R_N \gg R$. The nonlocal free energy is nearly independent of $N$ in this regime [it is easy to check that this is true in the $\eta^4$ approximation using Eq. (17)].

The general expression (16) can be simplified using the ground-state approximation. Solving Eq. (14) by separating variables $n$ and $(r,r')$ and keeping only the ground-state term we get

$$\Psi(r,r';n) \simeq \psi(r,r')e^{\gamma n} \quad \text{for } n \gg R^2/b^2, \tag{22}$$

where $\psi$ is the ground state

$$a^2\nabla_6^2\psi + u\psi = \gamma\psi. \tag{23}$$

Using the initial condition $\Psi(r,r';0)=1$ and orthogonality of eigenfunctions of $a^2\nabla_6^2+u$ we find the normalization condition

$$\int \psi(\psi-1)d^3r d^3r' = 0. \tag{24}$$

Typically $\psi$ is nearly constant far from the droplet [in particular, for $r_6 \sim R$, where $\boldsymbol{r}_6 \equiv (\boldsymbol{r},\boldsymbol{r}')$], and the above condition means that this constant is close to 1, or, more precisely

$$\frac{1}{V^2}\int \psi d^6r \simeq 1, \tag{25}$$

where $d^6r \equiv d^3r d^3r'$ and the integrations are restricted to one cell [this condition is obtained from Eq. (24) on using the identity $\psi(\psi-1)=\psi-1+(\psi-1)^2$ and neglecting $\frac{1}{V^2}\int(\psi-1)^2d^6r$ which is typically small being proportional to $p^2$]. Integrating Eq. (23) over the cell, and recalling the periodic boundary conditions we get

$$\gamma = \int u\psi d^6r \Bigg/ \int \psi d^6r \simeq \frac{1}{V^2}\int u\psi d^6r. \tag{26}$$

On using Eqs. (13) and (22) and the last equation we get $F_{\rm nloc}=\mathcal{N}\mathfrak{F}$, where the nonlocal energy per chain is $\mathfrak{F} \simeq \frac{1}{2}(e^{\gamma N}-1)$. Recalling that $\mathfrak{F} \simeq \frac{1}{2}\langle W^2\rangle_{\rm seq}$, and that $|W| \ll 1$ is the basic condition of validity of the theory [see Eq. (12) and above], we must demand: $\mathfrak{F} \ll 1$. Therefore $\gamma N \ll 1, \mathfrak{F} \simeq \gamma N/2$, and the total nonlocal energy (per cell) can be transformed to

$$F_{\rm nloc} \simeq \frac{c_0}{2V}\int u(\psi-1)d^6r, \tag{27}$$

where $\psi=\psi(r_6)$ is defined by Eqs. (23) and (25), and the obvious relation $\int ud^6r=0$ was used. This $F_{\rm nloc}$ is obviously independent of $N$. The result is valid for $\gamma N \ll 1$ and $N \gg N_R$, where $N_R=R^2/b^2$. The two conditions are compatible if $\gamma N_R \ll 1$. In this case Eq. (27) is valid also for infinitely long chains $N \to \infty$, since $F_{\rm nloc}$ is nearly constant for $N \gg N_R$. On using Eqs. (26) and (27) the condition $\gamma N_R \ll 1$ can be rewritten as

$$\frac{F_{\rm nloc}}{Vc_0}\frac{R^2}{b^2} \ll 1. \tag{28}$$

This is a necessary condition of validity of Eq. (27). In Sec. IV it is shown that a stronger condition is actually required.

### D. Adsorption threshold

Let us consider an example of $\eta(r)$ with "rectangular" profile: $\eta=-A$ if $r<R_d$ and $\eta=pA$ otherwise, where $p=V_d/V \ll 1, V_d=4\pi R_d^3/3, V$ is the volume per cell as before. The $\psi$ function satisfying Eq. (23) invites analogies with a delocalized quantum particle in the potential well $-u(r,r') = -\eta(r)\eta(r')/K_0$ in six dimensions, or with a long $6d$ polymer chain interacting with such well. The ground-state solution to Eq. (23) with $\gamma N_R \ll 1$ (for $p \ll 1$) exists only if the well is not too deep, $A<A^*$, when the $6d$ chain is not adsorbed on the well. The amplitude $A^*$ (or $u^*=A^{*2}/K_0$) corresponding to the adsorption threshold is $A^* \sim l_0/R_d$ ($u^* \sim b^2/R_d^2$), where $l_0 \equiv m^{1/2}a$. A numerical analysis of Eq. (23) yields $A^* \approx 1.6 l_0/R_d$ for the "rectangular" profile of $\eta(r)$. Thus the necessary condition of applicability of Eq. (27) is $A<A^*$.

It is enough to find $\delta\psi$ in the vicinity of the droplet [it is this region that provides the dominant contribution to $F_{\rm nloc}$ in Eq. (27)]. For $A \ll A^*$ the $\psi$ function is close to 1 everywhere: $\psi = 1+\delta\psi, |\delta\psi| \ll 1$. Then Eq. (23) can be approximated as

$$a^2\nabla_6^2\delta\psi + u = 0$$

with the formal boundary condition: $\delta\psi \to 0$ as $r_6 \to \infty$. Solving the equation we get

$$F_{\rm nloc} \simeq 3.2pc_0R_db^2(A/A^*)^4, \quad A \ll A^*. \tag{29}$$

The same result can be obtained using Eq. (1) since higher-order terms in the perturbation $\eta$ expansion are negligible for $A \ll A^*$.

In the general case, $A \lesssim A^*$, Eq. (23) can be approximated by

$$\nabla_6^2\psi \simeq 0$$

for $2R_d^2 < r_6^2 \ll R^2$, where $\boldsymbol{r}_6 \equiv (\boldsymbol{r},\boldsymbol{r}')$, $r_6^2=r^2+r'^2$. Therefore

$$\psi \simeq \bar{\psi} + C_6\left(\frac{R_d}{r_6}\right)^{d-2}, \quad d=6$$

for $R_d \ll r_6 \ll R$. Here $\bar{\psi} \simeq 1$ for $p \ll 1-A/A^*$ [the last condition ensures the validity of Eq. (25); the case when $A$ is even closer to $A^*, 1-A/A^* \ll p$, is not considered below since Eq. (27) is never applicable in this regime, see the next section]. The factor $C_6$ increases in the vicinity of $A^*$

$$C_6 \approx \frac{0.61}{1-A/A^*}, \quad 1-A/A^* \ll 1.$$

The nonlocal energy in this regime scales as

$$F_{\text{nloc}} \approx \frac{1.52}{1-A/A^*} p c_0 b^2 R_d, \quad 1-A/A^* \ll 1, \tag{30}$$

i.e., $F_{\text{nloc}}$ diverges as $A$ approaches $A^*$. The nonlocal energy was calculated numerically using Eqs. (27) and (23) in the general case $0 < A < A^*$. For $p \ll 1-A/A^*$ the last term $\gamma\psi$ in Eq. (23) can be neglected. The result is

$$F_{\text{nloc}} \simeq \frac{c_0 a^2}{2V} R_d^4 \tilde{F}(B),$$

where $B \equiv A^2 R_d^2/(K_0 a^2)$ and the function $\tilde{F}(B)$ can be approximated as

$$\tilde{F}(B) \approx \frac{B^2}{B^* - B}\left(15.7 - 0.05B - \frac{0.004B^2}{11.9 - B}\right), \quad B^* \approx 10.23 \tag{31}$$

with accuracy of 0.2%. Note the general relation between the factor $C_6$ and $\tilde{F}$

$$4\pi^3 C_6 \simeq \tilde{F}(B) + \frac{16\pi^2}{9} B.$$

Of course the qualitative behavior of $F_{\text{nloc}}$ defined in Eq. (30) is valid not only for the "rectangular" $\eta(r)$ [when $\eta(r)$ is constant inside the droplet]: This equation is valid in the general case. It is only the numerical factors that depend on the $\eta(r)$ profile.

Using the above result the condition (28) can be written as

$$1 - A/A^* \gg p^{4/3},$$

which is weaker than the condition $1-A/A^* \gg p$ assumed just above.

The following questions arise naturally: What is the upper boundary of the region of validity of Eq. (30)? What is the physical picture behind the rapid increase of $F_{\text{nloc}}$ near $A^*$? What is the behavior of $F_{\text{nloc}}$ for $A > A^*$? We try to clarify these issues in the next sections.

## IV. BEYOND THE REGION OF VALIDITY OF EQ. (27)

### A. The importance of adsorption

We start with the general Eq. (10) for the nonlocal energy. Taking into account that $Z = V(1+W), \langle W \rangle_{\text{seq}} = 0$ (see Sec. III A) we rewrite it as

$$F_{\text{nloc}} \simeq \mathcal{N}\langle W - \ln(1+W)\rangle_{\text{seq}}. \tag{32}$$

This equation is much more general than Eq. (12): It is not assumed that $|W| \ll 1$. The equation shows that $F_{\text{nloc}} \geq 0$ in the general case.

Let us focus on the most interesting regime $A \simeq A^*$ where $F_{\text{nloc}}$ is rapidly increasing with $A$. As before we consider $\eta(r)$ defining a dilute system of droplets of volume $V_d \sim R_d^3$. $\eta(r) \sim -A$ inside the droplets, $\eta \ll A$ outside. The typical distance between droplets is $R \sim R_d/p^{1/3}$, where $p = V_d/V$ is their volume fraction, $p \ll 1, V = 1/c_d$ is the cell volume, $c_d$ is number concentration of droplets.

In order to calculate $F_{\text{nloc}}$ using Eq. (32) we need to know the distribution of $W$ ($W$ is a random quantity depending on the copolymer sequence). The formal analysis of the previous section suggests that the increase of $F_{\text{nloc}}$ in the critical region $A \simeq A^*$ has something to do with polymer adsorption. Below we clarify this qualitative idea. Later on we present a semiquantitative argument allowing to obtain the essential part of $W$-distribution in the region $A \simeq A^*$ and above $A^*$.

Let us assume for convenience that $N \sim N_R = R^2/b^2$ (i.e., the chain size $R_N \sim$ the cell size $R$). It is appropriate to consider the copolymer as a chain of $N/g_d$ blobs of size $g_d^{1/2} b \sim R_d$. The probability that a given blob is overlapping with a droplet (i.e., that its potential energy deviates from 0)[3] is $p_{ov} \sim \frac{R_d^3}{R^3} \sim p$. The average number of blobs interacting with a droplet is small: it equals $\frac{N}{g_d} p_{ov} \sim p^{1/3}$. Therefore it is tempting to assume that no more than one blob is interacting with the droplet at a time. It is easy to estimate $F_{\text{nloc}}$ with this assumption. Let $E_i$ be the potential energy of the $i$th blob [$E_i = 0$ if the blob does not overlap with the droplet, otherwise $E_i \sim g_d(U + \varphi\sigma_i)$, where $\sigma_i$ is the average composition of the blob, and $U, \varphi$ are the average values of the corresponding fields over the droplet]. Then by definition

$$W = \left\langle e^{-\sum_i E_i} - 1\right\rangle_0,$$

where $\langle \cdot \rangle_0$ means averaging over all chain conformations with ideal (Gaussian) weights. If only one term in the sum above can be nonzero at a time, then $W$ can be represented as

$$W = \left\langle \sum_i (e^{-E_i} - 1)\right\rangle_0 = p_{ov} \sum W_i,$$

where $W_i = \langle e^{-E_i} - 1\rangle_{ov}$ and $\langle \cdot \rangle_{ov}$ means averaging under the condition that $i$th blob is overlapping with the droplet. It is easy to show that $\langle W_i^2 \rangle_{\text{seq}} \sim 1$ for $A \simeq A^*$. Taking also into account that $\langle W_i \rangle_{\text{seq}} = 0$ and that $\{W_i\}$ are *independent* variables ($W_i$ depends on the sequence of the $i$th blob, sequences of different blobs are not correlated since the blob size is much larger than the spin correlation length, $g_d \gg m$) we find

---

[3] Both potential fields $U$ and $\varphi$ are very small outside the droplets; for simplicity we assume here that they exactly vanish outside; this assumption is inessential for the conclusions drawn below.

$$\langle W^2\rangle_{\text{seq}} \sim p^2 \frac{N}{g_d} \sim p^{4/3} \ll 1 .$$

Therefore the typical $W$ is small (the probability that $|W| \gtrsim 1$ is exponentially low), so the expression $W - \ln(1+W)$ in Eq. (32) can be approximated by $W^2/2$

$$F_{\text{nloc}} \sim \mathcal{N}\langle W^2\rangle_{\text{seq}} \sim \mathcal{N} p^2 N/g_d = c_0 V p^2/g_d \sim p c_0 R_d b. \tag{33}$$

This result is in agreement with Eq. (30) for $A = A^*/2$, however Eq. (33) significantly underestimates the nonlocal energy if $A$ is close to the critical value $A^*$. This discrepancy suggests that the initial assumption that only one blob (or none) is overlapping with the droplet at a time is not correct in the critical regime. In other words the states with many overlapping blobs must provide significant (dominant) contribution to $F_{\text{nloc}}$, in this regime. This picture obviously corresponds to adsorption of a chain fragment (or fragments) on the droplet.

### B. Nonlocal energy generalized

The sequence dependent part of the potential energy of a blob interacting with the droplet is $\sim \varphi g_d \sigma$, where $\varphi = -\eta/K_0 \sim A/K_0$ and $\sigma$ is the average spin (composition). It is clear that adsorbed fragments must be characterized by large enough negative $\sigma$. It is important that many adsorbed fragments are less favorable than one continuous fragment. In fact, consider two adsorbed fragments $n_1$ and $n_2$ separated by a nonadsorbed loop $n$. The statistical weight of the loop $w_n$ is proportional to the return probability $w_n \sim V_d/(n^{1/2}b)^3$; the weight of all loops longer than $n, \Sigma_{m>n} w_m \sim \frac{V_d}{b^3} n^{-1/2}$, is small for large $n$. Therefore the contribution of long loops is negligible, i.e., typically $n \lesssim g_d$, meaning that the adsorbed fragments are in effect not separated. Thus the states when two or more distinct fragments of the same chain are simultaneously adsorbed can be disregarded. The partition function of a sequence containing an adsorbed fragment (i.e., a fragment with negative enough coarse-grained $\sigma$) is

$$Z \simeq V + V_d(e^E - \varsigma),$$

where the first term corresponds to nonadsorbed conformations, $V_d$ is the volume of adsorbing "well," $E$ is the total adsorption energy, and $\varsigma = \langle e^E\rangle_{\text{seq}} \sim 1$. In what follows we neglect $\varsigma$ in comparison with $e^E$ assuming $E \gg 1$. Therefore

$$W \simeq p e^E. \tag{34}$$

It is necessary to find the probability of sequences with a given $E = E_0$

$$\rho(E_0) = \frac{N}{g_d} e^{-S(E_0)}, \tag{35}$$

$$S(E_0) = -\ln\left\{ \int e^{-H[s]} \delta(E_0 - E[s]) D[s] \right\}, \tag{36}$$

where $s = \{\sigma_0, \sigma_1, \ldots,\}$ is an adsorbing sequence, $E[s]$ is the adsorption energy for this sequence, $e^{-H[s]}$ is the probability of the sequence $s$ starting in a given blob. The factor $N/g_d$ accounts for all different starting blobs. For each sequence $s = \{\sigma_0, \sigma_1, \ldots,\}$ we define the function $\epsilon(n)$, the adsorption energy of the subfragment $\{\sigma_0, \sigma_1, \ldots, \sigma_n\}$. Obviously $E[s] = \epsilon(\infty)$. Then we change variables considering the function $\nu(\epsilon) = \frac{dn}{d\epsilon}$ instead of $\sigma_n$ [here $n(\epsilon)$ is the function inverse to $\epsilon(n)$], and note that $H[s]$ can be represented as a superposition of contributions coming from different parts of the fragment

$$H[s] \simeq \int_0^E h[\nu(\epsilon)] d\epsilon,$$

where the density $h$ depends only on the local $\nu = \nu(\epsilon)$ and its local derivatives. Doing the similar change of variables in the integral in Eq. (36) we find

$$S(E_0) = -\ln\left\{ \int e^{-\int_0^{E_0} h^*(\nu(\epsilon)) d\epsilon} D[\nu(\epsilon)] \right\},$$

where the difference $h^* - h$ accounts for the Jacobian $\frac{D[s]}{D[\nu(\epsilon)]}$. Note that $\int h^* d\epsilon$ is formally analogous to the Hamiltonian, $E_0$ to the "mass," $1/\nu$ to "density," and $S(E_0)$ to the thermodynamic potential of a one-dimensional system of particles with local interactions. The asymptotic behavior of $S(E)$ suggested by this analogy for large $E$ is

$$S(E) = \alpha E + \alpha' ,$$

where $\alpha, \alpha'$ are constants, $\alpha E$ is the bulk contribution, and $\alpha'$ accounts for the end effects.

The typical energy of interaction of a blob with a near-critical well (for $A \sim A^*$) is $\sim 1$ ($k_B T$), therefore both $\alpha$ and $\beta$ must be $\sim 1$. Thus

$$\rho(E) \simeq \frac{N}{g_d} e^{-S(E)} \simeq \frac{3}{2\pi} \kappa \frac{N b^2}{R_d^2} e^{-\alpha E}, \tag{37}$$

where $g_d \sim R_d^2/b^2, \kappa \sim 1$ is an unknown numerical factor, and the additional factor $\frac{3}{2\pi}$ is introduced merely for convenience.

$\alpha$ is the most important parameter which depends on the composition contrast $A, \alpha = \alpha(A)$. For example, consider the function $z(\beta) = \langle Z^\beta\rangle_{\text{seq}}$. Using $Z = V(1 - p\varsigma + pe^E)$ we find

$$z(\beta) = \int V^\beta (1 - p\varsigma + pe^E)^\beta \rho(E) dE.$$

In view of Eq. (37) we observe that $z(\beta)$ must diverge at $\beta = \alpha$. Note that $F_{\text{nloc}}$ Eq. (27) is proportional to $\langle W^2\rangle_{\text{seq}}$ which is diverging together with $z(2) = \langle Z^2\rangle_{\text{seq}}$ at $A = A^*$. Therefore $\alpha(A^*) = 2$.

Unfortunately, there is no way to calculate $z(\beta)$ for noninteger $\beta$ analytically. Instead we take another approach to calculate $\alpha = \alpha(A)$ approximately: First we note that $E$ can be considered as a functional of a smoothed (coarse-grained) spin sequence $\sigma(n)$ with the length of coarse-graining $\Delta n > m$. The probability of a given $\sigma(n)$ is proportional to $e^{-\mathcal{F}[\sigma]}$, where $\mathcal{F}[\sigma] \simeq \frac{1}{2K_0} \int \sigma(n)^2 dn$. In the mean-field approximation $S(E)$ is equal to the minimum of $\mathcal{F}[\sigma]$ for a given $E=E[\sigma]$, therefore $S(E)$ is approximately proportional to $\frac{1}{K_0}$. The idea then is to formally increase the block size: $K_0 \to K=\beta K_0$, keeping the fields $U$ and $\varphi$ unchanged. This would result in a similar decrease of $S(E)$, i.e., the renormalization $\alpha \to \alpha/\beta$. Let us define the function $Z(\beta)=\langle Z\rangle_{\mathrm{seq}|K}$ where averaging is performed for sequences with the renormalized moment $K=\beta K_0$. This $Z(\beta)$ involves $\int e^E e^{-\alpha E/\beta} dE$ which diverges at $\beta=\alpha$. On the other hand, $\langle Z\rangle_{\mathrm{seq}|K}$ is equal to the partition function of the homopolymer chain in the effective potential $U^*=U-\frac{1}{2}K\varphi^2=-(\beta-1)\frac{1}{2}\eta^2/K_0$ (cf. Sec. III A). The depth of this potential well is proportional to $(\beta-1)A^2$. The divergence of $\langle Z\rangle_{\mathrm{seq}|K}$ corresponds to the critically adsorbing well (cf. Sec. III D), i.e., to $(\beta-1)A^2=A^{*2}$. Therefore

$$\alpha \approx 1+\frac{A^{*2}}{A^2}.$$

We are now in a position to analyze the behavior of the nonlocal energy $F_{\mathrm{nloc}}$ in the critical region $A \approx A^*$. Using Eqs. (32), (34), and (37) we obtain

$$F_{\mathrm{nloc}} \simeq \frac{3}{2\pi}\kappa \frac{Nb^2\mathcal{N}}{R_d^2} I(p,\alpha),$$

$$I(p,\alpha)=\int_0^\infty [pe^E-\ln(1+pe^E)]e^{-\alpha E}dE, \tag{38}$$

where $N\mathcal{N}=c_0V$ is the total number of units in $V$.

This equation is asymptotically exact if (i) the lion's share of the integral comes from the region of high $E\sim E_0, E_0 \gg 1$; (ii) $F_{\mathrm{nloc}}$ is small enough [see Eq. (11)]. The first condition is met if $A$ is close to $A^*$ or exceeds it, the second is valid if $A/A^*$ is not too high (see below).[4] Evaluating the integral we find a complicated behavior of $F_{\mathrm{nloc}}$ as a function of $A$ involving the following four asymptotic regimes:

(i) $I(p,\alpha)\simeq \frac{1}{2}\frac{p^2}{\alpha-2}$ if $\frac{1}{\ln(1/p)} \ll \alpha-2 \ll 1$ (here the dominant contribution to the integral comes from the region $E \gg 1, pe^E \ll 1$). Thus

$$F_{\mathrm{nloc}} \simeq \kappa b^2 R_d c_0 p \frac{1}{A^{*2}/A^2-1} \quad \text{for } \frac{1}{\ln(1/p)} \ll \frac{A^*}{A}-1 \ll 1. \tag{39}$$

The approach considered in Sec. III A is valid in this regime, therefore Eq. (30) is applicable in the case of "rectangular" composition profile. Comparing it with the result above we evaluate the coefficient $\kappa \approx 3.04$ for this case. The typical $E$ in this regime is $E\sim \frac{1}{\alpha-2} \sim \frac{1}{A^*/A-1}$.

(ii) $I(p,\alpha)\simeq \frac{p^2}{2}\ln(1/p)$ for $|\alpha-2| \ll \frac{1}{\ln(1/p)}$, and so

$$F_{\mathrm{nloc}} \simeq \kappa b^2 R_d c_0 p \ln\frac{1}{p} \quad \text{for } \left|\frac{A^*}{A-A^*}\right| \gg \ln\frac{1}{p}. \tag{40}$$

Here typically $E\sim \ln\frac{1}{p}$.

(iii) $I(p,\alpha)\simeq \frac{p^\alpha}{2(2-\alpha)}$ for $\frac{1}{\ln(1/p)} \ll 2-\alpha \ll 1$. So

$$F_{\mathrm{nloc}} \simeq \kappa b^2 R_d c_0 \frac{p^{A^{*2}/A^2}}{1-A^{*2}/A^2} \quad \text{for } 1 \ll \frac{A^{*2}}{A-A^*} \ll \ln\frac{1}{p}. \tag{41}$$

The typical $E$ here is the same as in the previous regime.

(iv) $I(p,\alpha)\simeq p^\alpha/(\alpha-1)$ for $1 \ll \frac{1}{\alpha-1} \ll \ln\frac{1}{p}$, and

$$F_{\mathrm{nloc}} \sim b^2 R_d c_0 p^{A^{*2}/A^2} \quad \text{for } 1 \lesssim \frac{A^2}{A^{*2}} \lesssim \ln\frac{1}{p}. \tag{42}$$

Here the typical $E\sim \ln\frac{1}{p}$ like in the previous regimes. In the last regime the preexponential factor (including $\kappa$) is omitted.

Note an exponential increase of $F_{\mathrm{nloc}}$ with $A$ in regimes (iii) and (iv).

Let us figure out the typical length $g$ of an adsorbed fragment. In regimes (i)–(iii) the adsorption energy per blob $g_d$ is of the order 1 ($k_{\mathrm{B}}T$), therefore $g\sim Eg_d$. On the other hand, in the last regime the adsorption energy $E_0$ per blob $g_d$ is large: $E_0 \sim g_d U$. With $g_d \sim \frac{R_d^2}{b^2}$ and $U\sim A^2/K_0$ we get $E_0 \sim \frac{R_d^2}{b^2}\frac{A^2}{m} \sim \frac{A^2}{A^{*2}}$, so that $g\sim \frac{g_d}{E_0}E \sim g_d \frac{A^{*2}}{A^2}\ln\frac{1}{p}$ in the last regime.

For $\frac{A^2}{A^{*2}} \gtrsim \ln\frac{1}{p}$ the condition (11) is not satisfied, i.e., the basic Eq. (38) is not valid. In this regime the adsorbed fragments are shorter than $g_d$ and are strongly stretched (cf. Ref. [10]). In fact, the fraction of $g_d$ blobs with mean composition $\eta\sim -A$ is $p(g_d)\sim \exp\left(-g_d\frac{A^2}{2K_0}\right) \ll p$ for $\frac{A^2}{A^{*2}} \gg \ln\frac{1}{p}$. Therefore the total number of units in all such fragments is much less than the number of units in the droplets. Hence the droplets must be filled by shorter fragments (of length $g<g_d$) with the same mean composition $-A$: These fragments are more numerous. Their size is defined by the condition $p(g)\sim p$, i.e., $g\sim g_d\frac{A^{*2}}{A^2}\ln\frac{1}{p}$. Each $g$ fragment must span the droplet, i.e., its end-to-end distance must be $\sim R_d$. The nonlocal energy equals to the elongation energy of all such fragments in a droplet [10]

$$F_{\mathrm{nloc}} \sim \frac{c_0 V_d}{g}\frac{R_d^2}{gb^2} \sim b^2 R_d c_0 \left[\frac{A^2}{A^{*2}\ln(1/p)}\right]^2, \quad \frac{A^2}{A^{*2}} \gtrsim \ln\frac{1}{p}. \tag{43}$$

The following $A$ dependence of the typical length of adsorbed fragments is thus predicted

$$g/g_d \sim \begin{cases} \dfrac{1}{A^*/A-1}, & \dfrac{1}{\ln(1/p)} \lesssim \dfrac{A^*}{A}-1 \lesssim 1 \\ \ln\dfrac{1}{p}, & \dfrac{1}{A^*/A-1} \gtrsim \ln\left(\dfrac{1}{p}\right). \\ \dfrac{A^{*2}}{A^2}\ln\dfrac{1}{p}, & A>A^* \end{cases}$$

---

[4] Note that formally the derivation of Eq. (38) is valid only if $N/g$ is not too high: In fact Eq. (35) is valid if $\rho \ll 1$, i.e., $N/g_d \ll e^{\alpha E_0}$. On the other hand it is easy to show that $F_{\mathrm{nloc}}$ must be independent of $N$ if $\frac{N}{g_d} \gg E_0$ (here we take into account that the typical number of $g_d$ blobs per adsorbed fragment is $\sim E_0$, see the end of this section). The two conditions are obviously compatible since $E_0 \gg 1, \alpha \sim 1$, meaning that Eq. (38) is actually valid for however large $N, N/g_d \gg E_0$.

It is interesting that $F_{\text{nloc}}$ is proportional to $A^4$ both in the perturbation regime [Eq. (29)] and in the regime of strongly stretched blobs [Eq. (43)]. We stress however that these two regimes are physically very different: They are separated by four qualitatively different intermediate regimes [see Eqs. (39)–(42)].

## V. MICELLE FORMATION

### A. Dropletlike micelles

We are now in a position to consider the disorder-to-order transition. In Sec. II we showed that this transition occurs at negative $\tau$ (i.e., at $\chi < \chi^*$), that it is driven by the local free energy Eq. (6), more precisely by the cubic term, and that it results in formation of micelles, i.e., spherical droplets with negative $\eta$. The transition point is defined by the local energy only; moreover it is sufficient to consider homogeneous phases. The local energy density is proportional to $\eta^2[-2\tau + \Gamma_4\eta(4\epsilon+\eta)]$, it has two minima at $\eta=0$ and at a negative $\eta$. The second minimum is more deep if $\tau > -\tau_0$, where

$$\tau_0 = 2\Gamma_4\epsilon^2.$$

The second minimum at $\tau=-\tau_0$ corresponds to $\eta=-2\epsilon$. Therefore for $\tau$ just above $-\tau_0(\tau=-\tau_0+\Delta\tau, \Delta\tau \ll \tau_0)$ the system tends to separate in two phases, the minor phase with $\eta=\eta^{(2)} \simeq -2\epsilon$ and major phase with $\eta=\eta^{(1)} \simeq 2\epsilon p$, where $p$ is the volume fraction of the minor phase. The local free energy density in the minor phase is $f^{(2)} \simeq -2\Delta\tau(2\epsilon)^2\frac{c_0}{m}$. The interphase tension $\gamma$ can be easily calculated by minimizing $\int f_{\text{loc}}dx$ with $f_{\text{loc}}$ defined in Eq. (6), $\eta=\eta(x), \eta(-\infty) = \eta^{(2)}, \eta(+\infty)=\eta^{(1)}$. The result is $\gamma \simeq \frac{1}{3}\frac{c_0 l}{m}\sqrt{\Gamma_4}(2\epsilon)^3$. The interfacial thickness is $\Delta \simeq \frac{1}{\sqrt{\Gamma_4}\epsilon}$.

The nonlocal energy diverges in the case of *macroscopic* phase separation (compare with Ref. [15]), hence it drives a transformation of the minor phase into a system of spherical droplets of certain size. The droplet radius $R_d$ and their volume fraction $p$ can be obtained by minimization of the reduced free energy $\mathcal{F}=\frac{m}{c_0 V}F=\mathcal{F}_{\text{loc}}+\mathcal{F}_{\text{nloc}}$, where

$$\mathcal{F}_{\text{loc}} \simeq \frac{m}{c_0(V_d/p)}(V_d f^{(2)} + 4\pi R_d^2\gamma) \simeq -8\epsilon^2 p\Delta\tau + 8\sqrt{\Gamma_4}\frac{l\epsilon^3}{R_d}p. \tag{44}$$

Here $V_d=\frac{4\pi}{3}R_d^3$ is the droplet volume, and we assume that $R_d \gg \Delta$. $\mathcal{F}_{\text{nloc}}$ can be obtained using Eqs. (39)–(43) in the previous section. After simple algebra we get

$$\mathcal{F}_{\text{nloc}} \simeq 4.35\frac{l_0^2 p}{R_d^2}\tilde{\mathcal{F}}(B,p), \tag{45}$$

$$\tilde{\mathcal{F}}(B,p) \simeq \begin{cases} 0.01pB^2, & B \ll B^* \\ \dfrac{p}{B^*/B-1}, & \dfrac{1}{\ln(1/p)} \ll 1-\dfrac{B}{B^*} \ll 1 \\ p\ln\dfrac{1}{p}, & \left|1-\dfrac{B}{B^*}\right| \ll \dfrac{1}{\ln(1/p)} \\ p^{B^*/B}/(1-B^*/B), & \dfrac{1}{\ln(1/p)} \ll \dfrac{B}{B^*}-1 \ll 1 \\ \text{const}\, p^{B^*/B}, & 1 \lesssim \dfrac{B}{B^*} \lesssim \ln\dfrac{1}{p} \\ \text{const}\left[\dfrac{B}{B^*\ln(1/p)}\right]^2, & \dfrac{B}{B^*} \gtrsim \ln\dfrac{1}{p} \end{cases}, \tag{46}$$

where $B=\frac{A^2R_d^2}{K_0a^2} \simeq \frac{16\epsilon^2R_d^2}{l_0^2}$, $l_0=m^{1/2}a$ is the typical block size, $B^* \approx 10.23$ [see Eq. (31)]. As nonlocal energy is always positive, the droplets can be stable only if $\mathcal{F}_{\text{loc}} < 0$, i.e., $R_d \gtrsim R_{d0}$

$$R_{d0} = \sqrt{\Gamma_4}\frac{l\epsilon}{\Delta\tau}.$$

Hence $B \gtrsim B_0=\frac{4\ell^2}{\Gamma_4\ell_0^2}\left(\frac{\tau_0}{\Delta\tau}\right)^2$, i.e., $B$ is large if $\Delta\tau \ll \tau_0$. It is therefore the last line in Eq. (46) that must be applicable for small $\Delta\tau$, i.e., $\mathcal{F}_{\text{nloc}} \sim \frac{p}{\ln(1/p)^2}\frac{R_d^2\epsilon^4}{l_0^2}$ for small $\Delta\tau$ (an unknown numerical factor is omitted). Minimizing $\mathcal{F}=\mathcal{F}_{\text{loc}}+\mathcal{F}_{\text{nloc}}$ with respect to $p, R_d$ we find

$$R_d \sim R_{d0}, \quad \ln\frac{1}{p} \sim \zeta\frac{\tau_0}{(\Delta\tau)^{3/2}}, \quad \text{for } \Delta\tau \lesssim \zeta^2\tau_0^2, \tag{47}$$

where

$$\zeta \equiv \frac{l}{\sqrt{\Gamma_4}l_0}, \tag{48}$$

is the copolymer sequence parameter (for example, $\zeta=1/\sqrt{2}$ for the correlated random model).

For larger $\Delta\tau$, in the range $\epsilon^2 \ll \frac{\Delta\tau}{\tau_0} \ll \zeta$, minimization of $\mathcal{F}$ yields the nonlocal energy which is much smaller than the surface energy, $\mathcal{F}_{\text{nloc}} \ll \mathcal{F}_{\text{surf}}$, and $\mathcal{F}_{\text{bulk}} \simeq \mathcal{F}_{\text{surf}}$ [$\mathcal{F}_{\text{bulk}}$ and $\mathcal{F}_{\text{surf}}$ correspond to the two last terms in the r.h.s. of Eq. (44), respectively]. These statements can be proved using the following relations:

$$\frac{\partial\mathcal{F}_{\text{nloc}}}{\partial\ln R_d} \gg \mathcal{F}_{\text{nloc}}, \quad \frac{\partial\mathcal{F}_{\text{nloc}}}{\partial\ln p} \sim \mathcal{F}_{\text{nloc}},$$

which are valid for the regimes corresponding to lines 2–5 in Eq. (46). Therefore $R_d \simeq R_{do}$ for these regimes, i.e., for $\epsilon^2 \ll \frac{\Delta\tau}{\tau_0} \ll \zeta$. As $\Delta\tau$ increases in this range, the fifth, fourth, third, second, and first lines in Eq. (46) become consequently applicable. Minimizing $\mathcal{F}_{\text{loc}}+\mathcal{F}_{\text{nloc}}$ we get ($\tau^* \simeq \frac{2}{\sqrt{B^*}}\zeta\tau_0 \approx 0.63\zeta\tau_0$ in equations below)

$$R_d \simeq \sqrt{\Gamma_4}\frac{l\epsilon}{\Delta\tau}, \quad \ln\frac{1}{p} \simeq 0.39\zeta^2\left(\frac{\tau_0}{\Delta\tau}\right)^2 \ln\frac{\Delta\tau}{\zeta^2\tau_0^2},$$
$$\text{for } \zeta^2\tau_0^2 \ll \Delta\tau \ll \zeta\tau_0, \tag{49}$$

$$R_d \simeq \sqrt{\Gamma_4}\frac{l\epsilon}{\Delta\tau}, \quad p \sim \frac{1-\Delta\tau/\tau^*}{\ln(1/\epsilon)}\epsilon^{2\left(\frac{\tau^*}{\Delta\tau}\right)^2},$$
$$\text{for } \frac{1}{\ln(1/\epsilon)} \lesssim 1 - \frac{\Delta\tau}{\tau^*} \lesssim 1, \tag{50}$$

$$R_d \simeq \sqrt{\Gamma_4}\frac{l\epsilon}{\Delta\tau}, \quad p \sim \frac{\epsilon^2}{\ln(1/\epsilon)^2}, \quad \text{for} \left|1 - \frac{\Delta\tau}{\tau^*}\right| \lesssim \frac{1}{\ln(1/\epsilon)}, \tag{51}$$

$$R_d \simeq \sqrt{\Gamma_4}\frac{l\epsilon}{\Delta\tau}, \quad p \simeq 0.163\zeta\tau_0\left(\frac{\Delta\tau}{\tau^*} - 1\right)^2,$$
$$\text{for } \frac{1}{\ln(1/\epsilon)} \ll \frac{\Delta\tau}{\tau^*} - 1 \ll 1, \tag{52}$$

$$R_d \simeq 2\sqrt{\Gamma_4}\frac{l\epsilon}{\Delta\tau}, \quad p \simeq 0.178\frac{1}{\zeta^2}\frac{(\Delta\tau)^3}{\tau_0^2}, \quad \text{for } \tau^* \ll \Delta\tau \ll \tau_0. \tag{53}$$

The last four regimes Eqs. (50)–(53) are valid if $\zeta \ll 1$ (this is true near the Lifshitz point [4]); these results are qualitatively applicable also for $\zeta \sim 1$.

For $\Delta\tau \gtrsim \tau_0$ the interfacial thickness $\Delta$ becomes comparable with $R_d$, and the droplet composition profile significantly deviates from the "rectangular" shape. If $\zeta \sim 1$ then the fourth-order approximation for the nonlocal energy [Eq. (1)] is not valid in the region $|\tau| \sim \tau_0$: Here the nonlocal energy must be calculated using the general expression, Eq. (27). The droplet (micelle) composition profile essentially depends on two parameters: $\zeta$ and $\tau/\tau_0$, and can be obtained numerically by an appropriate minimization procedure. As $\Delta\tau$ increases ($\tau$ increases) the profile shows more and more pronounced oscillations. We do not analyze these nonuniversal profiles, but rather turn to the more universal regime $\tau \gg \tau_0$. In this regime the fourth-order approximation for the nonlocal energy is applicable.

### B. Spherical-wave micelles

Let us consider a system of spherically symmetric micelles, their concentration is $c_d$. Each micelle is characterized by the composition profile $\eta(r)$. Below we neglect interactions of micelles and consider just one cell of volume $V_d = 1/c_d$. The total free energy over the total volume is

$$f = c_d F_{\text{loc}} + \frac{1}{2}c_d^2 f_{\text{nloc}}, \tag{54}$$

where

$$F_{\text{loc}} \simeq \frac{c_0}{m}\int \{-2\tau\eta^2 + l^2(\nabla\eta)^2 + 4\epsilon\Gamma_4\eta^3 + \Gamma_4\eta^4\}d^3r, \tag{55}$$

$$f_{\text{nloc}} \simeq \frac{16c_0}{ml_0^2}\int_{q,q'}\frac{|\eta_q|^2|\eta_{q'}|^2}{q^2+q'^2}. \tag{56}$$

(Note that $\eta_q = \int e^{iq\cdot r}\eta(r)d^3r$, and the integrals are taken over one cell.) Minimizing $f$ with respect to $c_d$

$$c_d = -\frac{F_{\text{loc}}}{f_{\text{nloc}}}, \quad f = -\frac{1}{2}\frac{F_{\text{loc}}^2}{f_{\text{nloc}}}. \tag{57}$$

The next step is to minimize $f$ (defined in the last equation) with respect to $\eta(r)$. In the first approximation we may disregard the local $\eta^3$ and $\eta^4$ terms. Then it is easy to prove [1] that at the minimum $\eta_q$ is concentrated on the sphere $q = q^*, q^{*2} = 2\tau/3l^2$, i.e., $\eta_q = 0$ for $q \neq q^*$. In this case $f = f_0$

$$f_0 = -\frac{1}{32}\frac{c_0}{m}\frac{l_0^2}{l^2}\left(\frac{4\tau}{3}\right)^3. \tag{58}$$

Recalling the spherical symmetry we find the order parameter profile: $\eta(r) \simeq A\frac{\sin(q^*r)}{q^*r}$.

With subdominant local $\eta^3$ and $\eta^4$ terms the spectrum $\eta_q$ must be still localized near $q = q^*: \eta_q = g(Q)$, where $Q = q - q^*$, and $g(Q)$ decays for $|Q| > \kappa, \kappa \ll q^*$. Evaluating $f$ in this case ($\kappa \ll q^*$) we find

$$f = f_0(1 - \Delta_f), \tag{59}$$

$$\Delta_f \simeq \frac{1}{2}\frac{\int Q^2g^2(Q)dQ}{\int g^2(Q)dQ} + \frac{3\Gamma_4}{2\tau}\frac{\int(4\epsilon\eta^3 + \eta^4)d^3r}{\int\eta^2(r)d^3r}. \tag{60}$$

It is easy to show that the last term in the r.h.s. depends on $g(Q)$ via just two integral parameters: $I_1 = \int g(Q)dQ$ and $I_2 = \int g^2(Q)dQ$. Therefore min $f$ corresponds to min $\int Q^2g^2(Q)dQ$ at fixed $I_1$ and $I_2$. Using the method of Lagrange multipliers we find: $g(Q) = \frac{\text{const}}{1+Q^2/\kappa^2}$. The corresponding composition profile is

$$\eta(r) \simeq Ae^{-\kappa\tau}\frac{\sin(q^*r)}{q^*r}, \quad q^* = \left(\frac{2\tau}{3}\right)^{1/2}\frac{1}{l}. \tag{61}$$

The profile corresponds to a decaying spherically symmetric composition wave. On using Eq. (60) we get

$$\Delta_f \simeq \frac{2\kappa^2}{q^{*2}} + \frac{3\pi}{2}\frac{\Gamma_4\kappa}{\tau q^*}(4\epsilon A + A^2).$$

Minimization of $\Delta_f$ with respect to $\kappa, A$ then yields

$$A = -2\epsilon, \quad \kappa = \frac{3\pi}{4}\frac{\tau_0}{\tau}q^*, \quad \Delta_f = -\frac{9\pi^2}{8}\left(\frac{\tau_0}{\tau}\right)^2,$$

$$f \simeq -\frac{1}{32}\frac{c_0}{m}\frac{l_0^2}{l^2}\left(\frac{4\tau}{3}\right)^3\left[1 + \frac{9\pi^2}{8}\left(\frac{\tau_0}{\tau}\right)^2\right]. \tag{62}$$

Thus $\kappa/q^* \sim \tau_0/\tau$ is indeed small if $\tau \gg \tau_0$. The micelle radius can be defined as $R_d = 1/\kappa$

$$R_d \simeq \frac{4}{3\pi}\left(\frac{3}{2}\right)^{1/2}\frac{l}{\sqrt{\tau_0}}\left(\frac{\tau}{\tau_0}\right)^{1/2}.$$

Note that $R_d \propto \tau^{1/2}$ and $1/q^* \propto \tau^{-1/2}$. Concentration of micelles [see Eq. (57)] is

$$c_d \simeq \sqrt{-2f/f_{\rm nloc}} \simeq \frac{1}{24\pi}\frac{l_0^2\tau}{\epsilon^2}q^{*4}\kappa \propto \tau^{5/2}.$$

The fraction of volume occupied by micelles is

$$p \sim c_d\frac{4\pi}{3}R_d^3 \simeq \frac{32}{3^5\pi^2}\frac{1}{\zeta^2}\frac{\tau^4}{\tau_0^3}.$$

Therefore $p \ll 1$ if $\tau/\tau_0 \ll \frac{1}{\sqrt{\epsilon}}$.

Let us verify the validity of the fourth-order approximation Eq. (56) for the nonlocal energy of the spherical micelle for $\tau \gg \tau_0$, $F^{(4)}_{\rm nloc}=\frac{1}{2}c_d^2 f_{\rm nloc}$. The correction to this approximation, $F^{(8)}_{\rm nloc}$ is defined in Eq. (21). Using this equation with $\eta(r)$ Eq. (61) we get

$$F^{(8)}_{\rm nloc}/F^{(4)}_{\rm nloc} \sim \left(\frac{\tau_0}{\tau}\right)^4.$$

Therefore $F^{(8)}_{\rm nloc}/F^{(4)}_{\rm nloc} \ll |\Delta_f|$, i.e., $F^{(8)}_{\rm nloc}$ produces a subdominant correction to the average free energy density $f$.

### C. bcc micelles

The spherical-wave micelles considered above are not stable at sufficiently large $\tau$'s: A structure of secondary domains with internal primary composition pattern must be favorable in the regime $\epsilon^2 \ll \tau \ll \epsilon$ [15]. The transition from spherical-wave micelles to secondary domains is considered below. The free energy of the secondary domain structure was calculated in Ref. [15]. Here we slightly generalize the result allowing for arbitrary values of the parameter $\zeta=\frac{1}{\sqrt{\Gamma_4}l_0}$. We consider spherical secondary domains of radius $R_s$, and mean concentration $c_s$. The most stable primary pattern is a body-centered cubic (bcc) structure of six plane waves with $q=q^* \simeq \left(\frac{2\tau}{3}\right)^{1/2}\frac{1}{l}$: $\eta(r) \simeq -2A\sum_{s=1}^{6}\cos(q_s\cdot r)$. The amplitude $A$ is nearly constant inside the secondary domain; $A \simeq 0$ in the matrix outside the domain.

The secondary structure can be analyzed using the general Eqs. (54)–(57) (with $c_d$ replaced by $c_s$). These equations stay valid except a modification of Eq. (56): Higher-order corrections [see Eqs. (19) and (21)] to the nonlocal energy must be taken into account

$$f_{\rm nloc} \simeq \frac{c_0}{m}\frac{16}{l_0^2}\left\{\int_{q,q'}\frac{|\eta_{\boldsymbol q}|^2|\eta_{\boldsymbol q'}|^2}{q^2+q'^2}+\frac{1}{q^{*4}l_0^2}\left[\int \eta(\boldsymbol r)^3 d^3r\right]^2 + \int_{q,q'}\frac{|\tilde\varphi_{\boldsymbol q}|^2|\tilde\varphi_{\boldsymbol q'}|^2}{q^2+q'^2}\right\}, \qquad (63)$$

where $\tilde\varphi(\boldsymbol r)=\frac{\sqrt{2}}{q^* l_0}\langle\eta^2(\boldsymbol r)\rangle_{\rm loc}$, $\langle\cdot\rangle_{\rm loc}$ means smoothing over a length-scale longer than $2\pi/q^*$, but shorter than $R_s$. Calculating the mean free energy density $f$ for $\tau \gg \tau_0$, we get in analogy with Eq. (59)

$$f = f_0[1-\Delta_{fs}],$$

where $f_0$ is defined in Eq. (58), and

$$\Delta_{fs} \simeq \Delta_p + \Delta_s + \Delta_i.$$

Here $\Delta_p$ is due to the $\eta^3$ and $\eta^4$ terms in the local energy and the sixth order nonlocal term

$$\Delta_p \simeq -\frac{3\Gamma_4}{2\tau}(16\epsilon A - 45\mu A^2), \quad \mu \equiv 1 + \frac{32}{45}\zeta^2.$$

Minimizing $\Delta_p$ with respect to $A$ we get

$$A = A_0 \simeq \frac{8\epsilon}{45\mu}, \quad \Delta_p \simeq -\frac{16}{15\mu}\frac{\tau_0}{\tau}.$$

The second correction $\Delta_s$ is due to the second nonlocal energy term [see Eq. (63)]

$$\Delta_s \simeq 0.151\frac{R_s^2\epsilon^4 l^2}{\tau l_0^4\mu^4}.$$

The last term $\Delta_i$ accounts for the surface energy of the secondary domain

$$\Delta_i \simeq 1.46\frac{l\epsilon\sqrt{\Gamma_4}}{\tau R_s\mu}.$$

Note that $\Delta_i$ is proportional to the surface tension $\gamma$ at the boundary between bcc and disordered regions. The tension was calculated in Ref. [15] [see Eq. (32) there]. The thickness of the interfacial region is $\xi \simeq 1.37\frac{l\mu}{\epsilon\sqrt{\Gamma_4}}$.

Minimizing $\Delta_s+\Delta_i$ with respect to $R_s$ we get

$$R_s \simeq \frac{1.69}{\zeta^{1/3}}\frac{l_0\mu}{\epsilon}, \quad \Delta_{fs} \simeq (0.65\zeta^{4/3} - 1.07\mu)\frac{\tau_0}{\tau\mu^2}.$$

The bcc secondary domains are more stable than the spherical-wave micelles if $\Delta_{fs}$ is smaller than $\Delta_f$ defined in Eq. (62). The transition ($\Delta_{fs}=\Delta_f$) occurs at $\tau=\tau_t$,

$$\frac{\tau_t}{\tau_0} \approx \frac{10.41\mu^2}{\mu - 0.61\zeta^{4/3}}. \qquad (64)$$

Thus, $\tau_t/\tau_0 \approx 20$ for $\zeta = 1/\sqrt{2}$ corresponding to the correlated random copolymers. This large value of $\tau_t/\tau_0$ approximately justifies the assumption $\tau \gg \tau_0$ used above to calculate the free energies of spherical-wave and bcc micelles. For example, the spherical-wave micelles are characterized by the ratio $\kappa/q^* \approx 0.12$ at the transition point, so the approximation $\kappa/q^* \ll 1$ is plausible.

The number of primary "spheres" (loops) per secondary domain is

$$N_p \simeq V_s/V_p,$$

where $V_s \simeq 4\pi R_s^3/3$ is the domain volume, and $V_p = 8\sqrt{2}\pi^3/q^{*3}$ is the volume per loop in the bcc structure. Using the results for $R_s$ and $q^*$ we obtain

$$N_p \simeq 0.0889\frac{\mu^3}{\zeta^4}\left(\frac{\tau}{\tau_0}\right)^{3/2}.$$

For $\zeta = 1/\sqrt{2}$ at the transition point we thus get $N_p \approx 77$. For smaller values of $\zeta$ (i.e., closer to the Lifshitz point) $N_p$ is larger. $N_p$ further increases for $\tau > \tau_t$. Therefore the secondary domains are always significantly larger than the primary domains.

The volume fraction of bcc micelles is

$$p = c_s V_s = -\frac{F_{\rm loc}}{f_{\rm nloc}} V_s \simeq \frac{75}{256}\frac{l_0^2}{l^2}\frac{\tau^2\mu^2}{\epsilon^2}$$

and their concentration is

$$c_s = \frac{p}{V_s} \simeq 0.0145\zeta\frac{\epsilon}{l^2 l_0 \mu}\tau^2.$$

The ratio of concentration of spherical-wave micelles to concentration of bcc micelles is

$$\frac{c_d}{c_s} \simeq 2.2\frac{\mu}{\zeta^4}\left(\frac{\tau}{\tau_0}\right)^{1/2}.$$

This ratio is large at the transition point: $c_d/c_s \gtrsim 50$ if $\zeta \lesssim 1/\sqrt{2}$.

It is interesting that the narrow interface approximation (assuming that $\xi \ll R_s$) becomes strictly valid near the Lifshitz point where $\zeta$ is small: Note that $\xi/R_s \simeq 0.81\zeta^{4/3}$. Therefore the theory of secondary domain structures developed in Ref. [15] and outlined above is asymptotically exact for $\tau \gg \tau_0$ if $\zeta \ll 1$.

## VI. DISCUSSION AND CONCLUSIONS

(1) Microphase-separation transition in irregular (partially random) block copolymers is considered in the paper. We analyze the most important case when the copolymer chemical sequence (the sequence of A and B units) is quenched; different chains, or different fragments of the same chain are generally characterized by different sequences which however are governed by a common statistical distribution. The relevant "order parameter" is the local copolymer composition, i.e., the local excess of A units over B units.

We focus on the weak segregation regimes (WSL) appropriate for compositionally nearly symmetric copolymer systems. It is shown that the transition from a disordered liquid (macroscopically homogeneous copolymer melt) to a microdomain superstructure necessarily involves an intermediate stage of micelle formation. Although block-copolymer micelles are well known, their relevance for *weak segregation* was not recognized so far. We considered different micelle types: plain spherical micelles with nearly homogeneous core (Sec. V A); spherical-wave micelles with space-oscillating composition profile (Sec. V B); and secondary micelles with internal periodic structure (Sec. V C).

(2) In the paper we present a rather detailed analysis of the nonlocal energy $F_{\rm nloc}$ in the most relevant case when micelle volume fraction is low $p \ll 1$. This energy plays a keyrole in stabilizing random copolymer micelles in the WSL. So far the nonlocal energy was treated using the well-known fourth-order expression [see Eq. (1)] which is valid if the amplitude of composition inhomogeneity $A = \Delta\eta$ is small enough. We showed that this classical fourth-order approximation for $F_{\rm nloc}$ is insufficient for the analysis of micelle formation. Some time ago [10] we argued that $F_{\rm nloc}$ must be also proportional to $A^4$ in the case of sufficiently large amplitude, when the relevant fragments of copolymer chains are strongly stretched. It is interesting that the regime of strongly stretched fragments does not necessarily imply a strong segregation regime: The composition inhomogeneity may be still relatively weak: $\Delta\eta/\eta_{\rm max} \ll 1$, see Sec. IV B and Ref. [10]. In the present paper we find that there are many intermediate regimes between the two $A^4$-behaviors for $p \ll 1$ [see Eqs. (39)–(42)].

The most essential features of these regimes are summarized below (points 3–5):

(3) If $A$ is not too high then $F_{\rm nloc}$ per micelle is proportional to $p$ in the limit $p \to 0$, so that $F_{\rm nloc}/p$ depends only on the micelle composition pattern (more precisely, we consider spherical micelles of volume $V_d$ and radius $R_d$, the composition $\eta =$ const in the matrix outside the micelles, $\eta$ deviates from this constant inside the micelle). We establish exact analytical expressions defining nonlocal energy in this regime, Eqs. (13)–(16). In the low-amplitude limit the classical $A^4$ behavior is recovered [see Eq. (1) for infinite chains, or Eq. (17) for chains with finite number of blocks]. In effect the general result includes all higher-order nonlocal terms in the $A$ expansion. We showed that in the case of a structure involving two essentially different length scales the dominant contributions to $F_{\rm nloc}$ may come from two terms: $A^4$ and $A^8$. It is demonstrated that the $A^8$ term [see Eqs. (21) and (20)] isequivalent to the nonlocal energy associated with the second-order parameter introduced in Ref. [15].

(4) Let us change the amplitude of the composition profile $\eta(\underline{\boldsymbol{r}})$ keeping its shape invariant and consider $F_{\rm nloc}/p$ is a function of $A$. In the case of infinite chains ($N \to \infty$) this function shows an interesting and nontrivial behavior: It diverges as $A$ tends to the critical value $A^*$ [$A^*$ depends on the shape of $\eta(\underline{\boldsymbol{r}})$]. In order to qualitatively account for this behavior let us consider a simple example: Instead of a micelle we consider a subvolume $V_d$ of the total volume $V, V_d \ll V$, but $R_d$ (the size of $V_d$) is much larger than the copolymer chain size. Then the chains can be treated as material points; their concentration is constant ($=c_0/N$) as the system is incompressible. To further simplify the model, we consider symmetric completely random copolymer chains, $N$ monomers per chain, mean number of A units per chain is $N/2$, $N \gg 1$. The chains differ in their mean composition $\sigma = N_A/N - 0.5$, where $N_A$ is the number of A units in a chain. The total number of chains with a given composition is $\mathcal{N}_\sigma \simeq \text{const}\ e^{-\sigma^2/(2\sigma_0^2)}$, where $\sigma_0^2 = 1/(4N)$, and const accounts for normalization. The imposed order parameter field is $\eta(\boldsymbol{r}) = (1-p)A$ for $\boldsymbol{r}$ in $V_d$, $\eta(\boldsymbol{r}) = -pA$ otherwise, where $p = V_d/V \ll 1$. The ideal-gas free energy of the system is

$$F = \sum_{\sigma} \int c_{\sigma}(r) \ln c_{\sigma}(r) d^3 r,$$

where $c_{\sigma}(r)$ is local concentration of chains with composition $\sigma$. The free energy for a given $\eta(r)$ can be obtained by minimizing $F$ with side conditions

$$\int c_{\sigma}(r) d^3 r = \mathcal{N}_{\sigma}, \quad \sum_{\sigma} c_{\sigma}(r) = c_0/N, \quad \sum_{\sigma} \sigma c_{\sigma}(r) = \eta(r) c_0/N.$$

The result is

$$F = \text{const} + F_{\text{loc}} + F_{\text{nloc}},$$

where const is irrelevant, $F_{\text{loc}} = 2c_0 \int \eta(r)^2 d^3 r = 2c_0 V_d (1-p) A^2$, and

$$F_{\text{nloc}} \simeq \frac{c_0 V_d p}{2N} (e^{4NA^2} - 1 - 4NA^2).$$

if $p$ is small enough: $pe^{12NA^2} \ll 1$. Thus $F_{\text{nloc}} \propto A^4$ for small $A(NA^2 \ll 1)$, but it exponentially increases with $A$ if $NA^2 \gtrsim 1$. The physical meaning of this strong increase is simple: For $NA^2 \gg 1$ the only way to achieve the required composition in $V_d$ is to accumulate there untypical chains with $\sigma \gg \sigma_0$. The number $\mathcal{N}^*$ of these chains exponentially decreases with $A$. Replacing typical chains in $V_d$ by the untypical chains results in a significant depletion of untypical chains outside $V_d$. The relative depletion strength is inversely proportional to $\mathcal{N}^*$, i.e., it exponentially *increases* with $A$. $F_{\text{nloc}}$ is related to this depletion effect and thus it also increases exponentially. For sufficiently large $A$ the total number of untypical chains (with composition $\sigma \gtrsim A$) is not enough to fill $V_d$, hence $F_{\text{nloc}}$ becomes formally infinite (the singularity is approximately defined by the condition $pe^{2NA^2} \sim 1$).

Of course the model treating copolymer chains as material points may seem oversimplified, but it captures all right the qualitative tendency of sharp increase of $F_{\text{nloc}}$ near a certain value of the composition contrast.

(5) Let us return to the more interesting case when polymer coils are much larger than the micelle size $R_d$ (more precisely, we assume that $N \to \infty$). In this case the nonlocal energy is related to interactions of the relevant *blobs* (copolymer fragments of Gaussian size $R_g \sim R_d$) with the micelle, i.e., with the region $V_d$ of nonuniform composition (see Sec. IV B). The blobs with the mean composition $\sigma$ of the same sign as $\eta$ in $V_d$ are referred to as proper blobs (the typical $\sigma$ in a proper blob is $\sim l_0/R_d$, where $l_0 = m^{1/2} a$ is the typical size of A or B blocks). The proper blobs are attracted by $V_d$; the attraction energy per proper blob is $k_B T A/A^*$, where $A^* \sim l_0/R_d$. If several proper blobs form a continuous sequence, it will tend to adsorb on $V_d$ if $A \sim A^*$.As $A$ increases toward $A^*$ longer and longer sequences provide the major contribution to $F_{\text{nloc}}$. The very $A^*$ is defined by the balance between the adsorption energy and the entropy loss associated with the low probability of a continuous sequence (see Sec. IV B). For $A > A^*$ the depletion effect considered in the previous point 4 becomes very significant because long sequences of proper blobs are extremely rare. The depletion results in a nonlinear dependence of $F_{\text{nloc}}$ on $p$ for $A > A^*$: $F_{\text{nloc}} \propto p^{\alpha-1}$ for $p \to 0$, where the exponent $\alpha - 1$ depends on $A$: It decreases with $A$ as $\alpha - 1 \approx A^{*2}/A^2$. For small $p$ this dependence of $\alpha$ results in an exponential increase of $F_{\text{nloc}}$ with $A$ in the region $A^* \lesssim A \lesssim A^*(\ln \frac{1}{p})^{1/2}$, see Eqs. (41) and (42). Therefore the nonlocal effects are significantly enhanced for $p \ll 1, A > A^*$ as compared to the classical $A^4$ prediction, Eq. (1). It is remarkable however that conformations of fragments of copolymer chains *averaged* with respect to *sequence variations* remain nearly Gaussian for $A \ll A^*(\ln \frac{1}{p})^{1/2}$, i.e., in all the regimes considered so far except the regime of strongly stretched blobs, Eq. (43). The idea is that although untypical long copolymer fragments with appropriately shifted composition tend to adsorb on the micelle and thus they significantly contribute to $F_{\text{nloc}}$, their contribution to the overall conformational distribution is negligible.[5]

(6) We show that the disorder-to-order transition in the copolymer system occurs when the interaction parameter $\chi$ is still below the critical (spinodal) point $\chi^*$: The transition point is $\chi = \chi_0 = \chi^*(1 - \text{const } \epsilon^2)$, where $\epsilon$ is the mean composition asymmetry (excess of A over B) of the copolymer sequence, and const is a numerical constant. This is in contrast with the previous theories [1,6,15] predicting the transition for random copolymers precisely at the spinodal $\chi = \chi^*$.[6] Above $\chi_0$ a structure of micelles is formed (see Sec. V). Close to $\chi_0$ the micelles are nearly uniform droplets with "reflected" composition (i.e., if the relative excess of A over B in the matrix outside the micelles is $\epsilon$, then a nearly equal excess of B over A, $-\epsilon$, is predicted in the micelles); the composition changes from $-\epsilon$ to $\epsilon$ in a relatively thin surface layer. Just above $\chi_0$ the micelles are very large and their volume fraction $p$ is exponentially small. The micelle size is inversely proportional to $x = \frac{\chi - \chi_0}{\chi^* - \chi_0}$ (note that $x = \frac{\tau}{\tau_0}$, see Sec. V); it decreases down to $R_d \sim l_0/\epsilon$ at $x \sim 1$ (in particular, at $\chi = \chi^*$). Concurrently the fraction of micelles increases to $p \sim \epsilon^2$. In the region $x \gtrsim 1$ the micelles are not uniform any more: They show progressively more pronounced oscillations. For $x \sim 10$ their structure is approximately described by the spherical-wave model [Eq. (61)]. A transformation of spherically symmetric micelles to micelles with internal (primary) pattern is predicted at $x = x_t \gtrsim 20$, see Eq. (64). This transformation is a first-order transition accompanied by a significant change of both the size and number of micelles: For example, the number of micelles decreases by a factor $\gtrsim 50$ at the transition point. The emerging internal composition pattern is a nearly periodic structure with body-centered cubic (bcc) symmetry inside each micelle. The number of internal subdomains (loops of bcc structure) per micelle $N_p$ is

---

[5] For example, consider all $g$ fragments starting at a given point $\boldsymbol{r}$ near $V_d$. Their overall distribution is nearly Gaussian at $A \sim A^*$ although some of these fragments are attracted by $V_d$ (those with proper mean composition), and some (with the opposite composition) are repelled.

[6] The order-disorder transition at $\chi_0 < \chi^*$ was predicted in Ref. [17]. The transition $\chi_0$ is not affected by the nonlocal free energy contribution. That is why the correct $\chi_0$ can be deduced from the results of Ref. [12] in spite of the incorrect treatment of the nonlocal energy adopted there.

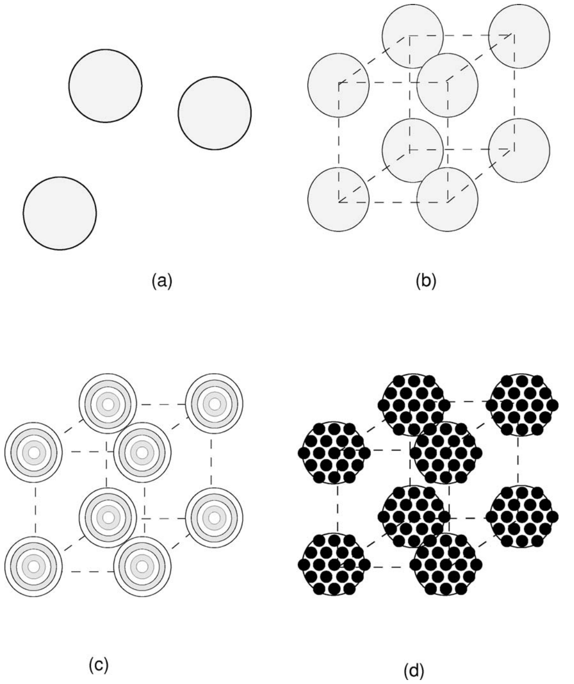

FIG. 1. The schematic sequence of micelle transformations as the interaction parameter $\chi$ increases beyond the threshold $\chi_0$: (a) disordered nearly uniform micelles; (b) ordered nearly uniform micelles (simple cubic lattice is shown instead of face-centered cubic, for simplicity); (c) spherical-wave micelles; and (d) micelles with internal bcc structure.

large at the transition point $N_p \gtrsim 80$ and it increases further with $\chi$. Since $N_p$ must change in a discontinuous way, we expect a series of auxiliary first-order structural transitions above $\chi_t$. These transitions are expected to be weak as $N_p$ is large. The predicted sequence of micelle transformations is illustrated in Fig. 1.

(7) A gas of micelles is predicted at $\chi$ just above $\chi_0$ when the micelle concentration is very low, and hence their interactions are negligible. However the interaction energy increases with $\chi$ as the micelle concentration rises, therefore micelles crystallize in a superlattice at some $\chi$. This is a first-order transition of a special kind that is not accompanied by a phase separation (see Appendix B). Using Eq. (B14) we estimate the interaction energy per micelle $F_{\mathrm{int}}=F^{(8)}_{\mathrm{nloc}}$ as $F_{\mathrm{int}} \sim k_{\mathrm{B}}T\frac{b^3}{v}m^{1/2}\epsilon^{11/3}$ for $x \sim 1$ ($v=1/c_0$ is the volume per monomer unit). Therefore micelles are ordered at $x \sim 1$ if $\epsilon m^{3/22} \gtrsim 1$, otherwise the ordering transition is shifted to $x \gg 1$. The most stable superlattice of micelles is of face-centred cubic (fcc) type both at $x \sim 1$ and $x \gg 1$ (see Appendix B).

(8) The free energy of a structure involving two essentially different length scales $1/q^*$ and $\Lambda \gg 1/q^*$ was calculated in Ref. [15] using the concept of the second-order parameter for the case when the primary structure is a superposition of weak harmonic waves ($A \ll A^*$) with nearly equal wave numbers $q \simeq q^*$. These results are generalized for the case when $A \sim A^*$ and for arbitrary primary pattern involving $q$'s of different magnitude (see Appendix A). It is shown that in the general case the second-order parameter is proportional to the nonlocal energy associated with the primary structure.

(9) The results obtained in the paper are applicable near the critical point of a system of stochastic copolymers (both second and third derivatives of the free energy density with respect to composition must vanish at the critical point). Otherwise the results are rather universal. They are applicable to copolymer melts, to their concentrated and semidilute solutions, including moderately selective solvents. The monomer units can be geometrically asymmetric: The assumptions that A and B blocks are characterized by the same statistical segments and the same volume per unit are not essential. The copolymer sequence must satisfy a few broad conditions: It must be (at least partially) irregular, quenched, characterized by finite-range correlations; the copolymer chain must be much longer than the correlation range which, in turn, must much exceed the unit size. Different chains are characterized by different (uncorrelated) sequences. This class includes, in particular, correlated random copolymers [11,15], and block copolymers with polydisperse blocks [4,5,10,14]. For $x \ll 1/\epsilon$ the only essential nondimensional parameter involved in the theory is $\zeta=\frac{1}{\sqrt{\Gamma_4}l_0}$ [see Eq. (48)]; $\zeta^2=1/2$ for correlated random copolymers; $\zeta^2$ is small in the vicinity of the Lifshitz point [4,5]. The narrow interface approximation used to analyze the structure of (secondary) micelles with internal bcc composition pattern in the range $1 \lesssim x \ll 1/\epsilon$ is asymptotically valid for small $\zeta$.

(10) Composition fluctuations are not considered in the paper. The fluctuation effects are negligible near the critical point if $\epsilon m^{1/4} \gg 1$ [2,12].

## ACKNOWLEDGMENTS

A partial support of NATO SfP Grant No. 974173 is acknowledged.

## APPENDIX A: FREE ENERGY OF A SECONDARY STRUCTURE

Let us consider a structure of periodically arranged secondary domains in a disordered matrix. Each secondary domain $V_2$ of size $\Lambda$ shows an internal periodic structure $\tilde{\eta}(\boldsymbol{r})$. The composition profile in one cell of the secondary structure (the cell volume is $V$) is $\eta(\boldsymbol{r})=\tilde{\eta}(\boldsymbol{r})\phi(\boldsymbol{r})$, where $\phi(\boldsymbol{r})=\begin{cases}1, & \boldsymbol{r} \text{ in } V_2\\ 0, & \text{otherwise}\end{cases}$. The function $\phi(\boldsymbol{r})$ defines the secondary structure, while $\tilde{\eta}(\boldsymbol{r})$ corresponds to the primary structure with period $\sim\lambda$. We assume that $\lambda \ll \Lambda$, and that $\langle\tilde{\eta}(\boldsymbol{r})\rangle=0$, where $\langle\cdot\rangle$ means averaging over the primary cell (the latter condition follows from the requirement $\int \eta(\boldsymbol{r})d^3r=0$).

We start formally with the case when the primary structure occupies the whole volume of the system ($V=V_2$). The nonlocal free energy of the system of infinite chains is then defined in Eq. (27), where $\psi=\tilde{\psi}$ satisfies Eq. (23)

$$a^2\nabla_6^2\tilde{\psi}+\tilde{u}\tilde{\psi}=\gamma_1\tilde{\psi}, \tag{A1}$$

where $\tilde{u}(\boldsymbol{r},\boldsymbol{r}')=\tilde{\eta}(\boldsymbol{r})\tilde{\eta}(\boldsymbol{r}')/K_0, \langle\tilde{\psi}\rangle=1$. Using the above equations and the periodicity of $\tilde{\psi}$ we find the average density of the nonlocal energy

$$f_1 = \frac{c_0}{2}\gamma_1.$$

These equations are valid if $\gamma_1$ is low enough

$$\gamma_1 \lambda^2 / a^2 \ll 1 \tag{A2}$$

[see end of Sec. III C, Eq. (28)]. Note that this condition ensures that $\tilde{\psi}$ must be close to unity everywhere, perhaps, apart from some regions occupying a small fraction of the volume (where $\tilde{u}$ is high).

Turning to the general case, $\eta(\boldsymbol{r}) = \tilde{\eta}(\boldsymbol{r})\phi(\boldsymbol{r})$ (primary structure in $V_2$ and disordered matrix in $V - V_2$) we demand that the function $\tilde{\psi}(\boldsymbol{r})$ satisfies Eq. (A1) when both $\boldsymbol{r}$ and $\boldsymbol{r}'$ are in $V_2$. Outside this region it must obey the Laplace equation

$$\nabla_6^2 \tilde{\psi} = 0.$$

Therefore for any $(\boldsymbol{r}, \boldsymbol{r}')$ $\tilde{\psi}$ satisfies the equation

$$a^2 \nabla_6^2 \tilde{\psi} + u\tilde{\psi} = \gamma_2 \psi, \tag{A3}$$

where $\gamma_2 = \gamma_2(\boldsymbol{r}, \boldsymbol{r}') = \gamma_1 \phi(\boldsymbol{r})\phi(\boldsymbol{r}')$ and $u = \eta(\boldsymbol{r})\eta(\boldsymbol{r}')/K_0 = \tilde{u}(\boldsymbol{r}, \boldsymbol{r}')\phi(\boldsymbol{r})\phi(\boldsymbol{r}')$. Obviously thus defined $\tilde{\psi}$ must be nearly periodic in $V_2$ and nearly constant, $\tilde{\psi} \simeq 1$, outside $V_2$ (here we disregard the interfacial layer(s) of thickness $\sim\lambda$ at the boundary between $V_2$ and the matrix).

Next we write $\psi = \tilde{\psi}\psi'$, where $\psi'$ is a modulation function corresponding to $\phi(\boldsymbol{r})$. Substituting this $\psi$ in Eq. (23) and using Eq. (A3) we get

$$a^2 \nabla_6^2 \psi' + 2a^2 (\nabla \ln \tilde{\psi}) \cdot \nabla \psi' = (\gamma - \gamma_2)\psi'. \tag{A4}$$

The second term in the l.h.s. of the last equation can be neglected since $\langle \nabla \ln \tilde{\psi} \rangle = 0$, and, more importantly, $\langle (\nabla \ln \tilde{\psi}) \cdot \nabla \psi' \rangle \simeq 0$ [the last statement can be verified by solving Eq. (A4) perturbatively treating the $\nabla \ln \tilde{\psi}$ term as a perturbation]. Therefore

$$a^2 \nabla_6^2 \psi' \simeq (\gamma - \gamma_2)\psi'. \tag{A5}$$

Recalling the periodicity of $\psi'$ (with elementary cell $V$) we find

$$\int (\gamma - \gamma_2)\psi' d^6 r = 0.$$

This equation defines $\gamma$ once $\psi'$ is known.

Taking into account that $\langle \tilde{\psi}\psi' \rangle_V \simeq 1$, and that $\langle \tilde{\psi} \rangle \simeq 1$ inside $V_2$, $\tilde{\psi} \simeq 1$ outside $V_2$, we get: $\langle \psi' \rangle_V \simeq 1$, where $\langle \cdot \rangle_V$ means averaging over the secondary cell $V \cdot V$. Let us consider now the most important case, when $\psi'$ is close to 1 everywhere: $\psi' = 1 + \delta\psi'$, $|\delta\psi'| \ll 1$. Then, using Eq. (A5) we get

$$\delta\psi'_{q,q'} \simeq \frac{\gamma_1 \phi_q \phi'_q}{q^2 + q'^2}, \quad (q, q') \neq 0,$$

where $\delta\psi'_{q,q'}$, $\phi_q$ are Fourier transforms of $\delta\psi'(\boldsymbol{r}, \boldsymbol{r}')$, $\phi(\boldsymbol{r})$, respectively. Finally, on using Eq. (27), we obtain

$$\begin{aligned} F_{\text{nloc}} &\simeq \frac{c_0}{2V} \int u\tilde{\psi}\psi' d^6 r \\ &\simeq \frac{c_0 V}{2}\gamma_1 p_2^2 + \frac{c_0}{2Va^2}\gamma_1^2 \int_{q,q'} \frac{|\phi_{\underline{q}}|^2 |\phi_{\underline{q}'}|^2}{q^2 + q'2}, \end{aligned} \tag{A6}$$

where $p_2 = V_2/V$ is the fraction of ordered (secondary) domains, and $F_{\text{nloc}}$ is the nonlocal energy per cell $V$. This equation is valid if $|\delta\psi'| \ll 1$, i.e.,

$$\gamma_1 \Lambda^2 / a^2 \ll 1, \tag{A7}$$

which is a stronger requirement that the condition (A2). The first term in the r.h.s. of Eq. (A6) is the nonlocal energy due to primary structure, and the second is that due to secondary structure. This second term generalizes the secondary nonlocal energy obtained in Ref. [15] for the case of a *weak* primary structure, when $\tilde{\eta}(r)$ is a superposition of weak harmonic waves with wave-vectors $q_i$, $|q_i| = q^*$. In this case $\gamma_1$ can be easily calculated using the classical fourth-order expression Eq. (1)

$$\gamma_1 \simeq \frac{8}{m^2 a^2 q^{*2}} \langle \tilde{\eta}^2 \rangle^2.$$

With $\gamma_1$ defined above, the last term in Eq. (A6) becomes identical to the secondary nonlocal energy obtained previously [15] using the concept of the second-order parameter $\tilde{\varphi}$. In the general case, when $\tilde{\eta}(r)$ involves wave numbers of different magnitude, we can still think of the second-order parameter $\tilde{\varphi}$ conjugate to the given primary structure: $\tilde{\varphi}$ may involve local fluctuations of the sequence correlation functions [the pair function $C_\sigma(n)$ Eq. (4), and higher-order functions]. We anticipate that $\tilde{\varphi}$ is nearly constant in the ordered domain $V_2$ and in the matrix: $\tilde{\varphi}(r) \simeq \text{const}[\phi(r) - p_2]$. Thus, following the argument explained in Ref. [15], one can obtain the general expression for the secondary nonlocal energy

$$F_{\text{nloc}}^{(8)} = \frac{\text{const}}{V} \int_{q,q'} \frac{|\phi_q|^2 |\phi_{q'}|^2}{q^2 + q'2} \tag{A8}$$

with unknown constant. By comparison with Eq. (A6) we find $\text{const} = \frac{c_0 \gamma_1^2}{2a^2}$.

There is one subtle point here: As the modulation function $\phi(r)$ is periodic, the integrals in Eqs. (A6) and (A8) must be replaced by the corresponding sums: $\int_{q,q'} \to \frac{1}{V^2}\Sigma_{q,q'}$. The sum in Eq. (A6) should include all terms with either $q \neq 0$ or $q' \neq 0$. On the other hand, the second-order parameter formalism yields the same sum, but with both $q \neq 0$ and $q' \neq 0$. The difference between $\Sigma_{(q,q') \neq 0}$ and $\Sigma_{q \neq 0, q' \neq 0}$ is negligible for $p_2 \to 0$, i.e., in the regime where the six-dimensional approach [Eq. (27)] is asymptotically exact. On the other hand, the validity of the second-order parameter ($\tilde{\varphi}$) approach does not depend on $p_2$ since $\tilde{\varphi}$ is a local parameter characterizing the copolymer sequence. Therefore it is likely that it is the second approach that yields the expression for the secondary nonlocal energy which is valid for any $p_2$

$$F_{\text{nloc}}^{(8)} \simeq \frac{c_0}{2V^3 a^2}\gamma_1^2 \sum_{q\neq 0, q'\neq 0} \frac{|\phi_q|^2|\phi_{q'}|^2}{q^2+q'^2}. \tag{A9}$$

The above results can be generalized to the case, when the mean order parameter $\eta$ averaged over the ordered domain is nonzero: $\langle \eta(r)\rangle_{V_2} \neq 0$. In this case the composition distribution can be represented as

$$\eta(r) = \tilde{\eta}(r)\phi(r) + \bar{\eta}(r),$$

where $\tilde{\eta}$ is a periodic function, $\langle \tilde{\eta}\rangle = 0$ as before, and $\bar{\eta}(r)$ is a smooth function which is nearly constant in the regions of size $\sim\lambda$ (the typical example: $\bar{\eta}(r) = \bar{\eta}_0[\phi(r) - p_2]$). Then the "potential" $u(r,r') = \{\tilde{\eta}(r)\tilde{\eta}(r')\phi(r)\phi(r') + \bar{\eta}(r)\bar{\eta}(r') + \tilde{\eta}(r)\bar{\eta}(r')\phi(r) + \tilde{\eta}(r')\bar{\eta}(r)\phi(r')\}/K_0$. It is possible to show that the mixed terms (the last two terms in curly brackets) are not significant: They produce just a subdominant correction to the nonlocal energy if the basic condition (A2) is valid. Keeping only the first two terms in curly brackets in the above expression for $u$, representing $\psi = \tilde{\psi}\psi'$, and proceeding along the line considered before Eq. (A9), we find

$$F_{\text{nloc}}^{(8)} \simeq \frac{c_0}{2V^3 a^2} \sum_{q\neq 0, q'\neq 0} \frac{\frac{1}{K_0^2}|\bar{\eta}_q|^2|\bar{\eta}_{q'}|^2 + \gamma_1^2|\phi_q|^2|\phi_{q'}|^2 + \frac{2\gamma_1}{K_0}\bar{\eta}_q\bar{\eta}_{q'}\phi_{-q}\phi_{-q'}}{q^2+q'^2}. \tag{A10}$$

Here, in addition to condition (A7), we assume that

$$\frac{\bar{\eta}^2\Lambda^2}{K_0 a^2} \ll 1. \tag{A11}$$

This equation can be also formally derived using the fourth-order perturbation approach [15] involving two independent order parameters $\bar{\eta}$ and $\tilde{\varphi}$.

## APPENDIX B: INTERACTION OF MICELLES

The (droplet) micelle concentration depends on the interaction parameter $\chi$. There is a dilute nearly ideal gas of micelles very close to $\chi_0$. On the other hand the micelles form a super-crystal at higher $\chi$'s. The corresponding gas-to-crystal transition and the super-lattice type are defined by micelle interactions.[7]

Below we analyze these interactions and determine which super-crystal structure is the most favorable. To this end the lattice-dependent part of the free energy must be established first. For infinite chains this can be done using the approach considered in Sec. III C. The composition parameter field is[8]

$$\eta(\boldsymbol{r}) = \sum_n \eta^{(0)}(\boldsymbol{r} - \boldsymbol{r}^{(n)}) - c_d\eta_0, \tag{B1}$$

where $\eta^{(0)}(\boldsymbol{r})$ is the composition profile of one droplet, $\eta^{(0)} \to 0$ as $\boldsymbol{r}\to\infty$, $\boldsymbol{r}^{(n)}$ are the positions of droplet centers, $c_d$ is their mean concentration, $\eta_0 = \int \eta^{(0)}(\boldsymbol{r})d^3r$. The potential field involved in Eq. (23) is $u(\boldsymbol{r}_1,\boldsymbol{r}_2) = \eta(\boldsymbol{r}_1)\eta(\boldsymbol{r}_2)/K_0$. We consider the general case $u \sim u^*$. The nonlocal free energy per micelle (per cell of volume $V = 1/c_d$) is defined in Eq. (27). Defining Fourier transforms of the functions $u(\boldsymbol{r}_1,\boldsymbol{r}_2) \equiv u(\boldsymbol{r})$ and $\psi(\boldsymbol{r}_1,\boldsymbol{r}_2) \equiv \psi(\boldsymbol{r})$,[9]

$$u_{\boldsymbol{q}} = \int_{V^2} u(\boldsymbol{r})e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}d^6r, \quad \psi_{\boldsymbol{q}} = \int_{V^2} \psi(\boldsymbol{r})e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}d^6r. \tag{B2}$$

We rewrite the nonlocal energy as

$$F_{\text{nloc}} \simeq \frac{c_0}{2V^3}\sum_{\boldsymbol{q}\neq 0} u_{\boldsymbol{q}}\psi_{-\boldsymbol{q}}. \tag{B3}$$

The integrals in Eqs. (B2) are taken over one cell. Taking into account that $\psi_0 \simeq V^2$ [see Eq. (25)] we define $\psi(\boldsymbol{r}) = 1 + \xi(\boldsymbol{r})$ and rewrite Eq. (23) in terms of Fourier transforms (note that $\xi_{\boldsymbol{q}} = \psi_{\boldsymbol{q}}$ for any $q \neq 0$)

---

[7] It is more appropriate to consider the ordering as a *liquid*-to-crystal transition since its concentration window is very narrow. In fact, the interaction of micelles is almost solely due to the nonlocal energy, which therefore is the major driving force for crystallization. However the nonlocal energy never favors phase separation: on the contrary, it always tends to suppress all sorts of long-range composition fluctuations in the system. Therefore crystallization of droplets is not accompanied by any significant phase separation as long as the contribution of the local energy to the micelle interaction is very small, which is true since the volume fraction of micelles is low.

[8] It is more physically meaningful to replace $c_d\eta_0$ by $c_d\eta_0[1 - \Sigma_n\Delta(\boldsymbol{r} - \boldsymbol{r}^{(n)})]$, where $\Delta(r) \simeq 1$ for $r \lesssim R_d$, $\Delta(r) \simeq 0$ for $r \gg R_d$, $R_d$ is the droplet radius. However this modification would not affect the non-local interaction energy calculated below.

[9] Note that $\boldsymbol{r} = (\boldsymbol{r}_1, \boldsymbol{r}_2)$ and $\boldsymbol{q} = (\boldsymbol{q}_1, \boldsymbol{q}_2)$ are six-dimensional vectors here and below in this section.

$$-(\gamma+a^2q^2)\xi_{\boldsymbol{q}}+u_{\boldsymbol{q}}+\frac{1}{V^2}\sum_{\boldsymbol{q}'\neq 0}u_{\boldsymbol{q}-\boldsymbol{q}'}\xi_{\boldsymbol{q}'}=0, \quad q\neq 0, \tag{B4}$$

where $\boldsymbol{q},\boldsymbol{q}'$ take all discrete values defined by the six-dimensional lattice. For example, for a simple cubic lattice $\boldsymbol{q}=\frac{2\pi}{R}\boldsymbol{n}$, where $\boldsymbol{n}$ is a six-dimensional vector with integer components $\boldsymbol{n}\in Z^6$, $R$ is the lattice period, = distance between the nearest micelles ($R^3=V$). Using Eqs. (26) and (29) we find $\gamma\sim p^2(b/R_d)^2$ for $A\sim A^*$. On the other hand, $a^2q^2=\frac{(2\pi)^2}{6}(b/R_d)^2p^{2/3}|\boldsymbol{n}|^2$, so that $\frac{a^2q^2}{\gamma}\gtrsim p^{-4/3}\gg 1$ for any nonzero $\boldsymbol{q}$. Therefore we can neglect $\gamma$ in Eq. (B4) for $q\neq 0$

$$-a^2q^2\xi_{\boldsymbol{q}}+u_{\boldsymbol{q}}+\frac{1}{V^2}\sum_{\boldsymbol{q}'\neq 0}u_{\boldsymbol{q}-\boldsymbol{q}'}\xi_{\boldsymbol{q}'}\simeq 0, \quad q\neq 0. \tag{B5}$$

Using Eq. (B1) we get $u_{\boldsymbol{q}}=u_{\boldsymbol{q}}^{(0)}+\delta u_{\boldsymbol{q}}$,

$$u_{\boldsymbol{q}}^{(0)}=\eta_{\boldsymbol{q}_1}^{(0)}\eta_{\boldsymbol{q}_2}^{(0)}/K_0, \tag{B6}$$

$$\delta u_{\boldsymbol{q}}=-\frac{\eta_0}{K_0}\Big[\eta_{\boldsymbol{q}_1}^{(0)}\Delta(\boldsymbol{q}_2)+\eta_{\boldsymbol{q}_2}^{(0)}\Delta(\boldsymbol{q}_1)\Big]+u_0\Delta(\boldsymbol{q}),$$

where $\boldsymbol{q}=(\boldsymbol{q}_1,\boldsymbol{q}_2)$, $\eta_{\boldsymbol{q}_1}^{(0)}=\int\eta^{(0)}(\boldsymbol{r}_1)e^{i\boldsymbol{q}_1\cdot\boldsymbol{r}_1}d^3r_1$, $\Delta(\boldsymbol{q}_1)=\begin{cases}1, & \boldsymbol{q}_1=0\\ 0, & \boldsymbol{q}_1\neq 0\end{cases}$, $u_0\equiv u_0^{(0)}=\eta_0^2/K_0$. In the main approximation we may replace $\frac{1}{V^2}\Sigma_{\boldsymbol{q}'}$ by $\int\frac{d^6q'}{(2\pi)^6}$, and neglect $\delta u$

$$-a^2q^2\xi_{\boldsymbol{q}}^{(0)}+u_{\boldsymbol{q}}^{(0)}+\int_{\boldsymbol{q}}u_{\boldsymbol{q}-\boldsymbol{q}'}^{(0)}\xi_{\boldsymbol{q}'}^{(0)}=0, \tag{B7}$$

which is equivalent to

$$a^2\nabla^2\xi^{(0)}+u^{(0)}[1+\xi^{(0)}]=0,$$

where $\nabla^2=\nabla_{\boldsymbol{r}_1}^2+\nabla_{\boldsymbol{r}_2}^2$, $\xi^{(0)}(\boldsymbol{r})\to 0$ for $r\to\infty$. Obviously $\xi^{(0)}$ is a single-micelle property that does not depend either on micelle concentration $c_d$ or on the super-lattice symmetry. Equation (B7) shows that $\xi_{\boldsymbol{q}}^{(0)}\simeq\frac{J+u_0}{a^2q^2}$ at small $q$'s, where

$$J=\int u^{(0)}(\boldsymbol{r})\xi^{(0)}(\boldsymbol{r})d^6r. \tag{B8}$$

It is clear that $\xi_{\boldsymbol{q}}$ must show a similar $1/q^2$ singularity at $q\to 0$. This singularity produces a correction to the integral representation of the sum in Eq. (B5)

$$\frac{1}{V^2}\sum_{\boldsymbol{q}'\neq 0}=\int_{q'}+\frac{1}{V^2}\widetilde{\sum_{\boldsymbol{q}'\neq 0}}, \tag{B9}$$

where $\widetilde{\Sigma}$ is the regularized sum which is effectively localized near the singular point. Substituting $u=u^{(0)}+\delta u$ and $\xi_{\boldsymbol{q}}=\xi_{\boldsymbol{q}}^{(0)}+\frac{\delta u_{\boldsymbol{q}}}{q^2a^2}+\delta\xi_{\boldsymbol{q}}$, $q\neq 0$, using the representation (B9) and neglecting inessential subdominant terms we get

$$-q^2\delta\xi_{\boldsymbol{q}}+\int_{\boldsymbol{q}'}u_{\boldsymbol{q}-\boldsymbol{q}'}^{(0)},\delta\xi_{\boldsymbol{q}'}=G_{\boldsymbol{q}}, \tag{B10}$$

where

$$G_{\boldsymbol{q}}\simeq-\frac{1}{V^2}\widetilde{\sum_{\boldsymbol{q}'\neq 0}}u_{\boldsymbol{q}-\boldsymbol{q}'}^{(0)}\xi_{\boldsymbol{q}'}^{(0)}-\frac{1}{V^2}\sum_{q'\neq 0}\delta u_{q-q'}\xi_{q'}^{(0)}-\frac{1}{V^2}\sum_{q'\neq 0}u_{q-q'}^{(0)}\frac{\delta u_{q'}}{q'^2a^2}.$$

Using Eqs. (B6) we obtain

$$\begin{aligned}G_{\boldsymbol{q}}\simeq{}&-\frac{1}{V^2}u_{\boldsymbol{q}}^{(0)}\frac{J+u_0}{a^2}\widetilde{\sum_{\boldsymbol{q}'\neq 0}}\frac{1}{q'^2}+\frac{1}{V}\frac{\eta_0}{K_0^2}\int_{q_3}\big[\xi_{(\boldsymbol{q}_1-\boldsymbol{q}_3,\boldsymbol{q}_2)}^{(0)}\\&+\xi_{(\boldsymbol{q}_1,\boldsymbol{q}_2-\boldsymbol{q}_3)}^{(0)}\big]\eta_{\boldsymbol{q}_3}^{(0)}+\frac{1}{V^2}\frac{\eta_0}{K_0^2a^2}\Bigg\{\eta_{\boldsymbol{q}_1}^{(0)}\sum_{\boldsymbol{q}_3\neq 0}\eta_{\boldsymbol{q}_2-\boldsymbol{q}_3}^{(0)}\eta_{\boldsymbol{q}_3}^{(0)}/q_3^2\\&+\eta_{\boldsymbol{q}_2}^{(0)}\sum_{\boldsymbol{q}_3\neq 0}\eta_{\boldsymbol{q}_1-\boldsymbol{q}_3}^{(0)}\eta_{\boldsymbol{q}_3}^{(0)}/q_3^2\Bigg\}\\\simeq{}&-u_{\boldsymbol{q}}^{(0)}\frac{1}{V^2a^2}\Bigg(J\widetilde{\sum_{\boldsymbol{q}'\neq 0}}\frac{1}{q'^2}+u_0\widetilde{\sum_{\boldsymbol{q}_1'\neq 0,\boldsymbol{q}_2'\neq 0}}\frac{1}{q'^2}\Bigg)\\&+\frac{1}{V}\frac{\eta_0}{K_0^2}\int_{q_3}\Bigg\{\xi_{(\boldsymbol{q}_1-\boldsymbol{q}_3,\boldsymbol{q}_2)}^{(0)}+\xi_{(\boldsymbol{q}_1,\boldsymbol{q}_2-\boldsymbol{q}_3)}^{(0)}\\&+\frac{1}{q_3^2a^2}\Big[\eta_{\boldsymbol{q}_1}^{(0)}\eta_{\boldsymbol{q}_2-\boldsymbol{q}_3}^{(0)}+\eta_{\boldsymbol{q}_2}^{(0)}\eta_{\boldsymbol{q}_1-\boldsymbol{q}_3}^{(0)}\Big]\Bigg\}\eta_{\boldsymbol{q}_3}^{(0)}.\end{aligned} \tag{B11}$$

Here $\boldsymbol{q}=(\boldsymbol{q}_1,\boldsymbol{q}_2)$, $\boldsymbol{q}'=(\boldsymbol{q}_1',\boldsymbol{q}_2')$ are six-dimensional vectors, $\boldsymbol{q}_1,\boldsymbol{q}_2,\boldsymbol{q}_3$ are three-dimensional vectors, $u_0=\eta_0^2/K_0$.

The last integral term in $G$ is not important since it does not depend on the lattice type, hence it produces a lattice-independent contribution to $\xi$ which is subdominant as compared with $\xi^{(0)}$. Neglecting this term, i.e., keeping only the first term which is proportional to $(u_{\boldsymbol{q}}^{(0)})$ in the r.h.s. of Eq. (B11) and solving Eq. (B10) we find

$$\delta\xi_{\boldsymbol{q}}\simeq\frac{1}{V^2a^2}\Bigg(J\widetilde{\sum_{\boldsymbol{q}'\neq 0}}\frac{1}{q'^2}+u_0\widetilde{\sum_{\boldsymbol{q}_1'\neq 0,\boldsymbol{q}_2'\neq 0}}\frac{1}{q'^2}\Bigg)\xi_{\boldsymbol{q}}^{(0)}.$$

Finally, on substituting $\xi_{\boldsymbol{q}}=\xi_{\boldsymbol{q}}^{(0)}+\frac{\delta u_g}{q^2a^2}+\delta\xi_{\boldsymbol{q}}$ and $u=u^{(0)}+\delta u$ in Eq. (B3) we get

$$F_{\text{nloc}}\simeq\frac{c_0}{2V}\Bigg\{J+\frac{1}{V^2a^2}\Bigg(J^2\widetilde{\sum_{\boldsymbol{q}\neq 0}}\frac{1}{q^2}+u_0(2J+u_0)\times\widetilde{\sum_{\boldsymbol{q}_1\neq 0,\boldsymbol{q}_2\neq 0}}\frac{1}{q^2}\Bigg)\Bigg\}, \tag{B12}$$

where $q^2=q_1^2+q_2^2$.

The second term in curly brackets corresponds to $F_{\text{nloc}}^{(8)}$ considered in Appendix A. Invoking the argument outlined at the end of Appendix A one can show that the lattice dependent part of $F_{\text{nloc}}^{(8)}$ must be proportional to $\widetilde{\Sigma}_{\boldsymbol{q}_1\neq 0,\boldsymbol{q}_2\neq 0}\frac{1}{q^2}$, which therefore must replace $\widetilde{\Sigma}_{\boldsymbol{q}\neq 0}\frac{1}{q^2}$ in the $J^2$ term. Thus modified $F_{\text{nloc}}^{(8)}$ reads (the lattice-independent terms are omitted)

$$F_{\text{nloc}}^{(8)}\simeq\frac{c_0}{2V}\frac{1}{V^2a^2}(J+u_0)^2\widetilde{\sum_{\boldsymbol{q}_1\neq 0,\boldsymbol{q}_2\neq 0}}\frac{1}{q^2}. \tag{B13}$$

Let us consider an example: Each droplet is characterized by a well-defined internal primary structure: $\eta^{(0)}(\boldsymbol{r})=[\tilde{\eta}(\boldsymbol{r})+\bar{\eta}]H(R_d-r)$, where $\tilde{\eta}(\boldsymbol{r})$ is a periodic function with the period $\lambda \ll R_d, \langle\tilde{\eta}\rangle=0, H(\cdot)$ is the Heaviside function. Then $J \simeq \gamma_1 V_d^2$, $u_0 \simeq (\bar{\eta}V_d)^2/K_0$, where $\gamma_1$ is defined in Appendix A [$\gamma_1=\frac{2}{c_0}$ times the nonlocal energy density of the bulk primary structure $\tilde{\eta}(r)$], and $V_d=\frac{4\pi}{3}R_d^3$ is the droplet volume. Therefore in this case

$$F_{\mathrm{nloc}}^{(8)} \simeq \frac{c_0}{2V}\frac{V_d^4}{V^2a^2}(\gamma_1+\bar{\eta}^2/K_0)^2 \widetilde{\sum_{\boldsymbol{q}_1\neq 0,\boldsymbol{q}_2\neq 0}} \frac{1}{q^2}.$$

The same result can be easily obtained using Eq. (A10) derived in Appendix A.

If the droplets are arranged in a simple cubic lattice, then the general result Eq. (B13) can be simplified as

$$F_{\mathrm{nloc}}^{(8)} \simeq \frac{c_0}{2V}\frac{1}{(2\pi)^2V^{4/3}a^2}(J+u_0)^2(S_6-2S_3), \tag{B14}$$

where

$$S_6 = \widetilde{\sum_{\boldsymbol{n}\in \mathrm{Z}^6}} \frac{1}{n^2}, \quad S_3 = \widetilde{\sum_{\boldsymbol{n}\in \mathrm{Z}^3}} \frac{1}{n^2}.$$

$Z^6$ is the space of all six-dimensional vectors with integer components, $Z^3$ is the same in three dimensions, and $\boldsymbol{n}=0$ is excluded from both sums. For the simple cubic lattice these constants are [14]

$$S_3 \approx -8.913\,633, \quad S_6 \approx -3.379\,685.$$

The same approach also works for other superstructures: Eq. (B14) stays generally valid, but the constants $S_6$ and $S_3$ depend on the superlattice. Their values for the most important lattices are: $S_3 \approx -9.074\,369, S_6 \approx -3.834\,713$ for body-centered cubic lattice (bcc); $S_3 \approx -9.073\,806$, $S_6 \approx -3.838\,360$ for face-centered cubic (fcc); $S_3 \approx -9.073\,446, S_6 \approx -3.837\,621$ for hexagonal closed packed (hcp). With this values it is obvious that the lowest $F_{\mathrm{nloc}}$ always corresponds to the fcc lattice since $J>0$ and $u_0>0$.

For weak composition contrast $A \ll A^*, J$ is much smaller than $u_0$, so the lattice dependent part of the free energy becomes

$$F_{\mathrm{nloc}}^{(8)} \simeq \frac{c_0}{2V}\frac{u_0^2}{(2\pi)^2V^{4/3}a^2}(S_6-2S_3)$$

in agreement with the results obtained in Ref. [14] in this weak regime. On the other hand, $J$ becomes much larger than $u_0$ if $A$ is close to $A^*$. In the latter regime the micelle interaction energy is proportional to $J^2 \propto \frac{1}{(1-A/A^*)^2}$, i.e., to the square of the nonlocal self-energy per micelle.

---

[1] E. I. Shakhnovich and A. M. Gutin, J. Phys. (France) **50**, 1843 (1989).

[2] A. M. Gutin, C. D. Sfatos, and E. I. Shakhnovich, J. Phys. A **27**, 7957 (1994).

[3] C. D. Sfatos, A. M. Gutin, and E. I. Shakhnovich, J. Phys. A **27**, L411 (1994).

[4] G. H. Fredrickson and S. T. Milner, Phys. Rev. Lett. **67**, 835 (1991).

[5] G. H. Fredrickson, S. T. Milner, and L. Leibler, Macromolecules **25**, 6341 (1992).

[6] C. D. Sfatos, A. M. Gutin, and E. I. Shakhnovich, Phys. Rev. E **51**, 4727 (1995).

[7] S. V. Panyukov and S. I. Kuchanov, Sov. Phys. JETP **72**, 368 (1991).

[8] S. V. Panyukov and S. I. Kuchanov, J. Phys. II **2**, 1973 (1992).

[9] S. V. Panyukov and I. I. Potemkin, JETP **85**, 183 (1997).

[10] A. N. Semenov, J. Phys. II **7**, 1489 (1997).

[11] H. Angerman, G. Ten Brinke, and I. Erukhimovich, Macromolecules **29**, 3255 (1996).

[12] I. I. Potemkin and S. V. Panyukov, Phys. Rev. E **57**, 6902 (1998).

[13] S. Panyukov and I. Potemkin, Physica A **249**, 321 (1998).

[14] A. N. Semenov and A. E. Likhtman, Macromolecules **31**, 9058 (1998).

[15] A. N. Semenov, Eur. Phys. J. B **10**, 497 (1999).

[16] S. I. Kuchanov and S. V. Panyukov, J. Phys.: Condens. Matter **18**, L43 (2006).

[17] A. V. Subbotin and A. N. Semenov, Eur. Phys. J. E **7**, 49 (2002).

[18] I. M. Lifshitz, A. Yu. Grosberg, and A. R. Khokhlov, Rev. Mod. Phys. **50**, 683 (1978); I. M. Lifshitz, A. Yu. Grosberg, and A. R. Khokhlov, Sov. Phys. Usp. **22**, 123 (1979).

[19] A. Yu. Grosberg, Usp. Fiz. Nauk **167**, 129 (1997).

[20] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Oxford, 1998).

[21] A. N. Semenov, S. H. Anastasiadis, N. Boudenne, G. Fytas, M. Xenidou, and N. Hadjichristidis, Macromolecules **30**, 6280 (1997).