Phase Separation of Grafted Copolymers

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ABSTRACT: We consider the demixing of diblock copolymers grafted densely to a surface in the melt state using mean-field methods. The layer contains equal numbers of A–B and complementary B–A chains. The incipient demixing leads to a density wave of composition, produced by splaying of the chains. In an equal mixture of A–C and B–C copolymers where only the free ends are immiscible, phase separation takes place in a thin zone near the free surface of the layer. Because the free end density is singular at the free surface, the A–B interaction strength required for demixing scales linearly with the length of the terminal A and B blocks, rather than quadratically, which would be the case for demixing of a blend of the same copolymers.

I. Introduction

Long polymer chains grafted on a surface are of general interest, especially when the chains are composed of two different kinds of monomers. A demixing interaction makes the two kinds of monomers tend to separate from each other spatially. A phase-segregated state is expected provided the demixing interaction reaches a sufficient strength. Grafted polymers were first studied by de Gennes and Alexander[1,2] and later by Semenov,[3] Milner, Witten, and Cates,[4] and Zhulina and Semenov.[5] They used the approximation which ignores the conformational fluctuations about the most likely conformations of the chains. Recently Marko and Witten[6] further studied the system's phase separation with two kinds of chains grafted on a surface, including conformational fluctuations. Their work generalizes the random-phase or mean-field approximation for the case of grafted chains. This approximation was first applied to polymer microphase separation in the classic work of Leibler.[7] Marko and Witten found that, as the demixing interaction is increased in strength, phase separation always begins with "rippling" in the x–y plane, rather than with "layering", or vertical stratification with no in-plane structure.

In this paper, we study how the chain architecture influences such phase separation. In particular we study the phase separation of grafted diblock chains. Our aim is to explore the variety of phase separation patterns that may occur by varying the architecture of the polymers. In section II, we discuss the general mechanism of phase separation of grafted polymers; we explain how phase separation can be studied by calculation of the two-point correlations in the absence of a demixing interaction. In section III, we discuss the computation of the correlation functions for the different systems of interest and give general results. In section IV we use numerical methods to calculate the eigenvalues and eigenfunctions of the correlation function. Thus we obtain the minimum demixing interaction strength Λ_c required to achieve phase separation, and the monomer density distribution of the phase-separated states. From our numerical results, we have observed that, in the limit where immiscibility is confined to short blocks at the free ends of the chains, the phase separation is confined to a thin layer near the ungrafted surface. We may account for the critical interaction strength Λ_c and the spatial pattern in this limit using a variational calculation, discussed in section V.

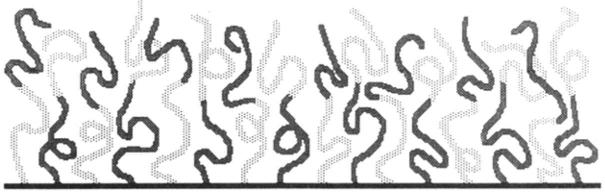

Figure 1. Grafted diblock copolymers without demixing interaction.

Figure 2. Polymers of Figure 1 in an A–B phase-separated state driven by demixing interaction.

II. Mechanism of Phase Separation of Grafted Polymers

We consider a system of long polymer chains end-grafted to the x–y plane. Each chain is fastened permanently to a point on the grafting surface.[8] There are σ chains per unit area grafted to the surface. The layer is in the melt state, with each chain occupying a fixed volume V. Thus the layer has thickness $h = \sigma V$. Each chain is composed of two kinds of monomers, which we label as A and B, as shown in Figure 1. The two are assumed to have identical properties before we turn on any demixing interaction or any external chemical potential to which A and B have opposite responses.

If we introduce an A–B demixing interaction, the chains will tend to demix into A and B regions to achieve the minimum free energy. We can expect the system to undergo A–B phase separation when the demixing interaction reaches a sufficient strength, as illustrated in Figure 2.

The total density is constrained by the "melt" condition: the total monomer density should be constant throughout the melt layer:

$$\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) = 1$$

in which $\phi_A(\mathbf{r})$ and $\phi_B(\mathbf{r})$ are A and B monomer volume fractions at $\mathbf{r}$.

Before we turn on any demixing interaction between A and B monomers (which means A and B are still identical), the free energy of a chain includes contributions from stretching and pressure:[4]

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

The "packing length" a depends on the chemical makeup of the chains and is usually of order 10 Å. Here and below, we express (free) energies in units of the thermal energy kT. Each chain is characterized by its conformation $\mathbf{r}(v)$. The variable v represents the volume of the polymer chain from the grafted point $\mathbf{r}_0$ to $\mathbf{r}$, and the pressure depends only on the height of z. To specify S explicitly, we suppose that the grafted layer is in contact with a melt of high-molecular-weight homopolymers of the same species. Then S is the work required to move a chain from some reference configuration in the melt to the configuration $\mathbf{r}(v)$ in the grafted layer. (We may take a reference configuration for which the stretching energy $\int(d\mathbf{r}/dv)^2$ is negligible.)

This representation of the chain energy uses several conventional and well-justified approximations. First, because the effects considered involve gentle spatial variations on the scale of many monomers, we have adopted the continuum, Gaussian description of the chains, following, *e.g.*, Edwards' many-body theory of polymers.[9] Second, we note that the bulk of the local interaction energy with other chains is the same as that in the reference state. Any difference in interaction free energy at a given height z can be expressed in terms of the work required to move a segment of chain from the reference melt at infinity to a point at height z. Work is required to introduce new monomers in the grafted layer. The work is necessary because the new monomers displace other grafted chains and thus increase the height of the layer, resulting in additional stretching of the other chains. Evidently the work is proportional to the amount of chain volume displaced, provided this volume causes a small perturbation in the layer. Thus the work to insert a volume dv of monomers at height z is dv times some z-dependent coefficient $p(z)$. This work per unit volume is by definition a pressure. The integral of this work over all the volume elements of the chain is thus one way to describe its interaction free energy. In this description, we assume that the insertion of a chain does not appreciably alter this pressure. Since the pressure at a given point is caused by the stretching of many chains (provided these have high molecular weight and interpenetrate strongly), this assumption is well justified. This representation is the basis for several analytical and numerical theories of high-molecular-weight grafted polymer layers.[4,10–14]

The single-chain partition function can be written as:

$$Z_1(\mathbf{r}_0) = \int d^3r_v \int D\mathbf{r}(v)\, e^{-S[\mathbf{r}]}$$

The integral $D\mathbf{r}$ is over all possible single chain configurations with grafted point $\mathbf{r}_0$ and free end $\mathbf{r}_v$ fixed. The free energy of the chain is the logarithm of this Z_1. This is the work required to introduce a new chain grafted at $\mathbf{r}_0$. Thus the free energy ΔF required to add $\Delta\sigma$ chains per unit surface is given by:

$$\Delta F = \Delta\sigma \int d^2\mathbf{r}_0 \log Z_1(\mathbf{r}_0)$$

This ΔF depends on the $p(z)$ from the chains already present; thus ΔF depends on the existing grafting density σ. To obtain the total free energy $F = \log(Z)$ of the layer, one must add the incremental ΔF's from zero grafting density to the final grafting density:[4]

$$F(\sigma) = \sum \Delta F = \int d\sigma \int d^2r_0 \log Z_1(\mathbf{r}_0,\sigma)$$

We now introduce a chemical potential $\mu(\mathbf{r})$, which is coupled to the A–B monomer concentration difference.

$$S_{\text{ext}} = -\int d^3r\, \mu(\mathbf{r})\, [\phi_A(\mathbf{r}) - \phi_B(\mathbf{r})] \equiv -\int d^3r\, \mu(\mathbf{r})\, \phi(\mathbf{r}) \tag{II-1}$$

A and B chains have opposite responses to this external field. The A–B monomer density difference $\phi_A(\mathbf{r}) - \phi_B(\mathbf{r})$ is defined as $\phi(\mathbf{r})$. (Many treatments consider a ϕ defined as $\phi_A - \langle\phi_A\rangle$ which is a factor of 2 smaller than our definition and that of refs 6 and 16.) The partition function of the system then is given by:

$$\log Z[\mu] = \int d\sigma \int d^2r_0 \log\left[\int d^3r_v \int D\mathbf{r}\, e^{-S[\mathbf{r}]-S_{\text{ext}}[\mathbf{r}]}\right]$$

The correlation functions of $\phi(\mathbf{r})$ are defined by:

$$G^{(n)}(\mathbf{r}_1,...,\mathbf{r}_n) \equiv \left.\frac{\delta^n \log Z[\mu]}{\delta\mu(\mathbf{r}_1)...\delta\mu(\mathbf{r}_n)}\right|_{\mu=0}$$

The one-point and two-point correlation functions are expectation values of the A–B density difference $\phi(\mathbf{r})$:

$$G^{(1)}(\mathbf{r}_1) = \langle\phi(\mathbf{r}_1)\rangle$$

$$G^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = \langle\phi(\mathbf{r}_1)\,\phi(\mathbf{r}_2)\rangle - \langle\phi(\mathbf{r}_1)\rangle\langle\phi(\mathbf{r}_2)\rangle$$

For our A–B symmetric system we have $\langle\phi(\mathbf{r})\rangle = 0$. In general we have the following relation:

$$G^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = \frac{\delta G^{(1)}(\mathbf{r}_1)}{\delta\mu(\mathbf{r}_2)} = \frac{\delta\langle\phi(\mathbf{r}_1)\rangle}{\delta\mu(\mathbf{r}_2)}$$

This gives us the linear response of the A–B density to a small perturbation of chemical potential, in terms of the second-order correlation function:

$$\langle\phi(\mathbf{r}_1)\rangle = \int d^3r_2\, G^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\, \mu(\mathbf{r}_2) + O(\mu^2)$$

We now turn on a demixing interaction between A and B monomers:

$$S_{\text{int}} = \Lambda \int d^3r\, \phi_A(\mathbf{r})\, \phi_B(\mathbf{r}) = -\frac{\Lambda}{4}\int d^3r\, \phi^2(\mathbf{r}) + \text{const.}$$

The demixing strength[17] Λ is related to the Flory parameter[18] χ by $\chi = \Lambda V/N$, where N is the polymerization index of the chains.[19] This A–B interaction can be expressed (making a mean-field approximation) as a shift in the external chemical potential (eq II-1):

$$\mu(\mathbf{r}) \rightarrow \mu(\mathbf{r}) - \left\langle\frac{\delta S_{\text{int}}}{\delta\phi(\mathbf{r})}\right\rangle = \mu(\mathbf{r}) + \frac{\Lambda}{2}\langle\phi(\mathbf{r})\rangle$$

In the presence of a demixing interaction, we thus have the modified linear response relation:

$$\langle\phi(\mathbf{r}_1)\rangle = \int d^3r_2\, G^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\left[\mu(\mathbf{r}_2) + \frac{\Lambda}{2}\langle\phi(\mathbf{r}_2)\rangle\right]$$

By definition, the correlation function in the presence of the demixing interaction $G_\Lambda^{(2)}$ satisfies

$$\langle\phi(\mathbf{r}_1)\rangle = \int d^3r_2\, G_\Lambda^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\, \mu(\mathbf{r}_2) \tag{II-2}$$

From the above two equations we can obtain the following integral equation:

$$G_\Lambda^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = G^{(2)}(\mathbf{r}_1,\mathbf{r}_2) + \frac{\Lambda}{2}\int \mathrm{d}^3r_3\, G^{(2)}(\mathbf{r}_1,\mathbf{r}_3)\, G_\Lambda^{(2)}(\mathbf{r}_3,\mathbf{r}_2)$$

This can be transformed into an expression which relates the correlation functions with and without the demixing interaction:

$$[G_\Lambda^{(2)}(\mathbf{r}_1,\mathbf{r}_2)]^{-1} = [G^{(2)}(\mathbf{r}_1,\mathbf{r}_2)]^{-1} - \frac{\Lambda}{2}\delta^3(\mathbf{r}_1-\mathbf{r}_2) \quad \text{(II-3)}$$

in which $[\ ]^{-1}$ denotes the matrix inverse. Since $G_\Lambda^{(2)}$ is a symmetric real operator, we can obtain its eigenfunctions ϕ_n and corresponding eigenvalues $\epsilon_{\Lambda n}$, which are real:

$$\int \mathrm{d}^3r_2\, G_\Lambda^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\, \phi_n(\mathbf{r}_2) = \epsilon_{\Lambda n}\phi_n(\mathbf{r}_1)$$

If the chemical potential $\mu(\mathbf{r})$ is simply an arbitrary infinitesimal perturbation of the A–B distribution of the system, we may express it as a superposition of the ϕ_n:

$$\mu(\mathbf{r}) = \sum_n \langle \mu|\phi_n\rangle \phi_n(\mathbf{r}) \quad \text{(II-4)}$$

in which the inner product is defined as:

$$\langle \mu|\phi_n\rangle \equiv \int \mathrm{d}^3r\, \mu(\mathbf{r})\, \phi_n(\mathbf{r})$$

Equations II-2 and II-4 may be combined to obtain:

$$\langle \phi(\mathbf{r}_1)\rangle = \sum_n \langle \mu|\phi_n\rangle \int \mathrm{d}^3r_2\, G_\Lambda^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\, \phi_n(\mathbf{r}_2) = \sum_n \epsilon_{\Lambda n}\phi_n(\mathbf{r}_1)\, \langle \mu|\phi_n\rangle \quad \text{(II-5)}$$

An alternative derivation of this result using free energy is given in Appendix D. From eq II-3, we see that the eigenfunctions of the $G_\Lambda^{(2)}$ are the same as the eigenfunctions of $G^{(2)}$, while their eigenvalues are related by:

$$\epsilon_{\Lambda n} = \left(\frac{1}{\epsilon_n} - \frac{\Lambda}{2}\right)^{-1} \quad \text{(II-6)}$$

We see that, if the demixing interaction strength Λ increases from 0 to such a value that one of the eigenvalues $\epsilon_{\Lambda m}$ goes to infinity (eq II-6), then the density distribution $\langle \phi(\mathbf{r})\rangle$ will develop into the corresponding eigenstate $\phi_m(r)$ (eq II-5) with a divergent magnitude. (This unphysical divergent magnitude is due to the fact that we only limit ourselves to linear response and neglect all higher order contributions.) In other words, in the presence of a demixing interaction with the particular strength which results in a divergent eigenvalue $\epsilon_{\Lambda m}$, the system will spontaneously phase separate into a state which is characterized by the corresponding eigenstate $\phi_m(\mathbf{r})$ of the correlation function $G_\Lambda^{(2)}$.

Thus, we shall study the second-order correlation function without the demixing interaction, $G^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ (which, for simplicity, we denote simply as $G(\mathbf{r}_1,\mathbf{r}_2)$ in what follows), and find its eigenfunctions and eigenvalues ϵ_n. By finding the biggest eigenvalue $\epsilon_{\max}$ of $G^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$, we can obtain the minimum strength $\Lambda_c = 1/\epsilon_{\max}$ for the system to begin to phase separate and predict the A–B demixing distribution in space.

III. Computation of the Correlation Function

We now calculate the correlation function for different polymer configurations, including diblock copolymer chains and chains with mixed composition.

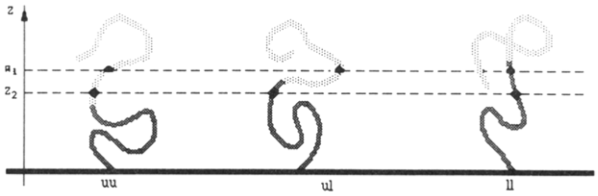

Figure 3. Three kinds of contributions to the correlation function $G(z_1,z_2)$, as expressed in eq III-1.

1. Diblock Copolymer System. Without the demixing interaction, the A and B monomers are identical except for labeling. The second-order correlation function $G(\mathbf{r}_1,\mathbf{r}_2)$ is, as in section II, the correlation of density difference $\phi(\mathbf{r}) \equiv \phi_A(\mathbf{r}) - \phi_B(\mathbf{r})$ of A and B monomers:

$$G(\mathbf{r}_1,\mathbf{r}_2) \equiv \langle \phi(\mathbf{r}_1)\, \phi(\mathbf{r}_2)\rangle_c \equiv \langle (\phi_A(\mathbf{r}_1) - \phi_B(\mathbf{r}_1))(\phi_A(\mathbf{r}_2) - \phi_B(\mathbf{r}_2))\rangle_c$$

in which, for simplicity, we define the cumulant correlation:

$$\langle fg\rangle_c \equiv \langle fg\rangle - \langle f\rangle\langle g\rangle$$

We shall consider the case in which the A and B portions are completely symmetric: for each chain with A at its upper block and B at its lower grafted block, there is a complementary chain with B at its upper block and A at its lower block (Figure 1). We denote $\phi_u(\mathbf{r})$ as the density contribution (either of A or B type) due to upper blocks and $\phi_l(\mathbf{r})$ as the density due to lower blocks. Directly from the definition of $G(\mathbf{r}_1,\mathbf{r}_2)$, we have

$$G(\mathbf{r}_1,\mathbf{r}_2) = \langle (\phi_l(\mathbf{r}_1) - \phi_u(\mathbf{r}_1))(\phi_l(\mathbf{r}_2) - \phi_u(\mathbf{r}_2))\rangle_c = \langle \phi_u(\mathbf{r}_1)\, \phi_u(\mathbf{r}_2)\rangle_c + \langle \phi_l(\mathbf{r}_1)\, \phi_l(\mathbf{r}_2)\rangle_c - \langle \phi_l(\mathbf{r}_1)\, \phi_u(\mathbf{r}_2)\rangle_c - \langle \phi_u(\mathbf{r}_1)\, \phi_l(\mathbf{r}_2)\rangle_c \quad \text{(III-1)}$$

From the above result, as illustrated in Figure 3, the correlation function can be divided into three parts, namely, upper–upper (both A–A or B–B are on the upper portion of the chain), upper–lower (A–B or B–A, one is on the upper portion of a chain and the other on the lower portion of the chain), and lower–lower (both A–A or B–B are on the lower portion of the chain).

In order to compute $G(\mathbf{r}_1,\mathbf{r}_2)$, we need correlations $\langle \phi_u(\mathbf{r}_1)\, \phi_u(\mathbf{r}_2)\rangle_c$, $\langle \phi_u(\mathbf{r}_1)\, \phi_l(\mathbf{r}_2)\rangle_c = \langle \phi_l(\mathbf{r}_2)\, \phi_u(\mathbf{r}_1)\rangle_c$, and $\langle \phi_l(\mathbf{r}_1)\, \phi_l(\mathbf{r}_2)\rangle_c$ which can be obtained by summing over the contributions from all the chains in the system. Thus the u–u contribution is given by:

$$\langle \phi_u(\mathbf{r}_1)\, \phi_u(\mathbf{r}_2)\rangle_c = \sum_{\mathbf{r}_0,\mathbf{r}_0'} \langle \psi_{\mathbf{r}_0,u}(\mathbf{r}_1)\, \psi_{\mathbf{r}_0',u}(\mathbf{r}_2)\rangle_c$$

The $\psi_{\mathbf{r}_0,u}(\mathbf{r})$ (also restricted to be upper monomers) are the monomer density distributions of a single chain grafted at point $\mathbf{r}_0$. Specifically

$$\psi_{\mathbf{r}_0,u}(\mathbf{r}) \equiv \int_{V/2}^{V} \mathrm{d}v\, \delta^3(\mathbf{r}-\mathbf{r}(v))$$

Since in our mean-field formalism the chains interact only via the one-body pressure field, they are statistically independent. The $\langle \psi\psi\rangle_c$ must vanish unless the two ψ factors refer to the same chain:

$$\langle \phi_u(\mathbf{r}_1)\, \phi_u(\mathbf{r}_2)\rangle_c = \Big[\sum_{\mathbf{r}_0=\mathbf{r}_0'} + \sum_{\mathbf{r}_0\neq\mathbf{r}_0'}\Big]\langle \psi_{\mathbf{r}_0,u}(\mathbf{r}_1)\, \psi_{\mathbf{r}_0',u}(\mathbf{r}_2)\rangle_c = \sum_{\mathbf{r}_0=\mathbf{r}_0'} \langle \psi_{\mathbf{r}_0,u}(\mathbf{r}_1)\, \psi_{\mathbf{r}_0,u}(\mathbf{r}_2)\rangle_c$$

In the continuum limit, the sum over all chains is just an integration over $\mathbf{r}_0$ in the x–y plane (i.e., integration over $\bar{x}_0 \equiv \{x_0, y_0\}$ with $z_0 = 0$), multiplied by chain density σ. The correlations of the total density of specific type on different blocks of the chains can be obtained by summing over all chains with different grafted points $\mathbf{r}_0$:

$$G_{\mathrm{uu}}(\mathbf{r}_1,\mathbf{r}_2) \equiv \langle \phi_{\mathrm{u}}(\mathbf{r}_1)\, \phi_{\mathrm{u}}(\mathbf{r}_2)\rangle_{\mathrm{c}} = \sigma \int \mathrm{d}^2\bar{x}_0\, \langle \psi_{\mathbf{r}_0,\mathrm{u}}(\mathbf{r}_1)\, \psi_{\mathbf{r}_0,\mathrm{u}}(\mathbf{r}_2)\rangle_{\mathrm{c}}$$

The G_{ul}, G_{lu}, and G_{ll} are defined similarly, with ϕ_{u} and ψ_{u} replaced by ϕ_{l} and ψ_{l} accordingly. With these partial G functions, we may reexpress the full response function of eq III-1 in terms of single-chain ψ correlations:

$$G(\mathbf{r}_1,\mathbf{r}_2) = G_{\mathrm{uu}}(\mathbf{r}_1,\mathbf{r}_2) + G_{\mathrm{ll}}(\mathbf{r}_1,\mathbf{r}_2) - G_{\mathrm{lu}}(\mathbf{r}_1,\mathbf{r}_2) - G_{\mathrm{ul}}(\mathbf{r}_1,\mathbf{r}_2)$$

We now need to compute the single-chain monomer density correlations:

$$\langle \psi_{\mathbf{r}_0,\mathrm{u}}(\mathbf{r}_1)\, \psi_{\mathbf{r}_0,\mathrm{u}}(\mathbf{r}_2)\rangle_{\mathrm{c}}, \quad \langle \psi_{\mathbf{r}_0,\mathrm{u}}(\mathbf{r}_1)\, \psi_{\mathbf{r}_0,\mathrm{l}}(\mathbf{r}_2)\rangle_{\mathrm{c}}, \quad \langle \psi_{\mathbf{r}_0,\mathrm{l}}(\mathbf{r}_1)\, \psi_{\mathbf{r}_0,\mathrm{l}}(\mathbf{r}_2)\rangle_{\mathrm{c}}$$

These can be calculated using the density distribution of a single chain in a grafted polymer system. This is already discussed in detail in ref 6, so here we quote the results.

The probability that a single chain has its free end located at height z_{v} in the melt state may be expressed in terms of the partial coverage of chains ending below height z_{v}, which we denote $\sigma(z_{\mathrm{v}})$, following ref 6. Evidently the total coverage σ defined before is $\sigma(h)$. Thus the desired probability may be written:

$$\frac{1}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}z} = \frac{z_{\mathrm{v}}}{h\sqrt{h^2 - z_{\mathrm{v}}^2}}$$

The monomers per unit height contributed at height z by a chain with the free end at height z_{v} is

$$\frac{\mathrm{d}v}{\mathrm{d}z} = \frac{2V}{\pi}\frac{1}{\sqrt{z_{\mathrm{v}}^2 - z^2}}$$

The height z can be expressed as a function of position v along the chain and the free end height z_{v}:

$$z(v,z_{\mathrm{v}}) = z_{\mathrm{v}} \sin \frac{\pi v}{2V}$$

The polymer section from v_0 to v_1 has a Gaussian end-to-end distance distribution in the x–y plane:

$$\gamma(\bar{x}_1,\bar{x}_0,v_1,v_0) = \frac{a}{2\pi(v_1 - v_0)} \exp\left(-\frac{a}{2}\frac{(\bar{x}_1 - \bar{x}_0)^2}{v_1 - v_0}\right)\theta(v_1 - v_0)$$

where $\theta(t)$ is the unit step function. We also denote:

$$(\bar{x}_1 - \bar{x}_0)^2 \equiv (x_1 - x_0)^2 + (y_1 - y_0)^2$$

From these results, the monomer density distribution at $\mathbf{r}$ of a single chain (grafted at point $\mathbf{r}_0$ with the free end at $\mathbf{z}_{\mathrm{v}}$) is the product:

$$\left(\frac{\mathrm{d}v}{\mathrm{d}z}\right)\gamma(\bar{x},\bar{x}_0,v(z,z_{\mathrm{v}}),0)$$

where $(\mathrm{d}v/\mathrm{d}z)$, although not explicitly indicated, is a function of z_{v}. By averaging the expression over all possible heights z_{v} of the free ends, we obtain the density distribution of monomers of specific type:

$$\langle \psi_{\mathbf{r}_0,\mathrm{l}}(\mathbf{r})\rangle = \int_z^h \mathrm{d}z_{\mathrm{v}} \left(\frac{1}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}z}\right)\theta(z(V_{\mathrm{l}},z_{\mathrm{v}})-z)\left(\frac{\mathrm{d}v}{\mathrm{d}z}\right)\gamma(\bar{x},\bar{x}_0,v(z,z_{\mathrm{v}}),0)$$

$$\langle \psi_{\mathbf{r}_0,\mathrm{u}}(\mathbf{r})\rangle = \int_z^h \mathrm{d}z_{\mathrm{v}} \left(\frac{1}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}z}\right)\theta(z-z(V_{\mathrm{l}},z_{\mathrm{v}}))\left(\frac{\mathrm{d}v}{\mathrm{d}z}\right)\gamma(\bar{x},\bar{x}_0,v(z,z_{\mathrm{v}}),0)$$

V_{l} is the volume displaced by the lower block of a chain, V_{u} is that of the upper block, and $V_{\mathrm{l}} + V_{\mathrm{u}} = V$. Thus $z(V_{\mathrm{l}},z_{\mathrm{v}})$ is the height of the junction point of the two blocks. The θ functions in the above expressions guarantee that only chains that can contribute will be summed: these are chains with end height z_{v} in the particular range such that z will be within the lower (for $\psi_{\mathrm{l}}(\mathbf{r})$) or upper (for $\psi_{\mathrm{u}}(\mathbf{r})$) block of the chains.

Similarly, the density correlation of monomers at z_1 and z_2 on a single chain is given by:

$$\left(\frac{\mathrm{d}v}{\mathrm{d}z}\right)_{z1}\left(\frac{\mathrm{d}v}{\mathrm{d}z}\right)_{z_2}\gamma(\bar{x}_<,\bar{x}_0,v(z_<,z_{\mathrm{v}}),0)\ \gamma(\bar{x}_>,\bar{x}_<,v(z_>,z_{\mathrm{v}}),v(z_<,z_{\mathrm{v}}))$$

We define $z_< \equiv \min\{z_1,z_2\}$ and $z_> \equiv \max\{z_1,z_2\}$, and $\bar{x}_<$ and $\bar{x}_>$ represent corresponding x–y coordinates. The product of two γ functions gives the probability that a chain stretches from the grafting point to $z_<$ and then continues to height $z_>$.

Averaged over all possible heights z_{v} of the chain, the density correlation between monomers depends on whether both are on the upper portion, both are on the lower portion, or one is on the upper portion and the other is on the lower portion of a chain. They are given by:

$$\langle \psi_{\mathbf{r}_0,\mathrm{u}}(\mathbf{r}_1)\, \psi_{\mathbf{r}_0,\mathrm{u}}(\mathbf{r}_2)\rangle = \int_{z_>}^h \mathrm{d}z_{\mathrm{v}} \left(\frac{1}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}z}\right)\theta(z_1-z(V_{\mathrm{l}},z_{\mathrm{v}}))\ \theta(z_2-z(V_{\mathrm{l}},z_{\mathrm{v}})) \times \left(\frac{\mathrm{d}v}{\mathrm{d}z}\right)_{z1}\left(\frac{\mathrm{d}v}{\mathrm{d}z}\right)_{z_2}\gamma(\bar{x}_<,\bar{x}_0,v(z_<,z_{\mathrm{v}}),0)\ \gamma(\bar{x}_>,\bar{x}_<,v(z_>,z_{\mathrm{v}}),v(z_<,z_{\mathrm{v}}))$$

$$\langle \psi_{\mathbf{r}_0,\mathrm{l}}(\mathbf{r}_1)\, \psi_{\mathbf{r}_0,\mathrm{l}}(\mathbf{r}_2)\rangle = \int_{z_>}^h \mathrm{d}z_{\mathrm{v}} \left(\frac{1}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}z}\right)\theta(z(V_{\mathrm{l}},z_{\mathrm{v}})-z_1)\ \theta(z(V_{\mathrm{l}},z_{\mathrm{v}})-z_2) \times \left(\frac{\mathrm{d}v}{\mathrm{d}z}\right)_{z_1}\left(\frac{\mathrm{d}v}{\mathrm{d}z}\right)_{z_2}\gamma(\bar{x}_<,\bar{x}_0,v(z_<,z_{\mathrm{v}}),0)\ \gamma(\bar{x}_>,\bar{x}_<,v(z_>,z_{\mathrm{v}}),v(z_<,z_{\mathrm{v}}))$$

$$\langle \psi_{\mathbf{r}_0,\mathrm{l}}(\mathbf{r}_1)\, \psi_{\mathbf{r}_0,\mathrm{u}}(\mathbf{r}_2)\rangle = \int_{z_>}^h \mathrm{d}z_{\mathrm{v}} \left(\frac{1}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}z}\right)\theta(z(V_{\mathrm{l}},z_{\mathrm{v}})-z_1)\ \theta(z_2-z(V_{\mathrm{l}},z_{\mathrm{v}})) \times \left(\frac{\mathrm{d}v}{\mathrm{d}z}\right)_{z_1}\left(\frac{\mathrm{d}v}{\mathrm{d}z}\right)_{z_2}\gamma(\bar{x}_<,\bar{x}_0,v(z_<,z_{\mathrm{v}}),0)\ \gamma(\bar{x}_>,\bar{x}_<,v(z,z_{\mathrm{v}}),v(z_<,z_{\mathrm{v}}))$$

The $z(V_{\mathrm{l}},z_{\mathrm{v}})$ is the height of the junction point of the two blocks (of different types) on a given chain, and the θ functions guarantee only the contribution from a chain with z_{v} in a certain range (so z_1 and z_2 fall within particular blocks of the chain) will be summed (Figure 3). By summing over these contributions from all the chains, we obtain the contributions to the second-order correlation function by monomers on different blocks of the chains, and the sum of them will be the correlation function.

From the above discussion, we can readily obtain the compositional correlation function $G(\mathbf{r}_1,\mathbf{r}_2)$. The actual mathematical derivation and simplification are straightforward and uninstructive, so we only illustrate the process in Appendix A. Here we simply list the results.

The system has translational and rotational symmetry in the x–y plane; this lets us simplify the problem by taking Fourier transform in the x–y variables of the correlation function. Then $G(\mathbf{r}_1,\mathbf{r}_2)$ may be expressed as a function of parameters $\bar{k}_1 \equiv \{k_{1x},k_{1y}\}$ and $\bar{k}_2 \equiv \{k_{2x},k_{2y}\}$ and variables z_1 and z_2: $\tilde{G}(\bar{k}_1,z_1;\bar{k}_2,z_2)$. After the mathematical simplification illustrated in Appendix A, we see that $\delta^2(\bar{k}_1+\bar{k}_2)$ appears as an overall factor in the correlation functions due to the translation invariance of the system in the x–y plane, and only magnitudes of momenta appear in the correlation function due to rotational symmetry in the x–y plane. The single characteristic length scale in the x–y plane is the lateral extent of a chain, of order $(V/a)^{1/2}$. It is thus natural to express the wavevector k in the reduced form:

$$\tilde{k}^2 \equiv \frac{\bar{k}_1^{\,2}V}{2a} = \frac{\bar{k}_2^{\,2}V}{2a}$$

The nonzero portion of the Fourier-transformed correlation function $\tilde{G}(\bar{k}_1,z;-\bar{k}_1,z_2)$ can be simply denoted as $\tilde{G}(\tilde{k}^2;z_1,z_2)$ times the area of the surface.

To simply the notation, we define

$$G^{\mathrm{I}}(\mathbf{r}_1,\mathbf{r}_2) \equiv \sigma\int \mathrm{d}^2\bar{x}_0\ \langle\psi_{\mathbf{r}_0}(\mathbf{r}_1)\ \psi_{\mathbf{r}_0}(\mathbf{r}_2)\rangle$$

$$G^{\mathrm{II}}(\mathbf{r}_1,\mathbf{r}_2) \equiv \sigma\int \mathrm{d}^2\bar{x}_0\ \langle\psi_{\mathbf{r}_0}(\mathbf{r}_1)\rangle\langle\psi_{\mathbf{r}_0}(\mathbf{r}_2)\rangle$$

So we have

$$G(\mathbf{r}_1,\mathbf{r}_2) = G^{\mathrm{I}}(\mathbf{r}_1,\mathbf{r}_2) - G^{\mathrm{II}}(\mathbf{r}_1,\mathbf{r}_2)$$

The corresponding Fourier-transformed correlation functions are defined similarly. Here we replace factors of V by h/σ:

$$\tilde{G}^{\mathrm{I}}_{\mathrm{uu}}(\tilde{k}^2;z_1,z_2) = \frac{16h}{\sigma}\int_{z_>}^{h}\mathrm{d}z_{\mathrm{v}}\ g_3(z_1,z_2,z_{\mathrm{v}})\ \theta(z'_<-z_{\mathrm{v}})$$

$$\tilde{G}^{\mathrm{I}}_{\mathrm{ll}}(\tilde{k}^2;z_1,z_2) = \frac{16h}{\sigma}\theta(h-z'_>)\int_{z'_>}^{h}\mathrm{d}z_{\mathrm{v}}\ g_3(z_1,z_2,z_{\mathrm{v}})$$

$$\tilde{G}^{\mathrm{I}}_{\mathrm{lu}}(\tilde{k}^2;z_1,z_2) = \frac{16h}{\sigma}\int_{z_>}^{h}\mathrm{d}z_{\mathrm{v}}\ g_3(z_1,z_2,z_{\mathrm{v}})\ \theta(z_{\mathrm{v}}-z'_1)\ \theta(z'_2-z_{\mathrm{v}})$$

$$\tilde{G}^{\mathrm{II}}_{\mathrm{uu}}(\tilde{k}^2;z_1,z_2) = \frac{16}{\sigma}g_1(z_1)\ g_1(z_2)$$

$$\tilde{G}^{\mathrm{II}}_{\mathrm{ll}}(\tilde{k}^2;z_1,z_2) = \frac{16}{\sigma}g_2(z_1)g_2(z_2)$$

$$\tilde{G}^{\mathrm{II}}_{\mathrm{lu}}(\tilde{k}^2;z_1,z_2) = \frac{16}{\sigma}g_2(z_1)\ g_1(z_2) \qquad \text{(III-2)}$$

where we have introduced

$$z' \equiv \frac{z}{\sin(\pi V_1/2V)}$$

If z is the junction point, z' is the free end height. The three functions g_1, g_2, and g_3 are given by:

$g_1(z) =$

$$\int_z^h \mathrm{d}z_{\mathrm{v}}\frac{z_{\mathrm{v}}}{\sqrt{h^2-z_{\mathrm{v}}^{\,2}}}\frac{1}{\sqrt{z_{\mathrm{v}}^{\,2}-z^2}}\theta(z'-z_{\mathrm{v}})\ \exp\left(-\frac{2\tilde{k}^2}{\pi}\varphi(z,z_{\mathrm{v}})\right)$$

$g_2(z) =$

$$\theta(h-z')\int_{z'}^{h}\mathrm{d}z_{\mathrm{v}}\frac{z_{\mathrm{v}}}{\sqrt{h^2-z_{\mathrm{v}}^{\,2}}}\frac{1}{\sqrt{z_{\mathrm{v}}^{\,2}-z^2}}\exp\left(-\frac{2\tilde{k}^2}{\pi}\varphi(z,z_{\mathrm{v}})\right)$$

$g_3(z_1,z_2,z_{\mathrm{v}}) =$

$$\frac{z_{\mathrm{v}}}{\sqrt{h^2-z_{\mathrm{v}}^{\,2}}}\frac{1}{\sqrt{z_{\mathrm{v}}^{\,2}-z_1^{\,2}}}\frac{1}{\sqrt{z_{\mathrm{v}}^{\,2}-z_2^{\,2}}}\times \exp\left(-\frac{2\tilde{k}^2}{\pi}\left|\varphi(z_2,z_{\mathrm{v}})-\varphi(z_1,z_{\mathrm{v}})\right|\right)$$

where the angle $\varphi(z,z_{\mathrm{v}})$ is defined by:

$$\varphi(z,z_{\mathrm{v}}) = \sin^{-1}(z/z_{\mathrm{v}})$$

For $k = 0$, we may express the correlation functions in terms of elementary functions and $F(\varphi,k)$, the incomplete elliptic integral of the first kind (Appendix A):

$\tilde{G}^{\mathrm{I}}_{\mathrm{uu}}(0;z_1,z_2) =$

$$\frac{16}{\sigma}\frac{h}{\sqrt{h^2-z_<^{\,2}}}\left[F\left(\frac{\pi}{2},\sqrt{\frac{h^2-z_>^{\,2}}{h^2-z_<^{\,2}}}\right)-F\left(\sin^{-1}\sqrt{\frac{h^2-z_<'^2}{h^2-z_>^{\,2}}},\sqrt{\frac{h^2-z_>^{\,2}}{h^2-z_<^{\,2}}}\right)\right]$$

$\tilde{G}^{\mathrm{I}}_{\mathrm{ll}}(0;z_1,z_2) =$

$$\frac{16}{\sigma}\frac{h}{\sqrt{h^2-z_<^{\,2}}}F\left(\sin^{-1}\sqrt{\frac{h^2-z_>'^2}{h^2-z_>^{\,2}}},\sqrt{\frac{h^2-z_>^{\,2}}{h^2-z_<^{\,2}}}\right)$$

$$\tilde{G}^{\mathrm{I}}_{\mathrm{lu}}(0;z_1,z_2) = \frac{16}{\sigma}\frac{h}{\sqrt{h^2-z_<^{\,2}}}\theta(z_2-z_1)\times \left[F\left(\sin^{-1}\sqrt{\frac{h^2-z_1'^2}{h^2-z_>^{\,2}}},\sqrt{\frac{h^2-z_>^{\,2}}{h^2-z_<^{\,2}}}\right)-F\left(\sin^{-1}\sqrt{\frac{h^2-z_2'^2}{h^2-z_>^{\,2}}},\sqrt{\frac{h^2-z_>^{\,2}}{h^2-z_<^{\,2}}}\right)\right]$$

$\tilde{G}^{\mathrm{II}}_{\mathrm{uu}}(0;z_1,z_2) =$

$$\frac{16}{\sigma}\cos^{-1}\sqrt{\frac{h^2-z_1'^2}{h^2-z_1^{\,2}}}\cos^{-1}\sqrt{\frac{h^2-z_2'^2}{h^2-z_2^{\,2}}}$$

$\tilde{G}^{\mathrm{II}}_{\mathrm{ll}}(0;z_1,z_2) =$

$$\frac{16}{\sigma}\sin^{-1}\sqrt{\frac{h^2-z_1'^2}{h^2-z_1^{\,2}}}\sin^{-1}\sqrt{\frac{h^2-z_2'^2}{h^2-z_2^{\,2}}}$$

$$\tilde{G}^{\mathrm{II}}_{\mathrm{lu}}(0;z_1,z_2) =$$

$$\frac{16}{\sigma}\sin^{-1}\overline{\sqrt{\frac{h^2-z_1'^2}{h^2-z_1^2}}}\cos^{-1}\overline{\sqrt{\frac{h^2-z_2'^2}{h^2-z_2^2}}} \quad \text{(III-3)}$$

Here for simplicity we have defined the operation $\overline{\sqrt{\ }}$ as:

$$\overline{\sqrt{X}} \equiv \begin{cases} 0 & \text{if } X < 0 \\ \sqrt{X} & \text{if } 0 \leq X \leq 1 \\ 1 & \text{if } X > 1 \end{cases}$$

2. Blocks with Mixed Composition. Besides the diblock configuration discussed above, we can also study the effect of blocks having composition intermediate between the pure A and B blocks treated above. On the lower portion of the chain, instead of A or B monomers, we consider blocks with A and B monomers mixed together. For example, the lower block may be a random copolymer of controlled composition. The density ratio $(1 - f)$ is defined as the proportion of upper species in the lower blocks. Thus, when $f = 1$, we have the A–B diblocks of section 1, while $f = 0$ gives us homopolymer chains (containing only a single type of monomer). So f is a measure of "contrast" of the two blocks of chains. The correlation function of this generalized system can be written as:

$$\begin{aligned} G(\mathbf{r}_1,\mathbf{r}_2) &= \langle(\phi_{\mathrm{A}}(\mathbf{r}_1) - \phi_{\mathrm{B}}(\mathbf{r}_1))(\phi_{\mathrm{A}}(\mathbf{r}_2) - \phi_{\mathrm{B}}(\mathbf{r}_2))\rangle_{\mathrm{c}} = \\ &\langle[f\phi_{\mathrm{l}}(\mathbf{r}_1) - (\phi_{\mathrm{u}}(\mathbf{r}_1) + (1-f)\phi_{\mathrm{l}}(\mathbf{r}_1))][f\phi_{\mathrm{l}}(\mathbf{r}_2) - (\phi_{\mathrm{u}}(\mathbf{r}_2) + \\ &(1-f)\phi_{\mathrm{l}}(\mathbf{r}_2))]\rangle_{\mathrm{c}} = \langle\phi_{\mathrm{u}}(\mathbf{r}_1)\ \phi_{\mathrm{u}}(\mathbf{r}_2)\rangle_{\mathrm{c}} + \\ &(1-2f)^2\langle\phi_{\mathrm{l}}(\mathbf{r}_1)\ \phi_{\mathrm{l}}(\mathbf{r}_2)\rangle_{\mathrm{c}} + (1-2f)\langle\phi_{\mathrm{l}}(\mathbf{r}_1)\ \phi_{\mathrm{u}}(\mathbf{r}_2)\rangle_{\mathrm{c}} + \\ &(1-2f)\langle\phi_{\mathrm{u}}(\mathbf{r}_1)\ \phi_{\mathrm{l}}(\mathbf{r}_2)\rangle_{\mathrm{c}} \end{aligned}$$

So we have

$$\begin{aligned} G(\mathbf{r}_1,\mathbf{r}_2) = G_{\mathrm{uu}}(\mathbf{r}_1,\mathbf{r}_2) + (1-2f)^2G_{\mathrm{ll}}(\mathbf{r}_1,\mathbf{r}_2) + \\ (1-2f)G_{\mathrm{lu}}(\mathbf{r}_1,\mathbf{r}_2) + (1-2f)G_{\mathrm{ul}}(\mathbf{r}_1,\mathbf{r}_2) \quad \text{(III-4)} \end{aligned}$$

This can be calculated using the results listed above. When $f = {}^1/_2$, we have

$$G(\mathbf{r}_1,\mathbf{r}_2) = G_{\mathrm{uu}}(\mathbf{r}_1,\mathbf{r}_2)$$

In this case, as will be discussed in more detail in later sections, the lower blocks are "neutral", the only tendency for phase separation comes from the upper blocks. Note that we cannot achieve the complementary case where only the lower blocks contribute.

As discussed in section II, to study A–B phase separation, we need to solve the following eigenvalue equation:

$$\int \mathrm{d}\mathbf{r}_1\ G(\mathbf{r}_1,\mathbf{r}_2)\ \phi(\mathbf{r}_1) = \epsilon\phi(\mathbf{r}_2)$$

or with x and y transformed into Fourier space and replaced by parameter $\bar{k}^2$:

$$\int_0^h \mathrm{d}z_1\ \tilde{G}(\bar{k}^2;z_1,z_2)\ \phi(\bar{k}^2;z_1) = (2\pi)^2\epsilon(\bar{k}^2)\ \phi(\bar{k}^2;z_2)$$

Our goal is to obtain the biggest eigenvalue and the corresponding eigenfunction. This corresponds to the A–B phase-separated state with lowest demixing interaction strength Λ_{c} and the density distribution of monomers of specific type in the demixed state. We use numerical methods as an approximate way to solve the eigenvalue problem and later use a variational principle to confirm some properties revealed by the numerical results.

IV. Numerical Method and General Result

In analyzing the properties of the correlation function $\tilde{G}(\bar{k}^2;z_1,z_2)$, we find that it is singular along the diagonal $z_1 = z_2$ line. This adds some difficulty to the numerical computation. As in the grafted homopolymer correlation function, this singularity is only logarithmic and hence integrable. The singularity may be removed by transforming to a basis set of smooth functions, such as Legendre polynomials. Alternatively, we may use a set of functions with localized support. For simplicity, we set $h = 1$, $V = 1$ (so $\sigma = h/V = 1$) in this section and the following section V, so all the lengths and volumes are in units of h and V, respectively.

1. Correlation Function and Eigenvalue Equation. The correlation function $G(z_1,z_2)$ with $k = 0$ is plotted in Figure 4a. From this we can notice that it diverges logarithmically along the diagonal line and diverges more strongly at the "corner" $z_1 = z_2 \rightarrow 1$ with power (-1). These divergences occur also for the homopolymer case treated by Marko and Witten.[6] As $z_1 \rightarrow z_2$, the volume fraction at z_2 of the chain passing through z_1 diverges, resulting in a divergence of G. The divergence at the corner arises from the $(1 - z_{\mathrm{v}}^2)^{-1/2}$ divergence of the end density $\mathrm{d}\sigma/\mathrm{d}z$. We can also see a "step" along $z_1 \approx 0.7$ or $z_2 \approx 0.7$: this can be explained by the fact that when z_1 and z_2 are higher than the maximum height that may be attained by the junction point (V_{l}), only the upper–upper portion of the correlation function will have a nonzero contribution. To illustrate the composition of the total correlation function G, we also plot the components $G^{\mathrm{I}}_{\mathrm{uu}}$, $G^{\mathrm{II}}_{\mathrm{uu}}$; $G^{\mathrm{I}}_{\mathrm{ll}}$, $G^{\mathrm{II}}_{\mathrm{ll}}$; and $G^{\mathrm{I}}_{\mathrm{lu}}$, $G^{\mathrm{II}}_{\mathrm{lu}}$ in Figure 4b–g. From these plots, the origins of divergences, dips, and steps of total $G(z_1,z_2)$ become clear.

For a kernel such as G, which is not smooth, we either can use a very small mesh in real space or project the G operator onto a basis of smooth functions such as the Legendre polynomials, in hopes that a smaller function space will give an adequate representation. We use both methods and obtain quite consistent results. Our numerical uncertainty is indicated by the difference between the curves in Figure 8.

2. Solving the Eigenvalue Equation in the Legendre Representation. First we use a projection method, in which we transform into a basis of Legendre polynomials. Since the Legendre polynomials are orthonormal, the eigenvalues of the correlation function will not be changed by this transformation. We define the matrix elements:

$$\langle P_i|G|P_j\rangle \int_0^1\int_0^1 \mathrm{d}z_1\ \mathrm{d}z_2\ P_i(2z_1-1)\ \tilde{G}(\bar{k}^2;z_1,z_2)\ P_j(2z_2-1) \equiv \tilde{G}(\bar{k}^2;i,j)$$

The $P_i(x)$ are Legendre polynomials defined for $x \in [-1, 1]$; thus, we use functions $P_i(2z-1)$ to allow $z \in [0, 1]$.

To simplify the mathematics, we use the following transformation formulas which are derived in detail in Appendix B. We neglect the factor $\delta^2(\bar{k}_1+\bar{k}_2)$ as before:

$$\langle f|\tilde{G}^{\mathrm{I}}_{\mathrm{uu}}|g\rangle = 4\pi^2\int_0^1\mathrm{d}\xi\int_{V_{\mathrm{l}}}^1\mathrm{d}\upsilon_1\int_{V_{\mathrm{l}}}^1\mathrm{d}\upsilon_2\ \mathrm{e}^{-\bar{k}^2|\upsilon_2-\upsilon_1|}K_{f,g}(\upsilon_1,\upsilon_2,\xi)$$

$$\langle f|\tilde{G}^{\mathrm{I}}_{\mathrm{ll}}|g\rangle = 4\pi^2\int_0^1\mathrm{d}\xi\int_0^{V_{\mathrm{l}}}\mathrm{d}\upsilon_1\int_0^{V_{\mathrm{l}}}\mathrm{d}\upsilon_2\ \mathrm{e}^{-\bar{k}^2|\upsilon_2-\upsilon_1|}K_{f,g}(\upsilon_1,\upsilon_2,\xi)$$

$$\langle f|\tilde{G}^{\mathrm{I}}_{\mathrm{lu}}|g\rangle = 4\pi^2\int_0^1\mathrm{d}\xi\int_0^{V_{\mathrm{l}}}\mathrm{d}\upsilon_1\int_{V_{\mathrm{l}}}^1\mathrm{d}\upsilon_2\ \mathrm{e}^{-\bar{k}^2|\upsilon_2-\upsilon_1|}K_{f,g}(\upsilon_1,\upsilon_2,\xi)$$

$$\langle f|\tilde{G}^{\mathrm{II}}_{\mathrm{uu}}|g\rangle = 4\pi^2\int_0^1\mathrm{d}\xi\int_{V_{\mathrm{l}}}^1\mathrm{d}\upsilon_1\ \mathrm{e}^{-\bar{k}^2\upsilon_1}K_f(\upsilon_1,\xi)\int_0^1\mathrm{d}\eta\int_{V_{\mathrm{l}}}^1\mathrm{d}\upsilon_2\ \mathrm{e}^{-\bar{k}^2\upsilon_2}K_g(\upsilon_2,\eta)$$

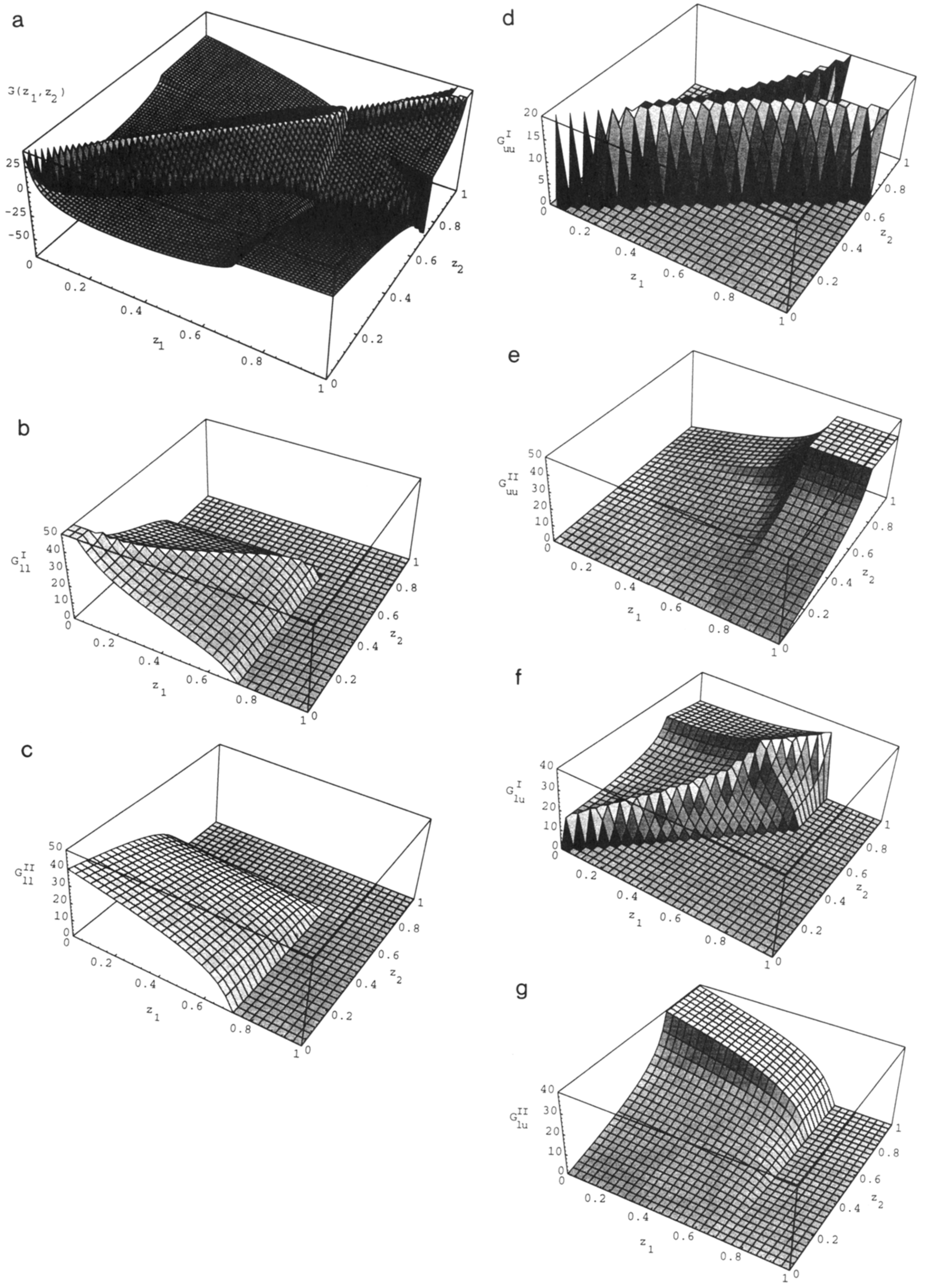

Figure 4. (a) Typical second-order correlation function $G(z_1,z_2)$ with $f = 1$, $V_l = {}^1/_2$, and $k = 0$, where $V = h = 1$. It is symmetric about the diagonal line, on which the eigenfunction diverges. The spikes along the diagonal are artifacts. (b) $G_{ll}^{I}(z_1,z_2)$ component. The vanishing region reflects the fact that there are no monomers from lower sections of chains above a certain height. (c) $G_{ll}^{II}(z_1,z_2)$ component. The vanishing region reflects the fact that there are no monomers from lower sections of chains above a certain height. (d) $G_{uu}^{I}(z_1,z_2)$ component. It diverges along the diagonal line. The spikes near the origin (0, 0) are an artifact of the plotting routine. (e) $G_{uu}^{II}(z_1,z_2)$ component. It is finite everywhere. (f) $G_{lu}^{I}(z_1,z_2)$ component. The vanishing region reflects the fact that there are no monomers from lower sections of chains above a certain height, and the monomers from the lower sections of a chain are lower than monomers from the higher sections of the same chain. The $G_{ul}^{I}(z_1,z_2)$ is just the transpose of it. (g) $G_{lu}^{II}(z_1,z_2)$ component. The vanishing region reflects the absence of monomers from lower sections of chains above a certain height. The $G_{ul}^{II}(z_1,z_2)$ is just the transpose of it.

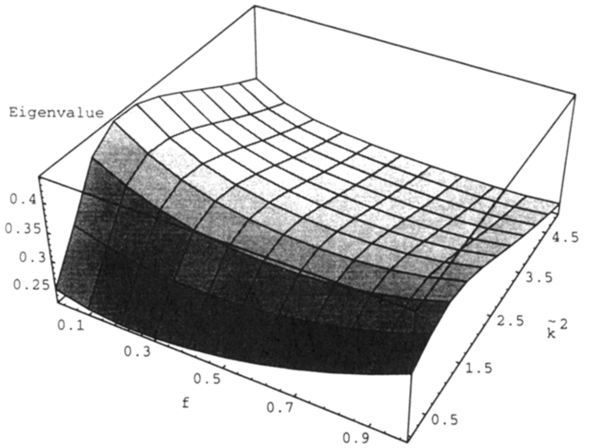

Figure 5. Biggest eigenvalue of $G(z_1,z_2)$ as a function of f and $\tilde{k}^2$ with $V_l = 0.5$, using a Legendre polynomial basis set. Numerical uncertainty estimated by the difference between the fifth- and fourth-order results is less than 0.05.

$$\langle f|\tilde{G}^{\rm II}_{\rm ll}|g\rangle = 4\pi^2 \int_0^1 {\rm d}\xi \int_0^{V_l} {\rm d}\upsilon_1\, {\rm e}^{-\tilde{k}^2\upsilon_1} K_f(\upsilon_1,\xi) \int_0^1 {\rm d}\eta \int_0^{V_l} {\rm d}\upsilon_2\, {\rm e}^{-\tilde{k}^2\upsilon_2} K_g(\upsilon_2,\eta)$$

$$\langle f|\tilde{G}^{\rm II}_{\rm lu}|g\rangle = 4\pi^2 \int_0^1 {\rm d}\xi \int_0^{V_l} {\rm d}\upsilon_1\, {\rm e}^{-\tilde{k}^2\upsilon_1} K_f(\upsilon_1,\xi) \int_0^1 {\rm d}\eta \int_{V_l}^1 {\rm d}\upsilon_2\, {\rm e}^{-\tilde{k}^2\upsilon_2} K_g(\upsilon_2,\eta)$$

The kernels K are defined as:

$$K_f(\upsilon,\xi) \equiv f\left(\sqrt{1-\xi^2}\sin\frac{\pi\upsilon}{2}\right),\quad K_g(\upsilon,\eta) \equiv g\left(\sqrt{1-\eta^2}\sin\frac{\pi\upsilon}{2}\right)$$

$$K_{f,g}(\upsilon_1,\upsilon_2,\xi) \equiv f\left(\sqrt{1-\xi^2}\sin\frac{\pi\upsilon_1}{2}\right) g\left(\sqrt{1-\xi^2}\sin\frac{\pi\upsilon_2}{2}\right)$$

Replacing the arbitrary functions $f(z)$ and $g(z)$ with Legendre polynomials $P_i(z)$, we find that the above integrals can be carried out in closed form. We thus obtain the correlation function components in Legendre space $\tilde{G}(\tilde{k}^2;i,j)$ in closed form as functions of $\tilde{k}^2$, the A–B contrast f, and the length of the lower block of the chain V_l. We find that the eigenvalues converge well when only a few low-order Legendre polynomials are used. Figure 5 shows the result obtained with up to fifth-order Legendre polynomials and with $V_l = 0.5$.

The dependence of eigenvalue ϵ on k for $f = 0$ may be compared directly with ref 6. We find our $\epsilon(k=0) = 0.25$ in agreement with their result. For $k = 1.95$, our ϵ has a maximum $\epsilon_{\rm max} = 0.44$. This agrees well with ref 6, where $\epsilon_{\rm max} = 0.440$ at $k = 1.841$. Since the largest eigenvalue occurs when $k \neq 0$, the phase separation requiring the smallest demixing interaction is always rippling and not layering. When we increase the demixing interaction strength, the system will first phase separate by rippling with finite wavelength in the x–y plane. If Λ is increased beyond Λ_c, we expect the rippling modulation to increase in strength. The concentration waves will, in general, interact to form, e.g., a lattice of alternating composition. Our linear-response picture is not sufficient to describe such phenomena, and we shall defer our treatment of them to a future publication.[20]

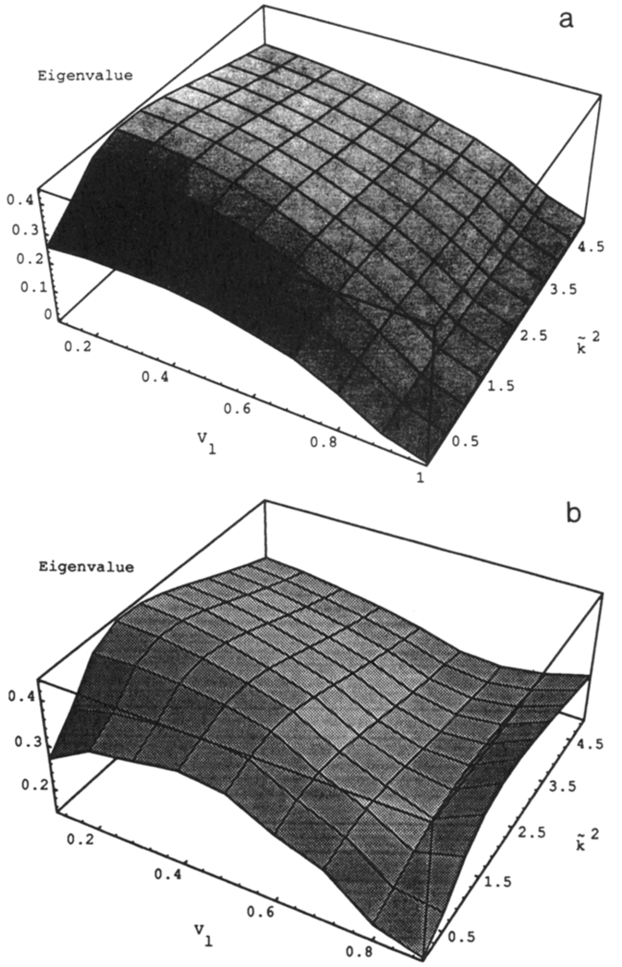

Figure 6. (a) Biggest eigenvalue of $G(z_1,z_2)$ as a function of $\tilde{k}^2$ and V_l with $f = 0.5$. (b) Biggest eigenvalue of $G(z_1,z_2)$ as a function of $\tilde{k}^2$ and V_l with $f = 1$.

We also notice that when $f \approx {}^1/_2$, i.e., when the lower block is neutral, the Λ_c is maximal. This is because, in this situation, neither A nor B from the upper block of the chain can easily penetrate into the lower region away from the upper blocks of unlike monomers. With $f \approx 0$ or $f \approx 1$, chains can easily penetrate into the lower portion without much repulsion (since there are few unlike monomers in the lower region). Thus the phase separation can be more easily achieved in these cases. Also we see generally the homopolymer chain system ($f = 0$) phase separates more easily than A–B diblocks ($f = 1$).

We also can obtain the dependence of the eigenvalues on the relative length of the two blocks (V_l) and $\tilde{k}^2$, as plotted in Figure 6a with $f = {}^1/_2$. For generic values of the contrast f, the effect of changing V_l is moderate: even if V_l is large and the upper sections are small, the homopolymer phase separation of the lower blocks dominates and controls the eigenvalue. But when $f = {}^1/_2$, there is no tendency for the lower blocks to phase separate. Then the overall tendency to phase separate must vanish as $V_l \rightarrow 1$, and the eigenvalue must go to zero, as can be seen in Figure 6a ($f = {}^1/_2$). The result shows that the longer the upper block is, the easier the phase separation will be. When the upper block is short, the relation is quite linear. This will be discussed more thoroughly later and in section V. When the upper block becomes a large fraction of the entire chain, the eigenvalue no longer strongly depends on the length.

For $f = 1$, the dependence of eigenvalues on V_l and $\tilde{k}^2$ is plotted in Figure 6b. We can see from Figure 6b that the easiest phase separation mode is one with $k \neq 0$ for any value of V_l, but the preference is less significant for bigger V_l values. At $V_l \approx 0.7$, the eigenvalues are almost independent of $\tilde{k}^2$, which means all the modes begin to contribute to compositional fluctuations for almost the same phase separation interaction strength. We plot the phase separation pattern of the first mode available with

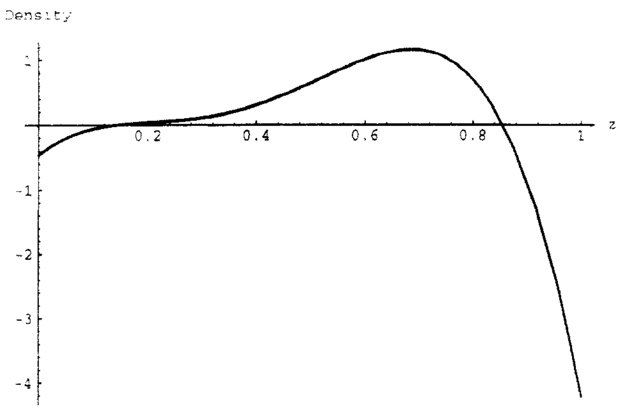

Figure 7. A–B density difference distribution of the phase-separated state with $f = 1$, $V_l = 0.7$, and $k^2 = 0.25$, calculated using Legendre representation.

$V = 0.7$ in Figure 7. We observe that the integral of this profile is nearly zero, indicating that there are nearly equal numbers of A or B monomers on any point on the x–y plane. This is in contrast with the $f = 0$ case, where the corresponding profile integral is much larger.

3. Neutral-Type System ($f = {}^1/_2$) Results Obtained in Real Space for $k = 0$. From the correlation formula (III-4):

$$G(\mathbf{r}_1,\mathbf{r}_2) = G_{\mathrm{uu}}(\mathbf{r}_1,\mathbf{r}_2) + (1 - 2f)^2 G_{\mathrm{ll}}(\mathbf{r}_1,\mathbf{r}_2) + (1 - 2f) G_{\mathrm{lu}}(\mathbf{r}_1,\mathbf{r}_2) + (1 - 2f) G_{\mathrm{ul}}(\mathbf{r}_1,\mathbf{r}_2)$$

When $f = {}^1/_2$, i.e., when the lower portion of the chain has an equal number of A or B monomers, we find

$$G(\mathbf{r}_1,\mathbf{r}_2) = G_{\mathrm{uu}}(\mathbf{r}_1,\mathbf{r}_2)$$

Thus the chains behave as if there is no lower (neutral) portion of the chain: all the demixing is due to the upper portion. This greatly simplifies the correlation function and makes it possible to study the properties of the system further with the expectation that there may exist some simple relation between the phase separation tendency and the system configuration (for example, V_{u}).

With $k = 0$ and $f = {}^1/_2$, we have the simplified correlation function:

$$\tilde{G}(z_1,z_2) \equiv \tilde{G}^{\mathrm{I}}(z_1,z_2) - \tilde{G}^{\mathrm{II}}(z_1,z_2) =$$

$$16\theta(z_<' - z_>) \frac{1}{\sqrt{1 - z_<^2}} \left[F\left(\frac{\pi}{2}, \sqrt{\frac{1 - z_>^2}{1 - z_<^2}}\right) - F\left(\sin^{-1} \sqrt{\frac{1 - \min\{z_<',1\}^2}{1 - z_>^2}}, \sqrt{\frac{1 - z_>^2}{1 - z_<^2}}\right)\right] - 16 \cos^{-1} \sqrt{\frac{1 - \min\{z_1',1\}^2}{1 - z_1^2}} \cos^{-1} \sqrt{\frac{1 - \min\{z_2',1\}^2}{1 - z_2^2}}$$

With a very small upper block length V_{u}, we expect that the phase-separated density distribution will no longer be so smooth and that the Legendre representation will no longer converge well. To solve this problem, we can compute the matrix elements in real space with a very small mesh. In other words, we divide the z interval into, e.g., 100 equally spaced intervals and use basis functions which are unity in the ith interval and zero elsewhere. On the diagonal line where the original $G(z_1,z_2)$ diverges, we use the average value of the correlation function obtained by integrating $G(z_1,z_2)$ over one square of the grid. The relation between the eigenvalue ϵ and V_{u} shown in Figure 8 is calculated using 200 × 200 and 100 × 100 size meshes. The consistency of the results shows that the numerical computation converges well at all but the smallest V_{u}.

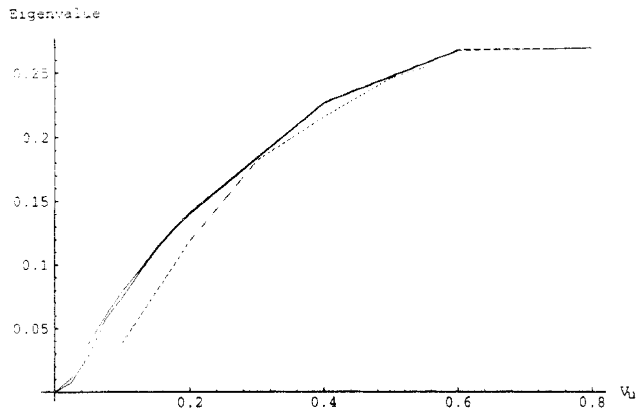

Figure 8. Biggest eigenvalue of $G(z_1,z_2)$ as a function of end block length V_{u}, with $k = 0$ and $f = 0.5$. The upper two solid lines are calculated using 100 × 100 and 200 × 200 meshes. The dashed line is the corresponding result using the Legendre basis. The three curves are all consistent for most V_{u} values. The Legendre calculation gives poorer results for small V_{u}; this is expected since for small V_{u} the eigenfunction is no longer so smooth.

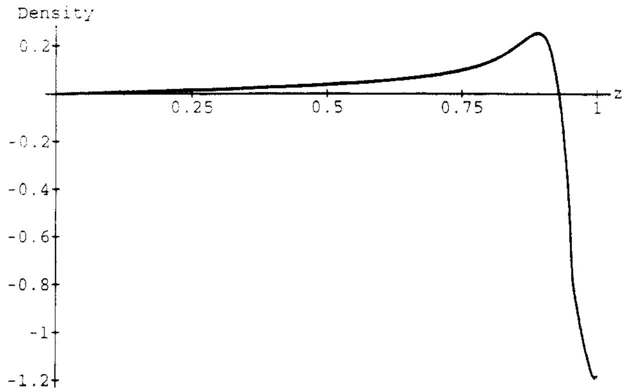

Figure 9. Typical A–B density difference distribution of a segregated state ($k = 0$, $V_l = 0.8$, $f = {}^1/_2$), calculated using 200 × 200 size mesh in real space.

One important property we observe from Figure 8 (Figure 11 shows an expanded scale) is that, for very small V_{u} (very short upper block), the eigenvalue ϵ, which is inversely proportional to minimum demixing interaction strength Λ_{c}, increases roughly linearly with V_{u}. Evidently the numerical convergence is poor for small V_{u}. This property is further studied in section V using a variational calculation (Figure 11).

A typical eigenfunction is shown in Figure 9. It is qualitatively similar to Figure 7, except that now the phase separation occurs in a narrower region near $z = 1$. Figure 9 clearly shows that the total A–B density difference $\phi = \phi_{\mathrm{A}} - \phi_{\mathrm{B}}$ changes sign along the z-axis and that the integral of the eigenfunction vanishes, reflecting the fact that there are equal values of A and B blocks and that $k = 0$.

V. Study of the Short End Block Limit via the Variational Principle for $k = 0$

It is clear from Figure 8 that our numerical methods are not suitable for treating the limit of short immiscible blocks. In this section we explore this limit using a variational approach.

From the eigenvalue equation:

$$\int \mathrm{d}^3 r_2 \, G(\mathbf{r}_1,\mathbf{r}_2) \, \phi_n(\mathbf{r}_2) = \epsilon_n \phi_n(\mathbf{r}_1)$$

we can obtain a complete orthonormal set of eigenfunctions

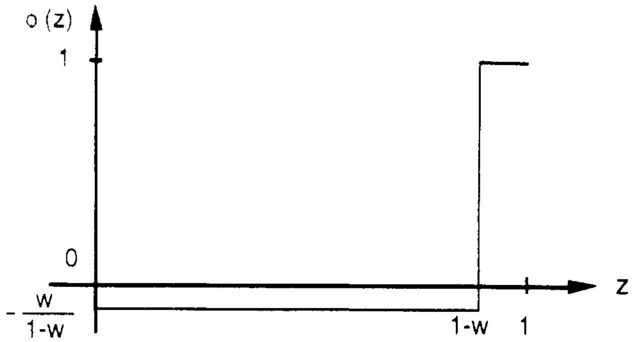

Figure 10. Trial demixed state density distribution function $\phi(z)$, without the normalizing prefactor.

$\phi_n(\mathbf{r})$ and eigenvalues ϵ_n, since $G(\mathbf{r}_1,\mathbf{r}_2)$ is symmetric and compact for our system. When G is applied to a function with unit norm, the result corresponds to a physical perturbed density distribution, so it must have a bounded norm. That is, G must be compact. Assuming that the biggest eigenvalue is ϵ, for an arbitrary trial function $\phi(\mathbf{r})$:

$$\phi(\mathbf{r}) = \sum_n \langle\phi|\phi_n\rangle\phi_n(\mathbf{r})$$

The "expectation" value of the correlation function is

$$\begin{aligned}\langle\phi|G|\phi\rangle &\equiv \int \mathrm{d}^3r_1\, \mathrm{d}^3r_2\, \phi(\mathbf{r}_1)\, G(\mathbf{r}_1,\mathbf{r}_2)\, \phi(\mathbf{r}_2)\\ &= \sum_{i,j}\langle\phi|\phi_i\rangle\langle\phi|\phi_j\rangle\int \mathrm{d}^3r_1\, \mathrm{d}^3r_2\, \phi_i(\mathbf{r}_1)\, G(\mathbf{r}_1,\mathbf{r}_2)\, \phi_j(\mathbf{r}_2)\\ &= \sum_{i,j}\langle\phi|\phi_i\rangle\langle\phi|\phi_j\rangle\epsilon_i\delta_{ij} = \sum_i \epsilon_i|\langle\phi|\phi_i\rangle|^2\\ &\leq \epsilon_1\sum_i|\langle\phi|\phi_i\rangle|^2 = \epsilon_1\end{aligned}$$

The equal sign is valid only when the trial function $\phi(\mathbf{r}) = \phi_1(\mathbf{r})$. Thus, we see that by choosing a trial function which is very close to the eigenfunction $\phi_1(\mathbf{r})$ corresponding to the maximum eigenvalue ϵ_1, the expectation value of $G(\mathbf{r}_1,\mathbf{r}_2)$ with respect to the trial function will give us a lower limit of the maximum eigenvalue. Due to the translational and rotational symmetry in the x–y plane, $\tilde{k}^2$ is a "good quantum number", and it appears in the problem only as a parameter. We can choose $\phi(\mathbf{r}) = \cos(kx)\phi(z)$; here we consider the behavior of ϵ when $\tilde{k}^2 = 0$, as in Figure 8.

We note that the correlation function has its peak (a strong divergence) at $z_1 = z_2 = 1$: we make full use of this region to make the expectation value as big as possible (hence closer to the real value ϵ_1) while choosing the trial function to be as simple as possible to simplify the mathematics. For the grafted chains with very short upper block $V_\mathrm{u} \ll 1$, the trial function $\phi(z)$ we choose, which is normalized and integrates to zero satisfying the condition that there is the same amount of A and B monomer in the system, can be written as:

$$\phi(z) = \sqrt{\frac{1-w}{w}}\left\{\theta[z-(1-w)] - \frac{w}{1-w}\theta[(1-w)-z]\right\}$$

with w small. The function is illustrated in Figure 10.

We make use of the transformation formulas listed in section IV, neglecting the mathematical details (which are listed in Appendix C). The expectation value of the first part of the correlation function G^I, in the limit $w \to 0$ and $V_\mathrm{u} \to 0$, is given by:

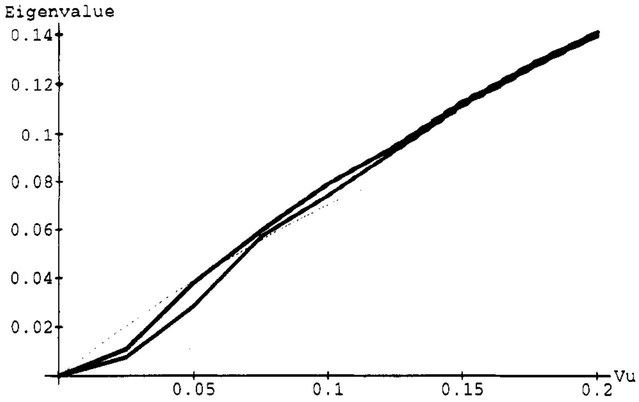

Figure 11. Near-linear relation of the biggest eigenvalue of G with short end block length. The dashed curve is a rigorous lower bound on the eigenvalue. The solid curves, from Figure 8, violate this bound at small V_u, owing to the effect of finite mesh size. From the bottom up, the solid curves are obtained using 100 × 100 and 200 × 200 meshes.

$$\langle\phi|\tilde{G}^\mathrm{I}|\phi\rangle \approx \frac{4\pi^3}{3}\frac{1-w}{w}[\xi^3 - (\xi^2 - {V_\mathrm{u}}^2)^{3/2}] \qquad \text{(V-I)}$$

The second part of the correlation can be obtained as:

$$\langle\phi|\tilde{G}^\mathrm{II}|\phi\rangle \approx \frac{\pi^4(1-w)^2}{w}\left[\frac{1}{2}V_\mathrm{u}\sqrt{\xi^2 - {V_\mathrm{u}}^2} + \frac{\xi^2}{2}\sin^{-1}\left(\frac{V_\mathrm{u}}{\xi}\right)\right]^2 \qquad \text{(V-II)}$$

in which the parameter ξ is defined by:

$$\xi \equiv \sqrt{\frac{4}{\pi^2}\frac{w(2-w)}{(1-w)^2}}$$

For small V_u, the expectation value of $G = G^\mathrm{I} - G^\mathrm{II}$ reaches its maximum when approximately:

$$w \approx 1 - \frac{1}{\sqrt{1 + \pi^2{V_\mathrm{u}}^2/4}} \approx \frac{\pi^2}{8}{V_\mathrm{u}}^2$$

Using this we have the expectation values:

$$\langle\phi|\tilde{G}^\mathrm{I}|\phi\rangle \approx (2\pi)^2\frac{8}{3\pi}V_\mathrm{u}$$

$$\langle\phi|\tilde{G}^\mathrm{II}|\phi\rangle \approx (2\pi)^2\frac{\pi^2}{8}{V_\mathrm{u}}^2$$

So the lower limit estimated from our trial function is

$$\epsilon = \frac{1}{4\pi^2}\langle\phi|\tilde{G}|\phi\rangle_\mathrm{max} = \frac{1}{4\pi^2}\langle\phi|\tilde{G}^\mathrm{I}|\phi\rangle - \frac{1}{4\pi^2}\langle\phi|\tilde{G}^\mathrm{II}|\phi\rangle \approx \frac{8}{3\pi}V_\mathrm{u}$$

We notice that the second part of the correlation function gives a contribution which is proportional to V_u^2 rather than V_u. This gives a negligible contribution to the eigenvalue when V_u is very small. The eigenvalue lower bound is about $0.85V_\mathrm{u}$ with $V_\mathrm{u} \approx 0$.

In Figure 11, the curved dashed line is the exact numerical result of the lower bound of ϵ using the trial function. It gives us a good estimation of ϵ for a very small V_u value. But not surprisingly, it gives a poor estimate for only a slightly bigger V_u. The solid lines are the numerical result we obtained before (Figure 8) by solving the eigenvalue equation directly. The dip at the small V_u region is due to the fact that the mesh we use is of finite size. Figures 8 and 11 show that, with a finer mesh, the dip will eventually disappear. Away from that region, the three curves agree well and the relation between eigenvalue $\epsilon = 2/\Lambda_\mathrm{c}$ and V_u is nearly linear.

We note that the end density distribution ($\mathrm{d}\sigma/\mathrm{d}z$) is singular at the top of the layer $z_v \approx 1$; this means when $V_u \rightarrow 0$, the short end blocks dominate the phase separation at the top of the layer, and the lower region can be neglected. In general:

$$\epsilon \equiv \langle \phi|\tilde{G}|\phi \rangle \approx \int\int \phi G^{\mathrm{I}} \phi \approx \int\int \phi \frac{\mathrm{d}v}{\mathrm{d}z}\frac{\mathrm{d}\sigma}{\mathrm{d}z}\frac{\mathrm{d}v}{\mathrm{d}z}\phi$$

We already see above, for short V_u, the eigenfunction ϕ has peak $\sim w^{-1/2}$ at the end $z = 1$; the width of it is about $w \sim V_u^2$. If the end density distribution $\mathrm{d}\sigma/\mathrm{d}z \sim (h - z)^{-p}$, the eigenvalue will have $\epsilon \sim w^{1-p} \sim V_u^{2-2p}$ (the $\mathrm{d}v/\mathrm{d}z$ only provides a smooth contribution above when we integrate z_v over the range 0–1). If $p = 0$, $\mathrm{d}\sigma/\mathrm{d}z$ is a smooth function, and $\epsilon \sim V_u^2$. But if $\mathrm{d}\sigma/\mathrm{d}z$ is divergent at the end $z = 1$ as in our system ($p = 1/2$), the ϵ will be much amplified and we have at the lowest order $\epsilon \sim V_u$ instead of V_u^2.

To further shed light on this behavior, we note that, if we neglect the second part of the correlation function G^{II}, the phase-separating pieces in fact behave like a dilute gas of immiscible atoms in the limit of small V_u. The gas is nonuniform, with a local density distribution ($\mathrm{d}\sigma/\mathrm{d}z$) which is divergent at the end $z = 1$. The result will be significantly different from a uniform gas system due to the highly inhomogeneous total density.

VI. Discussion

We have explored two aspects of the phase separation of grafted copolymers. The first was a general study of diblocks of an arbitrary length ratio. We also varied the relative demixing strength of the grafted block. Here the phase separation is qualitatively similar to that of homopolymers. The incipient phase separation pattern has a characteristic transverse wavelength comparable to the mean lateral extent of the grafted chains. For pure diblocks, the critical demixing strength Λ_c goes through a maximum when the upper block is about 20% of the chain. When the composition of the grafted block is varied, Λ_c is maximal when the composition is neutral—i.e., when $f = 1/2$. The neutral composition has no phase separation tendency. The phase separation profile with height z for diblocks typically has three regions of alternating composition, separated by two nodal surfaces.

In the second aspect of our study, we considered the limit in which only the free ends of the chains were immiscible. Such polymers in a free melt state would phase separate at Λ_c^{-1} of order V_u^2, where V_u is the immiscible fraction. When such chains are grafted, they show distinctive phase separation unlike that of the free chains or of grafted homopolymers. The phase separation resembles that of a nonuniform gas of immiscible blocks, with an overall density profile which is that of the chain ends. Because this end density profile is singular at the outer periphery of the grafted layer, the concentration of immiscible blocks is much higher than it would be in a uniform melt. Accordingly phase separation is easier: Λ_c^{-1} goes as V_u. The phase separation amplitude is concentrated at the extremity of the layer. We have not studied the transverse modulation in this limit. We expect this transverse modulation to be relatively structureless, since the immiscible blocks are free to migrate laterally over distances much larger than the size of the blocks. It is nearly as though the grafted ends were free to slide over the surface. Thus out to length scales comparable to the lateral extent of the chains, we expect uniform pancakes of phase-separated material.

We predict that chains with immiscible ends phase separate more readily when they are grafted. Our quantitative results in this limit are probably difficult to test experimentally. To do so requires substantial stretching of the grafted chains under melt conditions. Only mild stretching has been achieved in current experiments.[21] In addition, the theory requires the upper block to be a small fraction of the chain, yet still much larger than a monomer. Still, our theory should serve as a qualitative guide. To illustrate the magnitude of the predicted effects, we consider polystyrene and polybutadiene, whose $\Lambda \approx 2 \times 10^{-4}$ ($kT/\text{Å}^3$).[17] A blend composed of neutrally miscible chains with, say, 10% polystyrene or polybutadiene at the upper end ($V_u = 1/10$) would then undergo bulk demixing when the total molecular volume exceeds 1.1×10^6 Å^3. But when these chains are densely grafted the phase separation occurs at only $1/8$ of this molecular volume, which is about 1.4×10^5 Å$^3 \approx 80\,000$ amu, according to Figure 11.

In predicting these phase transitions, we have ignored several effects. Our approach has been to find the point at which the mixed system becomes linearly unstable. We identify such a point as a phase transition. This is correct as long as (a) the phase transition in question is continuous and (b) the mean-field approximation of replacing ϕ by $\langle \phi \rangle$ is justified.

We believe both of these conditions are sufficiently well satisfied for the long, grafted polymers treated here. In the mean-field approximation of simple liquids, polymer blends, or block copolymers, demixing is a continuous transition when the system is symmetric under interchange of the two components A and B.[7] Then the phase separation point is a critical point, and the departures fof $\langle \phi \rangle$ from zero may be made arbitrarily small. Our analysis assumes that this is the case for symmetric grafted layers as well. The validity of the mean-field approximation for long polymers is well accepted, as noted above. Still, if the molecular weight is finite, departures from mean-field behavior are known. Notably, symmetric diblock copolymers show fluctuations that render the transition to the lamellar phase weakly discontinuous.[22] This discontinuity, like other fluctuation effects, becomes arbitrarily small as the molecular weight goes to infinity. Our rippled phase has orientational degeneracy like a lamellar phase; accordingly, similar fluctuation effects are expected in our system.[16] Nevertheless, we expect our mean-field approach to describe the transition well except very near the transition point. These fluctuation effects can also determine which relative directions of ripples are favored. For example, the most stable configuration might be a square or a triangular pattern of ripples.

We have also ignored possible variations in the height $h(x,y)$ induced by phase separation. This is permissible because of the complete symmetry under interchange of A and B monomers. Any motion of an A segment of chain under phase separation is completely balanced by an opposite motion of the corresponding B segment. There cannot be any variation of height proportional to $\phi_A - \phi_B$, as this would distinguish between A and B and violate the symmetry. Any variation of height is of order $(\phi_A - \phi_B)^2$ and is thus negligible compared to the infinitesimal effects considered here. In mixed layers lacking this symmetry, height variations would accompany phase separation.

VII. Conclusion

This study illustrates how one may predict and control phase separation patterns in grafted polymer layers by varying the molecular architecture of the polymers used. Within limits one may tailor these patterns to achieve a desired goal, for information storage, controlled transport, or a structured environment for electronic or wave phenomena. For these purposes, it would be valuable to know how the patterns differ in the strong segregation regime, how they evolve in time, and how they respond to external influences such as flow or wetting effects. In this work we have only studied symmetric species, where the monomers are identical in their elasticity and their displaced volume. We have also not considered the potential effect of solvent in the layer. Such effects may have an important effect on the phase separation, and they should be explored.

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Appendix A: Calculation of the Correlation Function

In this appendix, we illustrate how the correlation functions in the text are simplified. The following is a mathematical manipulation of the formulas sketched previously. To avoid redundant computation, we only choose the correlation between an upper portion and a lower portion of chains and do the computation in detail. The other u–u and l–l contributions can be done similarly.

As in the text of this paper, we define the phase angle:

$$\varphi \equiv \frac{\pi}{2}\frac{V_{\mathrm{l}}}{V}$$

the "image" height:

$$z_1' \equiv \frac{z_1}{\sin\varphi} \quad \text{and} \quad z_2' \equiv \frac{z_2}{\sin\varphi}$$

and the probability that a single chain has free end height z_{v}:

$$\frac{1}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}z} = \frac{z_{\mathrm{v}}}{h\sqrt{h^2 - z_{\mathrm{v}}^2}}$$

The monomer density distribution of a chain with free end at height z_{v} is

$$\frac{\mathrm{d}\upsilon}{\mathrm{d}z} = \frac{2V}{\pi}\frac{1}{\sqrt{z_{\mathrm{v}}^2 - z^2}}$$

Thus, the height z can be expressed as a function of position υ along the chain:

$$z(\upsilon,z_{\mathrm{v}}) = z_{\mathrm{v}} \sin\frac{\pi\upsilon}{2V}$$

The polymer section $\upsilon_0 \sim \upsilon_1$ has its end-to-end distance distribution in the x–y plane given by the following Gaussian distribution:

$$\gamma(\bar{x}_1,\bar{x}_0,\upsilon_1,\upsilon_0) = \frac{a}{2\pi(\upsilon_1 - \upsilon_0)}\exp\left(-\frac{a}{2}\frac{(\bar{x}_1 - \bar{x}_0)^2}{\upsilon_1 - \upsilon_0}\right)\theta(\upsilon_1 - \upsilon_0)$$

We have the first part of the correlation function:

$$\begin{aligned} G^{\mathrm{I}}_{\mathrm{lu}}(\mathbf{r}_1,\mathbf{r}_2) &= \sigma\int \mathrm{d}^2\bar{x}_0\, [\langle \psi_{\mathbf{r}_0,\mathrm{l}}(\mathbf{r}_1)\, \psi_{\mathbf{r}_0,\mathrm{u}}(\mathbf{r}_2)\rangle] = \\ &\sigma\int \mathrm{d}^2\bar{x}_0 \Bigg[\int_{z_>}^{h}\mathrm{d}z_{\mathrm{v}}\left(\frac{1}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}z}\right)\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_1\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_2 \theta(z(V_{\mathrm{l}},z_{\mathrm{v}}) - z_1) \times \\ &\theta(z_2 - z(V_{\mathrm{l}},z_{\mathrm{v}}))\, \gamma(\bar{x}_<,\bar{x}_0,\upsilon(z_<,z_{\mathrm{v}}),0) \times \\ &\gamma(\bar{x}_>,\bar{x}_<,\upsilon(z_>,z_{\mathrm{v}}),\upsilon(z_<,z_{\mathrm{v}}))\Bigg] = \\ &\sigma\int \mathrm{d}^2\bar{x}_0 \Bigg[\int_{z_>}^{h}\mathrm{d}z_{\mathrm{v}}\left(\frac{1}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}z}\right)\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_1\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_2 \theta(z_{\mathrm{v}} - z_1') \times \\ &\theta(z_2' - z_{\mathrm{v}})\, \frac{a}{2\pi\upsilon_<}\exp\left(-\frac{a}{2}\frac{(\bar{x}_< - \bar{x}_0)^2}{\upsilon_<}\right)\frac{a}{2\pi|\upsilon_> - \upsilon_<|} \times \\ &\exp\left(-\frac{a}{2}\frac{(\bar{x}_> - \bar{x}_<)^2}{\upsilon_> - \upsilon_<}\right)\Bigg] \end{aligned}$$

Considering the translational symmetry in the x–y plane, we can simplify the previous expression by doing Fourier transforms with respect to x–y variables:

$$G(\bar{k}_1,z_1;\bar{k}_2,z_2) \equiv \int_{-\infty}^{+\infty}\mathrm{d}^2\bar{x}_1\, \mathrm{d}^2\bar{x}_2\, \mathrm{e}^{-i\bar{k}_1\bar{x}_1 - i\bar{k}_2\bar{x}_2} G(\mathbf{r}_1,\mathbf{r}_2)$$

The density distribution $(\mathrm{d}\upsilon/\mathrm{d}z)$ and probability $1/\sigma(\mathrm{d}\sigma/\mathrm{d}z)$ are substituted with the expressions listed above, and we have used $V = h/\sigma$ to eliminate V.

$$\begin{aligned} G^{\mathrm{I}}_{\mathrm{lu}}(\bar{k}_1,z_1;\bar{k}_2,z_2) &= \\ &\sigma(2\pi)^2\delta^2(\bar{k}_1+\bar{k}_2)\int_{z_>}^{h}\mathrm{d}z_{\mathrm{v}}\left(\frac{1}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}z}\right)\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_1\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_2 \times \\ &\theta(z_{\mathrm{v}} - z_1')\,\theta(z_2' - z_{\mathrm{v}})\exp\left(-\frac{\bar{k}_1^{\,2}}{2a}|\upsilon_2 - \upsilon_1|\right) = \\ &\frac{16h}{\sigma}\delta^2(\bar{k}_1+\bar{k}_2)\int_{z_>}^{h}\mathrm{d}z_{\mathrm{v}}\frac{z_{\mathrm{v}}}{\sqrt{h^2 - z_{\mathrm{v}}^2}}\frac{1}{\sqrt{z_{\mathrm{v}}^2 - z_1^2}}\frac{1}{\sqrt{z_{\mathrm{v}}^2 - z_2^2}} \times \\ &\theta(z_{\mathrm{v}} - z_1')\,\theta(z_2' - z_{\mathrm{v}})\exp\left(-\frac{\bar{k}_1^{\,2}}{2a}|\upsilon_2 - \upsilon_1|\right) \end{aligned}$$

The overall factor $\delta^2(\bar{k}_1+\bar{k}_2)$ allows us to use a single parameter:

$$\bar{k}^2 \equiv \frac{\bar{k}_1^{\,2}V}{2a} = \frac{\bar{k}_2^{\,2}V}{2a}$$

The polymer lengths υ_1 and υ_2 (or $\upsilon_<$ and $\upsilon_>$) are functions of free end height z_{v} of the chain and the height z_1 and z_2:

$$\upsilon_1 = \frac{2V}{\pi}\sin^{-1}\frac{z_1}{z_{\mathrm{v}}} \quad \text{and} \quad \upsilon_2 = \frac{2V}{\pi}\sin^{-1}\frac{z_2}{z_{\mathrm{v}}}$$

Thus we define the following angle:

$$\varphi(z,z_{\mathrm{v}}) = \sin^{-1}(z/z_{\mathrm{v}})$$

We can drop the δ function since we are only interested in correlation per unit area on the grafting surface. Thus we finally have

$$\tilde{G}^{\mathrm{I}}_{\mathrm{lu}}(\tilde{k}^2;z_1,z_2) =$$

$$\frac{16h}{\sigma}\int_{z_>}^{h}\mathrm{d}z_{\mathrm{v}}\,\frac{z_{\mathrm{v}}}{\sqrt{h^2-z_{\mathrm{v}}^{\,2}}}\,\frac{1}{\sqrt{z_{\mathrm{v}}^{\,2}-z_1^{\,2}}}\,\frac{1}{\sqrt{z_{\mathrm{v}}^{\,2}-z_2^{\,2}}}\,\theta(z_{\mathrm{v}}-z_1') \times \theta(z_2'-z_{\mathrm{v}})\exp\left(-\frac{2\tilde{k}^2}{\pi}\left|\varphi(z_2,z_{\mathrm{v}})-\varphi(z_1,z_{\mathrm{v}})\right|\right)$$

This is the result quoted in eq III-2.

With k set to zero, i.e., considering only layering, we obtain a simplified result after carrying out the integrations:

$$G^{\mathrm{I}}_{\mathrm{lu}}(0,z_1;z_2) = \frac{16}{\sigma}\frac{h}{\sqrt{h^2-z_<^{\,2}}}\theta(h-z_1')\,\theta(z_2-z_1) \times$$

$$\left[F\left(\sin^{-1}\sqrt{\frac{h^2-\max\{z_1',z_>\}^2}{h^2-z_>^{\,2}}},\sqrt{\frac{h^2-z_>^{\,2}}{h^2-z_<^{\,2}}}\right)-F\left(\sin^{-1}\sqrt{\frac{h^2-\min\{z_2',h\}^2}{h^2-z_>^{\,2}}},\sqrt{\frac{h^2-z_>^{\,2}}{h^2-z_<^{\,2}}}\right)\right]$$

For simplicity we define the operation $\overline{\sqrt{\ }}$ as:

$$\overline{\sqrt{X}} \equiv \begin{cases} 0 & \text{if } X<0 \\ \sqrt{X} & \text{if } 0\le X\le 1 \\ 1 & \text{if } X>1 \end{cases}$$

Then we have the result as quoted in eq III-3:

$$\tilde{G}^{\mathrm{I}}_{\mathrm{lu}}(0;z_1,z_2) = \frac{16}{\sigma}\frac{h}{\sqrt{h^2-z_<^{\,2}}}\theta(z_2-z_1) \times$$

$$\left[F\left(\sin^{-1}\overline{\sqrt{\frac{h^2-z_1'^2}{h^2-z_>^{\,2}}}},\sqrt{\frac{h^2-z_>^{\,2}}{h^2-z_<^{\,2}}}\right)-F\left(\sin^{-1}\overline{\sqrt{\frac{h^2-z_2'^2}{h^2-z_>^{\,2}}}},\sqrt{\frac{h^2-z_>^{\,2}}{h^2-z_<^{\,2}}}\right)\right]$$

The function $F(\varphi,k)$ is the elliptic integral of the first kind:[23]

$$F(\varphi,k) \equiv \int_0^{\sin\varphi}\frac{\mathrm{d}x}{\sqrt{(1-x^2)(1-k^2x^2)}}$$

For the second part of the correlation function, we carry out a similar derivation:

$$G^{\mathrm{II}}_{\mathrm{lu}}(\mathbf{r}_1,\mathbf{r}_2) = \sigma\int\mathrm{d}^2\bar{x}_0\,[\langle\psi_{\mathbf{r}_0,\mathrm{l}}(\mathbf{r}_1)\rangle\langle\psi_{\mathbf{r}_0,\mathrm{u}}(\mathbf{r}_2)\rangle] =$$

$$\sigma\int\mathrm{d}^2\bar{x}_0\left[\int_{z_1}^{h}\mathrm{d}z_{\mathrm{v}1}\left(\frac{1}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}z}\right)_1\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_1\theta(z(V_1,z_{\mathrm{v}1})-z_1) \times \gamma(\bar{x}_1,\bar{x}_0,\upsilon(z_1,z_{\mathrm{v}1}),0)\int_{z_2}^{h}\mathrm{d}z_{\mathrm{v}2}\left(\frac{1}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}z}\right)_2\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_2\theta(z_2-z(V_1,z_{\mathrm{v}2})) \times \gamma(\bar{x}_2,\bar{x}_0,\upsilon(z_2,z_{\mathrm{v}2}),0)\right] = \sigma\int\mathrm{d}^2\bar{x}_0\,\theta(h-z_1')\int_{z_1'}^{h}\mathrm{d}z_{\mathrm{v}1} \times$$

$$\left(\frac{1}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}z}\right)_1\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_1\frac{a}{2\pi\upsilon_1}\exp\left(-\frac{a}{2}\frac{(\bar{x}_1-\bar{x}_0)^2}{\upsilon_1}\right)\int_{z_2}^{h}\mathrm{d}z_{\mathrm{v}2} \times \left(\frac{1}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}z}\right)_2\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_2\theta(z_2'-z_{\mathrm{v}2})\,\frac{a}{2\pi\upsilon_2}\exp\left(-\frac{a}{2}\frac{(\bar{x}_2-\bar{x}_0)^2}{\upsilon_2}\right)$$

Substituting the density distribution $(\mathrm{d}\upsilon/\mathrm{d}z)$ and probability $1/\sigma(\mathrm{d}\sigma/\mathrm{d}z)$ with the expressions listed above and doing the Fourier transform with x–y variables as before,

$$G^{\mathrm{II}}_{\mathrm{lu}}(\bar{k}_1,z;\bar{k}_2,z_2) =$$

$$\frac{16}{\sigma}\delta^2(\bar{k}_1+\bar{k}_2)\,\theta(h-z_1')\int_{z_1'}^{h}\mathrm{d}z_{\mathrm{v}1}\frac{z_{\mathrm{v}1}}{\sqrt{h^2-z_{\mathrm{v}1}^{\,2}}}\frac{1}{\sqrt{z_{\mathrm{v}1}^{\,2}-z_1^{\,2}}} \times \exp\left(-\frac{\bar{k}_1^{\,2}\upsilon_1}{2a}\right)\int_{z_2}^{h}\mathrm{d}z_{\mathrm{v}2}\frac{z_{\mathrm{v}2}}{\sqrt{h^2-z_{\mathrm{v}2}^{\,2}}}\frac{1}{\sqrt{z_{\mathrm{v}2}^{\,2}-z_2^{\,2}}} \times \theta(z_2'-z_{\mathrm{v}2})\exp\left(-\frac{\bar{k}_2^{\,2}\upsilon_2}{2a}\right)$$

The polymer lengths υ_1 and υ_2 are functions of free end heights $z_{\mathrm{v}1}$ and $z_{\mathrm{v}2}$ of the chain and the heights z_1 and z_2:

$$\upsilon_1 = \frac{2V}{\pi}\sin^{-1}\frac{z_1}{z_{\mathrm{v}1}} \quad\text{and}\quad \upsilon_2 = \frac{2V}{\pi}\sin^{-1}\frac{z_2}{z_{\mathrm{v}2}}$$

We change to the new parameter $\tilde{k}^2$, use angles $\varphi(z,z_{\mathrm{v}})$ defined before, and drop the δ function. We have the final result:

$$G^{\mathrm{II}}_{\mathrm{lu}}(\bar{k}_1,z_1;\bar{k}_2,z_2) =$$

$$\frac{16}{\sigma}\theta(h-z_1')\int_{z_1'}^{h}\mathrm{d}z_{\mathrm{v}1}\frac{z_{\mathrm{v}1}}{\sqrt{h^2-z_{\mathrm{v}1}^{\,2}}}\frac{1}{\sqrt{z_{\mathrm{v}1}^{\,2}-z_1^{\,2}}} \times \exp\left(-\frac{2\tilde{k}^2}{\pi}\varphi(z_1,z_{\mathrm{v}1})\right)\int_{z_2}^{h}\mathrm{d}z_{\mathrm{v}2}\frac{z_{\mathrm{v}2}}{\sqrt{h^2-z_{\mathrm{v}2}^{\,2}}}\frac{1}{\sqrt{z_{\mathrm{v}2}^{\,2}-z_2^{\,2}}} \times \theta(z_2'-z_{\mathrm{v}2})\exp\left(-\frac{2\tilde{k}^2}{\pi}\varphi(z_2,z_{\mathrm{v}2})\right)$$

The result is what we quoted in eq III-2.

With $k = 0$, we obtained the explicit result:

$$G^{\mathrm{II}}_{\mathrm{lu}}(0,z_1;0,z_2) = \frac{16}{\sigma}\theta(h-z_1') \times \sin^{-1}\sqrt{\frac{h^2-z_1'^2}{h^2-z_1^{\,2}}}\cos^{-1}\sqrt{\frac{h^2-\min\{z_2',h\}^2}{h^2-z_2^{\,2}}}$$

Using the operation $\overline{\sqrt{\ }}$ defined previously, we have the result as quoted in eq III-3:

$$\tilde{G}^{\mathrm{II}}_{\mathrm{lu}}(0;z_1,z_2) = \frac{16}{\sigma} \times \sin^{-1}\overline{\sqrt{\frac{h^2-z_1'^2}{h^2-z_1^{\,2}}}}\cos^{-1}\overline{\sqrt{\frac{h^2-z_2'^2}{h^2-z_2^{\,2}}}}$$

Correlations corresponding to lower–lower and upper–upper blocks of the chains $G^{\mathrm{I}}_{\mathrm{ll}}$, $G^{\mathrm{II}}_{\mathrm{ll}}$, $G^{\mathrm{I}}_{\mathrm{uu}}$, and $G^{\mathrm{II}}_{\mathrm{uu}}$ can be derived similarly.

Appendix B: Derivation of the Transformation Relation

In this appendix, we define the formulas required for the calculation of matrix elements of G with respect to the Legendre basis set. To avoid redundant derivation, we only illustrate the process concerning the upper–lower part of the correlation; other parts can be derived similarly. We set $h = 1$ and $V = 1$ (so that $\sigma = 1$).

From the discussion we give in the main text, we have

$$\int_0^1\int_0^1 \mathrm{d}z_1\,\mathrm{d}z_2\,[f(z_1)\langle\psi_{\mathbf{r}_0,\mathrm{l}}(\mathbf{r}_1)\,\psi_{\mathbf{r}_0,\mathrm{u}}(\mathbf{r}_2)\rangle g(z_2)] =$$

$$\int_0^1\int_0^1 \mathrm{d}z_1\,\mathrm{d}z_2\int_{z_>}^1 \mathrm{d}z_\mathrm{v}\left(\frac{1}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}z}\right)\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_1\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_2\theta(z(V_\mathrm{l},z_\mathrm{v})-z_1)\times$$

$$\theta(z_2-z(V_\mathrm{l},z_\mathrm{v}))\,\gamma(\bar{x}_<,\bar{x}_0,\upsilon(z_<,z_\mathrm{v}),0)\times$$

$$\gamma(\bar{x}_>,\bar{x}_<,\upsilon(z_>,z_\mathrm{v}),\upsilon(z_<,z_\mathrm{v}))\,f(z_1)\,g(z_2)$$

We can easily prove the following relation, in which we change the integration order and the integration limits, but the volume in which the integration is carried out remains the same:

$$\int_0^1\int_0^1 \mathrm{d}z_1\,\mathrm{d}z_2\int_{z_>}^1 \mathrm{d}z_\mathrm{v} \equiv \int_0^1 \mathrm{d}z_\mathrm{v}\int_0^{z_\mathrm{v}} \mathrm{d}z_1\int_0^{z_\mathrm{v}} \mathrm{d}z_2$$

We thus have

$$\int_0^1\int_0^1 \mathrm{d}z_1\,\mathrm{d}z_2[f(z_1)\langle\psi_{\mathbf{r}_0,\mathrm{l}}(\mathbf{r}_1)\,\psi_{\mathbf{r}_0,\mathrm{u}}(\mathbf{r}_2)\rangle g(z_2)] =$$

$$\int_0^1 \mathrm{d}z_\mathrm{v}\int_0^{z_\mathrm{v}} \mathrm{d}z_1\int_0^{z_\mathrm{v}} \mathrm{d}z_2\frac{z_\mathrm{v}}{\sqrt{1-{z_\mathrm{v}}^2}}\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_1\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_2\times$$

$$\theta(z(V_\mathrm{l},z_\mathrm{v})-z_1)\,\theta(z_2-z(V_\mathrm{l},z_\mathrm{v}))\,\gamma(\bar{x}_<,\bar{x}_0,\upsilon(z_<,z_\mathrm{v}),0)\times$$

$$\gamma(\bar{x}_>,\bar{x}_<,\upsilon(z_>,z_\mathrm{v}),\upsilon(z_<,z_\mathrm{v}))\,f(z_1)\,g(z_2) =$$

$$\int_0^1 \mathrm{d}\xi\int_0^{V_\mathrm{l}} \mathrm{d}\upsilon_1\int_{V_\mathrm{l}}^1 \mathrm{d}\upsilon_2\,\frac{a}{2\pi\upsilon_<}\exp\left(-\frac{a}{2}\frac{(\bar{x}_<-\bar{x}_0)^2}{\upsilon_<}\right)\times$$

$$\frac{a}{2\pi(\upsilon_>-\upsilon_<)}\exp\left(-\frac{a}{2}\frac{(\bar{x}_>-\bar{x}_<)^2}{\upsilon_>-\upsilon_<}\right)f\left(\sqrt{1-\xi^2}\sin\frac{\pi}{2}\upsilon_1\right)\times$$

$$g\left(\sqrt{1-\xi^2}\sin\frac{\pi}{2}\upsilon_2\right)$$

In the above derivation we change variables from $\mathrm{d}z$ to $\mathrm{d}\upsilon = (\mathrm{d}\upsilon/\mathrm{d}z)\,\mathrm{d}z$ and replace z_v by $\xi \equiv \sqrt{h^2-{z_\mathrm{v}}^2}$. The θ functions are absorbed into the integration limits.

Summing over contributions from all chains and doing Fourier transforms of the x–y variables, we have:

$$\int_0^1\int_0^1 \mathrm{d}z_1\,\mathrm{d}z_2\,f(z_1)\,G_\mathrm{lu}^\mathrm{I}(\bar{k}_1,z_1;\bar{k}_2,z_2)\,g(z_2) =$$

$$\int \mathrm{d}^2\bar{x}_0\,\{\int_{-\infty}^{+\infty}\mathrm{d}^2\bar{x}_1\,\mathrm{d}^2\bar{x}_2\,\mathrm{e}^{-i\bar{k}_1\bar{x}_1-i\bar{k}_2\bar{x}_2}\int_0^1\int_0^1 \mathrm{d}z_1\,\mathrm{d}z_2\,[f(z_1)\times$$

$$\langle\psi_{\mathbf{r}_0,\mathrm{l}}(\mathbf{r}_1)\,\psi_{\mathbf{r}_0,\mathrm{u}}(\mathbf{r}_2)\rangle g(z_2)]\} =$$

$$4\pi^2\delta^2(\bar{k}_1+\bar{k}_2)\int_0^1 \mathrm{d}\xi\int_0^{V_\mathrm{l}} \mathrm{d}\upsilon_1\int_{V_\mathrm{l}}^1 \mathrm{d}\upsilon_2\times$$

$$\mathrm{e}^{-\bar{k}^2|\upsilon_2-\upsilon_1|}f\left(\sqrt{1-\xi^2}\sin\frac{\pi\upsilon_1}{2}\right)g\left(\sqrt{1-\xi^2}\sin\frac{\pi\upsilon_2}{2}\right)$$

Note that the overall factor $\delta^2(\bar{k}_1+\bar{k}_2)$ allows us to use a single parameter as before (note that we set $V = 1$):

$$\bar{k}^2 \equiv \frac{{\bar{k}_1}^2}{2a} = \frac{{\bar{k}_2}^2}{2a}$$

The result is what we listed in section IV after dropping the δ function, since we are only interested in correlation per unit area on the grafting surface.

Similarly, we have the result for the second part of the correlation function:

$$\int_0^1\int_0^1 \mathrm{d}z_1\,\mathrm{d}z_2\,[f(z_1)\,\langle\psi_{\mathbf{r}_0,\mathrm{l}}(\mathbf{r}_1)\rangle\langle\psi_{\mathbf{r}_0,\mathrm{u}}(\mathbf{r}_2)\rangle g(z_2)] =$$

$$\int_0^1 \mathrm{d}z_1\int_{z_1}^1 \mathrm{d}z_{\mathrm{v}1}\left(\frac{1}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}z}\right)_1\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_1\theta(z(V_\mathrm{l},z_{\mathrm{v}1})-z_1)\times$$

$$\gamma(\bar{x}_1,\bar{x}_0,\upsilon(z_1,z_{\mathrm{v}1}),0)f(z_1)\int_0^1 \mathrm{d}z_2\int_{z_2}^1 \mathrm{d}z_{\mathrm{v}2}\left(\frac{1}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}z}\right)_2\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_2\times$$

$$\theta(z_2-z(V_\mathrm{l},z_{\mathrm{v}2}))\,\gamma(\bar{x}_2,\bar{x}_0{}',\upsilon(z_2,z_{\mathrm{v}2}),0)g(z_2) =$$

$$\int_0^1 \mathrm{d}\xi\int_0^{V_\mathrm{l}} \mathrm{d}\upsilon_1\,\frac{a}{2\pi\upsilon_1}\exp\left(-\frac{a}{2}\frac{(\bar{x}_1-\bar{x}_0)^2}{\upsilon_1}\right)\times$$

$$f\left(\sqrt{1-\xi^2}\sin\frac{\pi\upsilon_1}{2}\right)\int_0^1 \mathrm{d}\eta\int_{V_\mathrm{l}}^1 \mathrm{d}\upsilon_2\,\frac{a}{2\pi\upsilon_2}\times$$

$$\exp\left(-\frac{a}{2}\frac{(\bar{x}_2-\bar{x}_1)^2}{\upsilon_2}\right)g\left(\sqrt{1-\eta^2}\sin\frac{\pi\upsilon_2}{2}\right)$$

In the derivation we change variables from $\mathrm{d}z$ to $\mathrm{d}\upsilon = (\mathrm{d}\upsilon/\mathrm{d}z)\,\mathrm{d}z$ and replace $z_{\mathrm{v}1}$ and $z_{\mathrm{v}2}$ by $\xi \equiv \sqrt{h^2-{z_{\mathrm{v}1}}^2}$, and $\eta \equiv \sqrt{h^2-{z_{\mathrm{v}2}}^2}$. The θ functions are absorbed into the integration limits.

Summing over contributions from all the chains and carrying out the Fourier transforms of the x–y variables, we have the final result:

$$\int_0^1\int_0^1 \mathrm{d}z_1\,\mathrm{d}z_2\,f(z_1)\,G_\mathrm{lu}^\mathrm{II}(\bar{k}_1,z_1;\bar{k}_2,z_2)\,g(z_2) =$$

$$\int \mathrm{d}^2\bar{x}_0\,\{\int_{-\infty}^{+\infty}\mathrm{d}^2\bar{x}_1\,\mathrm{d}^2\bar{x}_2\,\mathrm{e}^{-i\bar{k}_1\mathrm{I}-i\bar{k}_2\bar{x}_2}\int_0^1\int_0^1 \mathrm{d}z_1\,\mathrm{d}z_2\,[f(z_1)\times$$

$$\langle\psi_{\mathbf{r}_0,\mathrm{l}}(\mathbf{r}_1)\rangle\langle\psi_{\mathbf{r}_0,\mathrm{u}}(\mathbf{r}_2)\rangle g(z_2)]\} = 4\pi^2\delta^2(\bar{k}_1+\bar{k}_2)\times$$

$$\int_0^1 \mathrm{d}\upsilon_1\,\mathrm{e}^{-\bar{k}^2\upsilon_1}f\left(\sqrt{1-\xi^2}\sin\frac{\pi\upsilon_1}{2}\right)\int_0^1 \mathrm{d}\eta\int_{\upsilon_1}^1 \mathrm{d}\upsilon_2\times$$

$$\mathrm{e}^{-\bar{k}^2\upsilon_2}g\left(\sqrt{1-\eta^2}\sin\frac{\pi\upsilon_2}{2}\right)$$

The result is what we use in section IV after dropping the δ function. The formulas corresponding to upper–upper and lower–lower correlations can be derived similarly.

Appendix C: Calculation of the Lower Bound of Eigenvalues of *G*

In this Appendix, we evaluate the "expectation value" of the correlation function with the trial function we chose in section V. We make the approximation that w is very small and make use of the transform formulas listed in section IV and Appendix B. After a change of integration order and carrying out the first integration, we have the expectation value:

$$\langle \phi|\tilde{G}^{\mathrm{I}}|\phi\rangle =$$

$$\frac{(2\pi)^2}{w + \frac{w^2}{1-w}} \int_{1-V_{\mathrm{u}}}^{1} \mathrm{d}\upsilon_2 \int_{\upsilon_2}^{1} \mathrm{d}\upsilon_1 \left\{ \sqrt{1 - \left(\frac{1-w}{\sin(\pi\upsilon_2/2)}\right)^2} + \right.$$

$$\left[1 - \sqrt{1 - \left(\frac{1-w}{\sin(\pi\upsilon_1/2)}\right)^2}\right] \left(\frac{w}{1-w}\right)^2 -$$

$$2\left[\sqrt{1 - \left(\frac{1-w}{\sin(\pi\upsilon_2/2)}\right)^2} - \right.$$

$$\left.\left.\sqrt{1 - \left(\frac{1-w}{\sin(\pi\upsilon_1/2)}\right)^2}\right] \left(\frac{w}{1-w}\right) \right\} \approx$$

$$(2\pi)^2 \frac{2}{w} \int_0^{V_{\mathrm{u}}} \mathrm{d}\upsilon_2' \int_{\upsilon_2'}^{1} \mathrm{d}\upsilon_1 \sqrt{1 - \left(\frac{1-w}{\cos(\pi\upsilon_2'/2)}\right)^2} \approx$$

$$(2\pi)^2 \frac{2}{w} \int_0^{V_{\mathrm{u}}} \mathrm{d}\upsilon_2' \int_{\upsilon_2'}^{1} \mathrm{d}\upsilon_1 \sqrt{1 - (1-w)^2 (1 + \pi^2 \upsilon_2'^2/8)^2} =$$

$$\frac{(2\pi)^2 \pi}{3} \frac{1-w}{w} \left\{ \left[\frac{4}{\pi^2} \frac{w(2-w)}{(1-w)^2}\right]^{3/2} - \right.$$

$$\left. \left[\frac{4}{\pi^2} \frac{w(2-w)}{(1-w)^2} - V_{\mathrm{u}}^2\right]^{3/2} \right\} = \frac{4\pi^3}{3} \frac{1-w}{w} [\xi^3 - (\xi^2 - V_{\mathrm{u}}^2)^{3/2}]$$

Under the condition $V_{\mathrm{u}} \approx 0$, we assume $w \approx 0$ and neglect higher order corrections in w and V_{u} where convenient. In section V we have shown $w \sim V_{\mathrm{u}}^2$. This is consistent with the $w \approx 0$ assumption. The parameter ξ is defined as:

$$\xi \equiv \sqrt{\frac{4}{\pi^2} \frac{w(2-w)}{(1-w)^2}}$$

The above result is what we used in eq V-I.

The second part of the correlation function is given by:

$$\langle \phi|\tilde{G}^{\mathrm{II}}|\phi\rangle =$$

$$\frac{(2\pi)^2}{w + w^2/(1-w)} \left\{ \int_{1-V_{\mathrm{u}}}^{1} \mathrm{d}\upsilon \left[\sqrt{1 - \left(\frac{1-w}{\sin(\pi\upsilon/2)}\right)^2} + \right.\right.$$

$$\left.\left. \left[1 - \sqrt{1 - \left(\frac{1-w}{\sin(\pi\upsilon/2)}\right)^2}\right] \left(\frac{w}{1-w}\right) \right] \right\}^2 \approx$$

$$\frac{(2\pi)^2}{w} \left[\int_{1-V_{\mathrm{u}}}^{1} \mathrm{d}\upsilon \sqrt{1 - \left(\frac{1-w}{\sin(\pi\upsilon/2)}\right)^2} \right]^2 \approx$$

$$\frac{(2\pi)^2}{w} \left[\frac{\pi}{2}(1-w) \int_0^{V_{\mathrm{u}}} \mathrm{d}\upsilon' \sqrt{\frac{4}{\pi^2} \frac{w(2-w)}{(1-w)^2} - \upsilon'^2} \right]^2 \approx$$

$$\frac{\pi^4 (1-w)^2}{w} \left[\frac{1}{2} V_{\mathrm{u}} \sqrt{\xi^2 - V_{\mathrm{u}}^2} + \frac{\xi^2}{2} \sin^{-1}\left(\frac{V_{\mathrm{u}}}{\xi}\right) \right]^2$$

The result is what we used in eq V-II.

Appendix D: Relation between the Free Energy and Response Function

Equation II-5 may be obtained equivalently by writing the free energy F of the system in Landau form,[24] expanding for small values of the order parameter $\phi(\mathbf{r})$:

$$F = \frac{1}{2} \int \mathrm{d}^3 r_1\, \mathrm{d}^3 r_2 \Big(\phi(\mathbf{r}_1)\, K(\mathbf{r}_1,\mathbf{r}_2)\, \phi(\mathbf{r}_2) -$$

$$\frac{\Lambda}{2}(\mathbf{r}_1)\, \delta(\mathbf{r}_1 - \mathbf{r}_2)\, \phi(\mathbf{r}_2) \Big) - \int \mathrm{d}^3\mathbf{r}\, \mu(\mathbf{r})\, \phi(\mathbf{r}) + O(\phi^4)$$

The kernel K can be expressed in terms of its eigenvalues η_n and eigenfunctions $\phi_n(\mathbf{r})$. These eigenfunctions can be taken to be orthonormal, since K is symmetric. An arbitrary field $\phi(\mathbf{r})$ can also be expressed as $\phi(\mathbf{r}) = \sum_n f_n \phi_n(\mathbf{r})$. Likewise, the arbitrary external field $\mu(\mathbf{r})$ can be expressed as $\mu(\mathbf{r}) = \sum_n m_n \phi_n(\mathbf{r})$. In terms of the eigenamplitudes f_n and m_n, the free energy takes the simple form

$$F = \frac{1}{2} \sum_n f_n^2 \left(\eta_n - \frac{\Lambda}{2} \right) - f_n m_n$$

Each eigenmode n is independent of the others. The chemical-potential amplitude m_n may be written $m_n = \int \mathrm{d}^3 r\, \mu(\mathbf{r})\, \phi_n(\mathbf{r}) \equiv \langle \mu|\phi_n \rangle$, since the ϕ_n are orthonormal. We may now find the expectation value of the amplitude ϕ_n by minimizing F: $f_n = m_n/(\eta_n - {}^1/_2\Lambda)$. From these amplitudes, the induced $\phi(\mathbf{r})$ be reconstituted:

$$\langle \phi(\mathbf{r}) \rangle = \sum_n \frac{\langle \mu|\phi_n \rangle}{\left(\eta_n - \frac{1}{2}\Lambda \right)} \phi_n(\mathbf{r})$$

This is the exact form as eq II-5, identifying $\epsilon_{\Lambda n} = \eta_n - {}^1/_2\Lambda$. We conclude that (1) the eigenfunctions of F are the same as those of the response function G_Λ and (2) the eigenvalues η_n of F are the inverse of those of G_0: $\eta_n = 1/\epsilon_n$.

A phase transition occurs when the uniform state with $\phi(\mathbf{r}) \equiv 0$ no longer gives the minimum F for $\mu = 0$. This happens when any of the eigenvalues $\eta_n - {}^1/_2\Lambda$ becomes negative. For then any small $\phi(\mathbf{r}) = \delta\phi_n(\mathbf{r})$ decreases as $F = {}^1/_2(\eta_n - {}^1/_2\Lambda)\delta^2$.

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