Correlations in Grafted Polymer Layers

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ABSTRACT: We discuss compositional fluctuations in densely end-grafted polymers when two species of chains are present. When the two species are identical except for labeling, we relate the two-point spatial correlation function of local composition to density–density correlations within a *single* chain and calculate it under melt and solvent-swollen conditions. We deduce structure factors that could be observed in scattering from a layer composed of two chain species that differ only in their coupling to the scatterers. We generalize these results to describe compositional fluctuations when the two species have a nonzero free energy of mixing. These fluctuations diverge at a critical molecular weight. We analyze the divergence to corroborate the recently predicted phase transition to a "rippled" phase.

I. Introduction

Long polymers grafted to a surface are strongly perturbed from their ideal Gaussian coil state. As the molecular weight is increased, excluded-volume interactions between the chains force the chains to stretch. This picture of grafted polymer layers was first discussed by de Gennes and Alexander[1,2] and later was elaborated by Semenov[3] and Milner, Witten, and Cates.[4] The central approximation adopted by these authors has been to ignore conformational fluctuations about the most likely conformations of the chains: we will refer to this throughout this paper as the "classical" approximation.

Fluctuations about the most likely conformations are small (of order of the free-chain radius of gyration) and, as the chain length is taken to infinity, become arbitrarily less than the typical distance that a chain is extended (the layer height). Single-point averages, such as the monomer density, the thermodynamical pressure, or the density of free ends, are well described by the classical calculations. Recently, the classical picture has been used to study the layer boundaries,[5] the effect of chain length polydispersity,[6] and the effect of curving the grafting surface.[7] However, these classical studies can say nothing about correlations at scales of less than the layer height. One should note that, in directions parallel to the grafting plane, the layer is structureless at these scales. The correlation length for in-plane fluctuations is roughly the free-chain radius.

The self-consistent stretching of grafted chains makes them behave fundamentally differently from simpler polymer liquids. The studies cited above make it clear that these layers show nonlocal interaction and forms of anisotropy with no counterpart in other physical systems. For this reason it is important to explore the basic properties of these layers in a systematic way, so as to identify the main ways in which their behavior is distinctive.

In studying a new material, it is important to know its temporal and spatial linear-response properties. Some basic time scales governing temporal response have been explored previously.[8,9] Our focus here is on static spatial response: the response of the local state of the layer to a local disturbance elsewhere. We expect some response properties to be dramatically affected by the grafted state. In this paper we discuss such a response property: the *compositional* response in a layer with two species of chains. As in any equilibrium system, this compositional response may be inferred from spontaneous thermal fluctuations. Understanding compositional response is central to the study of polymer liquids for two reasons. First, compositional fluctuations are directly measured in scattering experiments.[10] Second, this response controls the incipient phase separation when the two species are incompatible.[10–13]

In what follows we develop a systematic theory of two-point monomer–monomer correlations in grafted polymer layers. Our theory uses the well-established "random-phase approximation" (RPA),[14,15] valid generally for strongly interpenetrating polymer systems.[12–14] We extend this theory to account for the constraints of the grafted layer. As in simpler systems, we find that the spatial fluctuations in composition are essentially the fluctuations of monomer density within an arbitrary single chain. The stretching of grafted chains introduces a large anisotropy in these correlations: the range of the response along the stretch direction is indefinitely greater than that in lateral directions for long grafted chains. These lateral correlations require a treatment of the stretched chains at a more subtle level than the usual classical approximation. These give unexpected features to the response function that go beyond mere anisotropy. Since these fluctuations are most directly observable through scattering, we present the compositional scattering function for polymer layers in the melt and the solvent-swollen regimes.

Because of the disparity between the entropy and mixing energy per chain, segregation is inevitable for bulk mixtures of long polymers.[14] Halperin has shown that the same mechanism acts in end-constrained layers and micelles when the chains are free to migrate laterally.[16] Recently[17–19] we have shown that, even when the chains are unable to migrate laterally, microphase separation occurs almost as readily as in the case when the chains are free to migrate. In this case the microphase separation takes a distinctive form. Of course, any tendency to phase separate also influences the spatial correlation and response functions of the layer. As in ordinary polymer blends there is a simple matrix equation giving the interacting system correlations, in terms of the noninteracting correlations; we derive it in section III. As the demixing interaction strength is increased to the phase-transition point, the compositional fluctuations diverge. By examining the correlation function at this divergence, we recover our previous results for the microphase-transition properties.[17]

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II. Grafted Polymer Layers in the Strong Stretching Limit

We consider identical flexible polymers with one end grafted to a flat surface. The surface contains σ chains per unit area. In the incompressible melt state, each chain displaces a volume V, which is proportional to the chain chemical length. Under melt conditions, the thickness of the layer is simply $h = V\sigma$.

To extend a section of chain of volume Δv costs an elastic free energy $K\Delta v$, where K is proportional to the extension squared $(\Delta \mathbf{r})^2$

$$K = kT\frac{a}{2}\left(\frac{\Delta \mathbf{r}}{\Delta v}\right)^2 \tag{1}$$

where the "packing length" a depends on the chemical makeup of the chains and is on the order of 10 Å. In the ungrafted melt state, this section would have a mean-squared end-to-end distance of $3\Delta v/a$, and its mean elastic energy would be $3kT/2$. Henceforth, energy will be expressed in units of kT.

The section Δv also contains (free) energy, owing to its interactions with neighboring chains: work is required to insert such a section into the grafted layer at height z, as chains must be displaced and stretched. This additional elastic energy is of the form $p(z)\ \Delta v$. Thus, there is a pressure $p(z)$ that forces a chain to assume a stretched state.

Labeling a point on a chain by the volume of chain v between that point and the grafted end, we express a conformation as a space curve $\mathbf{r}(v)$. The free energy functional for a chain is an Edwards model for a polymer in an external field[15]

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

from which the single-chain partition function is obtained by functional integration:[15]

$$Z_1(\mathbf{r}_0,\mathbf{r}_V) = \int \mathcal{D}\mathbf{r}(v)\, \exp(-s[\mathbf{r}]) \tag{3}$$

The functional integral $\int \mathcal{D}\mathbf{r}$ over polymer configurations must be carried out subject to a constraint on the free end location $\mathbf{r}(V) = \mathbf{r}_V$ and also with the grafted end fixed as $\mathbf{r}(0) = \mathbf{r}_0$, where $\mathbf{r}_0$ is a particular grafting point on the $z = 0$ plane. The free energy of the entire system is obtained by summing Z_1 over positions $\mathbf{r}_V$ of the free end and then summing the resulting single-chain free energies (under strong-overlap conditions, there are no chain–chain correlations):

$$\log Z = \sigma \int \mathrm{d}^2 r_0 \log \left[\int \mathrm{d}^3 r_V\, Z_1(\mathbf{r}_0,\mathbf{r}_V)\right] \tag{4}$$

In the limit of long chains ($Va\sigma^2 \gg 1$) under melt conditions, the chains extend over distances of order $h = \sigma V$, which are much larger than their ideal radius of order $(V/a)^{1/2}$ (we presume that h is much less than the maximum extension of the chains). Any chain thus fluctuates only narrowly about that path $\mathbf{r}(v)$, which minimizes the free energy functional (eq 2). This optimal path is of the form $\mathbf{r}(v) = \hat{\mathbf{z}} z(v) + \mathbf{r}_0$ (where $\hat{\mathbf{z}}$ is the unit vector along the z-axis) and is the solution to the Euler–Lagrange equation

$$a\frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}v^2} = \hat{\mathbf{z}}\frac{\mathrm{d}p}{\mathrm{d}z} \tag{5}$$

subject to the boundary conditions $z(V) = z_V$ and $z(0) = 0$. We also know that $\mathrm{d}\mathbf{r}/\mathrm{d}v(V) = 0$ for any chain since there are no forces acting on the free ends. This conformation is precisely analogous to the trajectory of a Newtonian particle released from height z_V arriving at the grafting surface ($z = 0$) after a "time" V (to obtain this analogy precisely, define time $t = V - v$). The operation of replacing the functional integral (eq 3) with a saddle-point contribution satisfying eq 5 is exact in the $V \to \infty$ limit: we shall refer to this limit as classical or "strong-stretching".

The hypothesis that there are free ends distributed throughout the layer allows us to conclude the form of the potential, since it must be a potential in which a particle released at rest falls to the ground in a fixed time V. The potential must be parabolic[4,5]

$$p(z) = P[1 - (z/h)^2] + \mathcal{O}(V^{-1}) \tag{6}$$

where the pressure at the grafting surface is $P = \pi^2 a h^2/8V^2$. The trajectory of a chain with the free end at height z_V is explicitly

$$z(v;z_V) = z_V \sin(\pi v/2V) \tag{7}$$

Once the trajectories are determined, we must specify the distribution of free ends per unit area per unit height $\mathrm{d}\sigma/\mathrm{d}z$. This distribution can be obtained by inversion of the integral equation that determines the melt volume fraction ϕ at a height z

$$\phi(z) = \int_z^h \mathrm{d}z_V \left(\frac{\mathrm{d}v}{\mathrm{d}z}\right)_{z_V} \frac{\mathrm{d}\sigma}{\mathrm{d}z_V} \tag{8}$$

where $(\mathrm{d}v/\mathrm{d}z)_{z_V}$ is the chain volume per unit height contributed at z by a chain with the free end at height z_V. In the case of the melt layer, for $z < h$, $\phi = 1$, which leads to an end distribution

$$\frac{\mathrm{d}\sigma}{\mathrm{d}z} = \frac{\sigma}{h^2}\frac{z}{[1 - (z/h)^2]^{1/2}} \tag{9}$$

In the case of a layer swollen by a marginal solvent, the action is again given by eq 2, where the potential $p(z)$ is again the free energy required to insert a unit volume of chain into the layer at z (because the layer is no longer incompressible as in the melt case, p should not be identified as the pressure). The hypothesis that free ends are found throughout the layer and the resultant equal-time constraint follow exactly as in the melt case, leading us to conclude that $p(z)$ has exactly the form eq 6 and that the conformations are again given by eq 7.

Under marginal solvent conditions, the monomer osmotic pressure behaves as $\Pi = \alpha^{-1}\phi^2$, where α is a constitutive constant with the dimensions of a volume.[4,7] The osmotic pressure Π is the work required to insert a unit volume of chain per *total volume*; thus, the work $p(z)$ required to insert a unit volume of chain is linearly related to the polymer volume fraction ϕ by $\phi(z) = \alpha p(z)$. Since the form of p is known, we can compute the ends per unit height for the layer in the solvent:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}z} = \frac{3\sigma z}{h^2}[1 - (z/h)^2]^{1/2} \tag{10}$$

In the solvent-swollen case, the height of the layer can be determined to be $h = \sigma V/(\pi^2 a\sigma^2\alpha/12)^{1/3}$.

We note that the value of the single-chain action (eq 2) is independent of the free-end height z_V when computed using the parabolic $p(z)$; however, by the definition of the chain partition function (eq 3), we note that $\exp[-s(z_V)]$ should be proportional to the probability of the chain end being at z_V, i.e., proportional to $\mathrm{d}\sigma/\mathrm{d}z_V$. This apparent paradox is resolved by realizing that there are corrections of order V^{-1} to the potential (eq 6) that do not affect the trajectories to lowest order but that do affect the distribution of ends.[5]

III. Two-Point Correlation Function

In a grafted layer containing a single species of chain, spatial fluctuations are strongly suppressed. Under melt conditions, any spatial nonuniformity in monomer density is confined to the monomeric length scale. The spatial correlations are like those found generally in dense liquids of small compressibility. The range of the correlations is of the order of the monomer size, and thus they are insensitive to the large-scale structure of the polymers. The same is true in semidilute solution: density fluctuations are strongly suppressed beyond distances far smaller than the size of the chains. In a grafted layer as well, the overall monomer density cannot fluctuate appreciably: the monomer density profile is clamped by self-consistency requirements outlined in the last section. However, in a blend of two components, there is an additional degree of freedom—the local composition—which may fluctuate freely without changing the overall density from its prescribed profile. It is these compositional correlations that we treat below.

We consider a polymer layer composed of two species of chains, denoted A and B, with identical chain volumes V and packing lengths a. The A and B grafts are presumed to be evenly mixed at the surface, with graft fractions f_{A} and f_{B} ($f_{\mathrm{A}} + f_{\mathrm{B}} = 1$), respectively. Because the two types of chains displace the same volumes, the volume fractions of A and B chains are also f_{A} and f_{B}. For the present, we presume that the A–A, B–B, and A–B monomer–monomer interactions are all identical (i.e., there is no tendency for a bulk A–B blend to demix, even for long chains).

We suppose the existence of a spatially varying externally imposed chemical potential $\mu(\mathbf{r})$ (here a factor of $1/kT$ has been absorbed into the definition of μ), which linearly couples to the A–B concentration difference. The chemical potential leads to an addition to the total free energy functional (the sum of single-chain free energies $s[\mathbf{r}_i]$ of the form eq 2)

$$S_{\mathrm{ext}} = -\int \mathrm{d}^3r\, \mu(\mathbf{r})\, [\phi_{\mathrm{A}}(\mathbf{r}) - \phi_{\mathrm{B}}(\mathbf{r})] \tag{11}$$

where $\phi_{\mathrm{A}}(\mathbf{r})$ and $\phi_{\mathrm{B}}(\mathbf{r})$ are functions of the chain conformations that measure the local volume fractions of A and B monomers, respectively. The partition function for the grafted layer is thus

$$Z[\mu] = \Big(\prod_{i\in \mathrm{A}} \int \mathrm{d}^3r_{Vi} \int \mathcal{D}\mathbf{r}_i e^{-s[\mathbf{r}_i]}\Big) \times \Big(\prod_{j\in \mathrm{B}} \int \mathrm{d}^3r_{Vj} \int \mathcal{D}\mathbf{r}_j e^{-s[\mathbf{r}_j]}\Big) e^{-S_{\mathrm{ext}}[\{\mathbf{r}\}]} \tag{12}$$

where the indices $i \in \mathrm{A}$ and $j \in \mathrm{B}$ refer to individual chains of specific types and grafting locations $\{\mathbf{r}_{0i}\}$.

The cumulant correlation functions of the monomer volume fraction difference are given as successive functional derivatives of the free energy log Z with respect to μ:

$$G^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) = \left.\frac{\delta^n \log Z(\mu)}{\delta\mu(\mathbf{r}_1)\ldots\delta\mu(\mathbf{r}_n)}\right|_{\mu=0} \tag{13}$$

For any equilibrium system these correlation functions can be expressed in terms of the A–B volume fraction difference $\phi \equiv \phi_{\mathrm{A}} - \phi_{\mathrm{B}}$

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

$$G^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = \langle \phi(\mathbf{r}_1)\, \phi(\mathbf{r}_2) \rangle - \langle \phi(\mathbf{r}_1) \rangle \langle \phi(\mathbf{r}_2) \rangle \tag{14}$$

and so on. For the case of the melt, the one-point function is just a constant: $G^{(1)}(\mathbf{r}) = f_{\mathrm{A}} - f_{\mathrm{B}}$, while in solvent, it is a function of height: $G^{(1)}(\mathbf{r}) = (f_{\mathrm{A}} - f_{\mathrm{B}})\alpha p(z)$. We note also that the two-point function, which we have interpreted as a correlation function for spontaneous fluctuations, may be thought of as the linear response function describing the change in ϕ when a small potential μ is placed on the system

$$G^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = \delta\langle \phi(\mathbf{r}_1) \rangle / \delta\mu(\mathbf{r}_2) \tag{15}$$

or equivalently

$$\langle \phi(\mathbf{r}_1) \rangle = \int \mathrm{d}^3r_2\, G^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\, \mu(\mathbf{r}_2) + \mathcal{O}(\mu^2) \tag{16}$$

We turn now to precisely specifying the volume fraction functions in terms of the individual polymer conformations in the symmetric case $f_{\mathrm{A}} = f_{\mathrm{B}} = {}^1/_2$. The A volume fraction is the sum of the ith chain local volume fraction functions ψ_i:

$$\phi_{\mathrm{A}}(\mathbf{r}) = \sum_{i\in \mathrm{A}} \psi_i(\mathbf{r}) \tag{17}$$

The local volume fraction for the ith chain is in turn related to the chain contour $\mathbf{r}_i(v)$:

$$\psi_i(\mathbf{r}) = \int_0^V \mathrm{d}v\, \delta^3(\mathbf{r} - \mathbf{r}_i(v)) \tag{18}$$

We note that the sum over A chains may be replaced by the A total grafting density times an integral over grafting positions, as was done for all the chains in eq 4. The function ϕ_{B} is obtained by replacing A with B in eq 17.

We may thus extend the single-chain partition function (eq 3) to be that for an A chain in the external field μ:

$$Z_1(\mathbf{r}_{0i},\mathbf{r}_{Vi};\mu) = \int \mathcal{D}\mathbf{r}_i \exp\{-s[\mathbf{r}_i] + \int \mathrm{d}^3r\, \mu(\mathbf{r})\, \psi_i(\mathbf{r})\} \tag{19}$$

Since the chains are thus statistically independent, we may rewrite the layer partition function (eq 12) as

$$\log Z(\mu) = \sigma \int \mathrm{d}^2r_0 \Big(f_{\mathrm{A}} \log \big[\int \mathrm{d}^3r_V\, Z_1(\mathbf{r}_0,\mathbf{r}_V;\mu)\big] + f_{\mathrm{B}} \log \big[\int \mathrm{d}^3r_V\, Z_1(\mathbf{r}_0,\mathbf{r}_V;-\mu)\big]\Big) \tag{20}$$

The A and B volume fractions in the correlation functions (eq 15) may now be expressed as sums of single-chain volume fraction functions as in eq 17. The A and B volume fractions are sums of statistically independent single-chain volume fractions, allowing us to write

$$\langle \phi_{\mathrm{A}}(\mathbf{r}_1)\, \phi_{\mathrm{B}}(\mathbf{r}_2) \rangle = \langle \phi_{\mathrm{A}}(\mathbf{r}_1) \rangle \langle \phi_{\mathrm{B}}(\mathbf{r}_2) \rangle \tag{21}$$

The two-point function is thus

$$G^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = \sum_{i,j\in \mathrm{A}} (\langle \psi_i(\mathbf{r}_1)\, \psi_j(\mathbf{r}_2) \rangle - \langle \psi_i(\mathbf{r}_1) \rangle \langle \psi_j(\mathbf{r}_2) \rangle) + (\mathrm{A} \leftrightarrow \mathrm{B}) \tag{22}$$

The terms with $i \neq j$ in this sum vanish, since, again, the chains are statistically independent. Since the ψ functions are the same for A or B chains, we can combine the A and B contributions of eq 22 to obtain

$$G^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = \sum_i (\langle \psi_i(\mathbf{r}_1)\, \psi_i(\mathbf{r}_2) \rangle - \langle \psi_i(\mathbf{r}_1) \rangle \langle \psi_i(\mathbf{r}_2) \rangle) \tag{23}$$

where the sum is over *all chains*.

Up to this point we have treated the response function $G^{(2)}$ as though the grafted chains did not interact but were statistically independent; interactions affect each chain only through the pressure field p. According to our hypotheses of incompressibility and validity of a mean-field (RPA) approach to interactions, p must be adjusted to maintain the proper total volume fraction $\Phi(\mathbf{r}) = \phi_{\mathrm{A}}(\mathbf{r})$

$+ \phi_B(\mathbf{r})$ (for the melt, $\Phi(\mathbf{r}) = 1$, while in the solvent case, $\Phi(\mathbf{r}) = \alpha p(z)$). The external field μ perturbs Φ by an amount of order μ. This perturbation is offset by a change in $p(\mathbf{r})$ (that we will call $\nu(\mathbf{r})$) of order μ; in turn, Φ is changed by an amount of order μ. Thus, the change in $G^{(2)}$ is of order unity.

Above we have worked out that the response of ϕ of μ is the two-point function $G^{(2)}$. The additional field ν may be included in our model by augmenting the expression eq 11 for S_{ext}:

$$S_{\text{ext}} = -\int \mathrm{d}^3 r\, [\mu(\mathbf{r})\, \phi(\mathbf{r}) - \nu(\mathbf{r})\, \Phi(\mathbf{r})] \tag{24}$$

The change in ϕ and Φ due to μ and ν may be worked out as above and may be expressed as the linear response equations:

$$\delta\langle\phi\rangle = G^{(2)}\mu - (f_A - f_B)G^{(2)}\nu \tag{25}$$

$$\delta\langle\Phi\rangle = (f_A - f_B)G^{(2)}\mu - G^{(2)}\nu = 0$$

Here we have used a matrix notation to simplify the equations; $G^{(2)}\mu$ replaces $\int \mathrm{d}^3 r'\, G^{(2)}(\mathbf{r},\mathbf{r}')\, \mu(\mathbf{r}')$. The condition that the response of Φ vanishes determines the field ν

$$\nu = (f_A - f_B)\mu \tag{26}$$

which when substituted back into the response equation for ϕ, yields

$$\delta\langle\phi\rangle = [1 - (f_A - f_B)^2]G^{(2)}\mu \tag{27}$$

We may read off the corrected two-point correlation of ϕ:

$$G^{*(2)} = [1 - (f_A - f_B)^2]G^{(2)} \tag{28}$$

We see that the RPA two-point correlation of ϕ differs from the $G^{(2)}$ derived above by only an overall constant factor of $1 - (f_A - f_B)^2$. In the fully symmetric case where $f_A = f_B = {}^1/_2$, there is no RPA correction to the two-point correlation of ϕ. We note that our approach is precisely analogous to the computation of correlation functions in the simpler case of a bulk polymer melt, where again strong interpenetration conditions lead to strong screening of correlations and allow an independent chain model to be adopted.[14]

A. Classical Limit. We may easily compute the two-point function in the "classical limit" where we ignore any fluctuations of chain conformations about the saddle-point trajectory. Since the fluctuations will be excursions of distances of order $(V/a)^{1/2}$ and the layer height is of order $\sigma^{\delta}V$ ($\delta = 1$ for melt, $^1/_3$ for marginal solvent), we expect nontrivial correlations in this limit. We expect the classical correlations to be relevant if we coarse-grain over distances larger than $(V/a)^{1/2}$ or look at scattering at wave numbers less than order $(a/V)^{1/2}$.

We consider first the expectation value of the volume fraction for a chain with grafting point $\mathbf{r}_0 = (x_0, y_0, 0)$, which we denote as $\langle\psi_{\mathbf{r}_0}(\mathbf{x})\rangle$. If the free end of the chain is found at a height z_V, we know that the chain volume contributed per volume element at an arbitrary point $\mathbf{r} = (x, y, z)$ is

$$\delta(x - x_0)\, \delta(y - y_0) \left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_{z_V} \Theta(z_V - z) \tag{29}$$

The inverse velocity follows directly from eq 7

$$\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_{z_V} = \frac{2V}{\pi}(z_V^{\,2} - z^2)^{-1/2} \tag{30}$$

The probability of the chain having a particular z_V is just the free-end distribution normalized so that its integral is unity. This allows us to write

$$\langle\psi_{\mathbf{r}_0}(\mathbf{r})\rangle = \int_z^h \mathrm{d}z_V \frac{1}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}z_V}\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_{z_V} \delta(x - x_0)\, \delta(y - y_0) \tag{31}$$

We can compute the two-chain density expectation value $\langle\psi_{\mathbf{r}_0}(\mathbf{r}_1)\, \psi_{\mathbf{r}_0}(\mathbf{r}_2)\rangle$ in a similar way. A chain with the free end at a height z_V contributes volume fractions at the two heights z_1 and z_2 in proportion to the product of two factors of the form eq 29 evaluated at the two test points $\mathbf{r}_1$ and $\mathbf{r}_2$. This product must then be integrated over end positions, weighted by the free-end distribution

$$\langle\psi_{\mathbf{r}_0}(\mathbf{r}_1)\, \psi_{\mathbf{r}_0}(\mathbf{r}_2)\rangle = \int_{z_>}^h \mathrm{d}z_V \frac{1}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}z_V}\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z_1}\right)_{z_V} \delta(x_1 - x_0)\, \delta(y_1 - y_0) \left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z_2}\right)_{z_V} \delta(x_2 - x_0)\, \delta(y_2 - y_0) \tag{32}$$

where $z_> = \max\,\{z_1, z_2\}$. Finally, we add up the contributions of all of the grafted chains to obtain the two-point function:

$$\begin{aligned} G^{(2)}(\mathbf{r}_1,\mathbf{r}_2) &= \\ &\sigma \int \mathrm{d}^2 r_0\, (\langle\psi_{\mathbf{r}_0}(\mathbf{r}_1)\, \psi_{\mathbf{r}_0}(\mathbf{r}_2)\rangle - \langle\psi_{\mathbf{r}_0}(\mathbf{r}_1)\rangle\langle\psi_{\mathbf{r}_0}(\mathbf{r}_2)\rangle) = \\ &\delta(x_1 - x_2)\, \delta(y_1 - y_2) \left[\int_{z_>}^h \mathrm{d}z_V \frac{\mathrm{d}\sigma}{\mathrm{d}z_V}\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z_1}\right)_{z_V}\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z_2}\right)_{z_V} - \right. \\ &\left. \frac{1}{\sigma}\int_{z_1}^h \mathrm{d}z_V \frac{\mathrm{d}\sigma}{\mathrm{d}z_V}\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z_1}\right)_{z_V} \int_{z_2}^h \mathrm{d}z'_V \frac{\mathrm{d}\sigma}{\mathrm{d}z'_V}\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z_2}\right)_{z'_V} \right] \end{aligned} \tag{33}$$

B. Addition of Transverse Fluctuations. We now turn to the problem of taking into account fluctuations about the classical trajectories. The statistical weight (often called the Edwards propagator) of a segment of chain from υ_0 to υ_1 to travel from position $\mathbf{r}_0$ to $\mathbf{r}_1$ in the presence of a field $p(z)$ is given by the functional integral[15]

$$\mathcal{G}(\mathbf{r}_1,\mathbf{r}_0;\upsilon_1,\upsilon_0) = \int \frac{\mathcal{D}\mathbf{r}}{Z} \exp\left\{-\int_{\upsilon_0}^{\upsilon_1} \mathrm{d}\upsilon \left[\frac{a}{2}\left(\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}\upsilon}\right)^2 + p(z)\right]\right\} \tag{34}$$

where the integration is constrained so that $\mathbf{r}(\upsilon_0) = \mathbf{r}_0$ and $\mathbf{r}(\upsilon_1) = \mathbf{r}_1$ and where the normalization factor Z is defined by the condition

$$\int \mathrm{d}^3 r_1\, \mathcal{G}(\mathbf{r}_1,\mathbf{r}_0,\upsilon_1,\upsilon_0)|_{p(z)=0} = 1 \tag{35}$$

The weight $\mathcal{G}$ is the product of independent factors governing the statistics of the $x - y$ and z components of the chain contour

$$\mathcal{G}(\mathbf{r}_1,\mathbf{r}_0;\upsilon_1,\upsilon_0) = \gamma_z(z_1,z_0;\upsilon_1,\upsilon_0)\, \gamma_{xy}(\bar{\mathbf{x}}_1,\bar{\mathbf{x}}_0;\upsilon_1,\upsilon_0) \tag{36}$$

where the notation $\bar{\mathbf{x}}$ refers to the two-dimensional vector consisting of the x and y components of $\mathbf{r}$. The z and $x - y$ propagators are

$$\gamma_z(z_1,z_0;\upsilon_1,\upsilon_0) = \int \frac{\mathcal{D}z}{\zeta_z} \exp\left\{-\int_{\upsilon_0}^{\upsilon_1} \mathrm{d}\upsilon \left[\frac{a}{2}\left(\frac{\mathrm{d}z}{\mathrm{d}\upsilon}\right)^2 + p(z)\right]\right\}$$

$$\gamma_{xy}(\bar{\mathbf{x}}_1,\bar{\mathbf{x}}_0;\upsilon_1,\upsilon_0) = \int \frac{\mathcal{D}\bar{\mathbf{x}}}{\zeta_{xy}} \exp\left\{-\int_{\upsilon_0}^{\upsilon_1} \mathrm{d}\upsilon \left[\frac{a}{2}\left(\frac{\mathrm{d}\bar{\mathbf{x}}}{\mathrm{d}\upsilon}\right)^2\right]\right\} \tag{37}$$

where the normalizations ζ_z and ζ_{xy} are defined to be

$$\int_0^h \mathrm{d}z_1\, \gamma_z(z_1,z_0;\upsilon_1,\upsilon_0)|_{p(z)=0} = 1$$

$$\int \mathrm{d}^2 x_1\, \gamma_{xy}(\bar{\mathbf{x}}_1,\bar{\mathbf{x}}_0;\upsilon_1,\upsilon_0) = 1 \tag{38}$$

The $x - y$ propagator is precisely that of a free two-dimensional Gaussian chain segment:

$$\gamma_{xy}(\bar{\mathbf{x}}_1,\bar{\mathbf{x}}_0;\upsilon_1,\upsilon_0) = \frac{a}{2\pi(\upsilon_1 - \upsilon_0)} \exp\left\{-\frac{a}{2}\frac{(\bar{\mathbf{x}}_1 - \bar{\mathbf{x}}_0)^2}{\upsilon_1 - \upsilon_0}\right\}\Theta(\upsilon_1 - \upsilon_0) \tag{39}$$

We turn now to the problem of determining the z-propagator. We wish to examine an expansion about the classical trajectory. For a segment extended from $z(\upsilon_0) = z_0$ to $z(\upsilon_1) = z_1$, there is a unique classical conformation given by the solution to the equation $a\mathrm{d}^2z^*/\mathrm{d}\upsilon^2 = \mathrm{d}p/\mathrm{d}z$. The action of eq 34 may be expanded about this trajectory

$$-\int_{\upsilon_0}^{\upsilon_1}\mathrm{d}\upsilon \left[\frac{a}{2}\left(\frac{\mathrm{d}z^*}{\mathrm{d}\upsilon}\right)^2 + p(z^*) + a\frac{\mathrm{d}z^*}{\mathrm{d}\upsilon}\frac{\mathrm{d}q}{\mathrm{d}\upsilon} + q\frac{\mathrm{d}p(z^*)}{\mathrm{d}z} + \frac{a}{2}\left(\frac{\mathrm{d}q}{\mathrm{d}\upsilon}\right)^2 + \frac{1}{2}q^2\frac{\mathrm{d}^2p(z^*)}{\mathrm{d}z^2} + \mathcal{O}(q^3\mathrm{d}^3p/\mathrm{d}z^3)\right] \tag{40}$$

where $q = z - z^*$ is the difference between the actual and most likely trajectory. We note that $q(\upsilon_0) = q(\upsilon_1) = 0$. The first two terms comprise the q-independent classical action, which we will be denoted $-s^*(z_1,z_0;\upsilon_1,\upsilon_0)$. The next term may be integrated by parts and when added to the term from the expansion of the pressure linear in q, vanishes (because z^* is a solution to the Euler–Lagrange equation). We may thus rewrite the action as

$$-s^*(z_1,z_0;\upsilon_1,\upsilon_0) - \int_{\upsilon_0}^{\upsilon_1}\mathrm{d}\upsilon \left[\frac{a}{2}\left(\frac{\mathrm{d}q}{\mathrm{d}\upsilon}\right)^2 + \frac{1}{2}q^2\frac{\mathrm{d}^2p(z^*)}{\mathrm{d}z^2}\right] + \mathcal{O}(q^3\mathrm{d}^3p/\mathrm{d}z^3) \tag{41}$$

We now with to examine the scaling of these various terms with the chain length V. The classical action s^* is of order V for any finite fraction of the chain. If the fluctuations about this saddle point are to be small, the correction terms should be of lower order than V. We consider the final integral. The free fluctuations of q (which for a segment of length ΔV are of order $(\Delta V/a)^{1/2}$) give rise to a typical scale for $(\mathrm{d}q/\mathrm{d}\upsilon)^2$ of ΔV^{-1}, which when integrated over the chain, are of order 1. These fluctuations give rise to a contribution from the q^2 term also of order 1; the higher order q^n terms from the Taylor expansion of the pressure give rise to contributions of order $V^{1-n/2}$. We conclude that the diffusive fluctuations of the z-positions of monomers do not significantly change the propagator over any finite fraction of stretched chain and that they may be ignored.

In this paper, we will only use strings of propagators that cover an entire chain. Thus our attention falls on the string of γ_z's:

$$\gamma_z(z_V,z_n;V,\upsilon_n)\ \gamma_z(z_n,z_{n-1};\upsilon_n,\upsilon_{n-1})...\gamma_z(z_1,0;\upsilon_1,0) \tag{42}$$

This quantity is proportional to the statistical weight for a chain with the free end at height z_V to pass through heights z_i at chain positions υ_i. This function is of course maximized (for fixed z_V and $\{\upsilon_i\}$) by $z_i = z(\upsilon_i;z_V) = z_V \sin(\pi\upsilon_i/2V)$, when it takes on the value of the exponential of the classical action for this trajectory. If we change one of the z_i's away from $z(\upsilon_i,z_V)$ by an amount δz, the action increases by an amount of order $s^*(\delta z)^2/h^2 \approx (\delta z)^2/V$. Evidently the expression eq 42 falls off from its maximum on a scale $\delta z \approx V^{1/2}$. This narrow Gaussian dispersion may be ignored compared to the classical motion. We may thus write eq 42 as

$$e^{-s^*(z_V,0;V,0)}\delta(z_n - z[\upsilon_n,z_V])...\delta(z_1 - z[\upsilon_1,z_V]) \tag{43}$$

This formula is the statement that, on the scale of the layer height, there is a unique relation between position υ along a chain and height z once the free-end position z_V is specified; this height is given by the classical trajectory $z(\upsilon;z_V)$.

Given this result, we may compute the volume fraction at $\mathbf{r}$ contributed by a chain grafted at $\mathbf{r}_0$:

$$\begin{aligned}\langle\psi_{\mathbf{r}_0}(\mathbf{r})\rangle &= \left[\int \mathrm{d}^3r_V\int_0^V \mathrm{d}\upsilon\ \mathcal{G}(\mathbf{r}_V,\mathbf{r};V,\upsilon)\ \mathcal{G}(\mathbf{r},\mathbf{r}_0;\upsilon,0)\right]\Big/\left[\int \mathrm{d}^3r_V\ \mathcal{G}(\mathbf{r}_V,\mathbf{r}_0;V,0)\right] \\ &= \left[\int_0^h \mathrm{d}z_V\int_0^V \mathrm{d}\upsilon\ \gamma_z(z_V,z;V,\upsilon)\ \gamma_z(z,0;\upsilon,0) \times \int \mathrm{d}^2x_V\ \gamma_{xy}(\bar{\mathbf{x}}_V,\bar{\mathbf{x}};V,\upsilon)\ \gamma_{xy}(\bar{\mathbf{x}},\bar{\mathbf{x}}_0;\upsilon,0)\right]\Big/ \\ &\qquad \left[\int_0^h \mathrm{d}z_V\ \gamma_z(z_V,0;V,0)\int \mathrm{d}^2x_V\ \gamma_{xy}(\bar{\mathbf{x}}_V,\bar{\mathbf{x}}_0;V,0)\right]\end{aligned} \tag{44}$$

Here, the probability of a particular monomer υ being at a particular point $\mathbf{r}$ is calculated by using the segment propagator $\mathcal{G}$. This probability is integrated over all monomers to give the total volume fraction at $\mathbf{r}$. We note the relation between the classical action and the total free-end distribution:

$$\frac{e^{-s^*(z,0;V,0)}}{\int_0^h \mathrm{d}z'\ e^{-s^*(z',0;V,0)}} = \frac{1}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}z} \tag{45}$$

This, combined with the γ_{xy} sum rule (eq 39), allows us to write

$$\langle\psi_{\mathbf{r}_0}(\mathbf{r})\rangle = \int_z^h \frac{\mathrm{d}z_V}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}z_V}\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_{z_V}\gamma_{xy}(\bar{\mathbf{x}},\bar{\mathbf{x}}_0;\upsilon[z;z_V],0) \tag{46}$$

The two-point volume fraction of a chain grafted at $\mathbf{r}_0$ is similarly computed (we assume $z > z'$):

$$\begin{aligned}\langle\psi_{\mathbf{r}_0}(\mathbf{r})\ \psi_{\mathbf{r}_0}(\mathbf{r}')\rangle &= \left[\int \mathrm{d}^3r_V\int_0^V \mathrm{d}\upsilon\int_0^V \mathrm{d}\upsilon'\ \mathcal{G}(\mathbf{r}_V,\mathbf{r};V,\upsilon) \times \mathcal{G}(\mathbf{r},\mathbf{r}';\upsilon,\upsilon')\ \mathcal{G}(\mathbf{r}',\mathbf{r}_0;\upsilon',0)\right]\Big/\left[\int \mathrm{d}^3r_V\ \mathcal{G}(\mathbf{r}_V,\mathbf{r}_0;V,0)\right] \\ &= \int_z^h \frac{\mathrm{d}z_V}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}z_V}\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_{z_V}\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z'}\right)_{z_V}\gamma_{xy}(\bar{\mathbf{x}},\bar{\mathbf{x}}';\upsilon[z;z_V],\upsilon[z';z_V]) \times \gamma_{xy}(\bar{\mathbf{x}}',\bar{\mathbf{x}}_0;\upsilon[z';z_V],0)\end{aligned} \tag{47}$$

Note that a "time-ordering" of z occurs because the classical trajectory $z(\upsilon;z_V)$ is monotonic in υ. To convert the single-chain densities to the two-point monomer correlation function for the entire layer, we sum over the grafting positions:

$$G^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = \sigma\int \mathrm{d}^2r_0(\langle\psi_{\mathbf{r}_0}(\mathbf{r}_1)\ \psi_{\mathbf{r}_0}(\mathbf{r}_2)\rangle - \langle\psi_{\mathbf{r}_0}(\mathbf{r}_1)\rangle\langle\psi_{\mathbf{r}_0}(\mathbf{r}_2)\rangle) \tag{48}$$

The interpretation of these expressions for the one-point and two-point correlations is obvious. For a chain grafted at $\mathbf{r}_0$, we compute the probability of contributing monomer at $\mathbf{r}$ by propagating it from the grafting point to the observation point(s) and then to the free-end position $\mathbf{r}_V$. In the z-direction, we worry only about structure on the scale of h, the layer height. This allows us to use the classical trajectory to convert heights z to distances along the chain υ. The amount of monomer contributed per unit height at $\mathbf{r}$ by such a chain is given by its inverse velocity $\mathrm{d}\upsilon/\mathrm{d}z$. The probability of the chain fluctuating in the x–y plane is given by propagators for a free chain, since there are no inhomogeneities in the potential in the plane. An overall factor of the end density is required, and then we sum over all possible end positions. Finally, we sum up the contributions of all of the grafted chains. Generalization of these results to n-point expectations is straightforward.

To complete the calculation, it is useful to work in terms of Fourier transforms with respect to the two-dimensional x–y coordinate

$$\tilde{G}^{(2)}(\bar{\mathbf{k}}_1,\bar{\mathbf{k}}_2,z_1,z_2) = \int \mathrm{d}^2r_1\,\mathrm{d}^2r_2\, e^{i(\bar{\mathbf{k}}_1\cdot\bar{\mathbf{x}}_1+\bar{\mathbf{k}}_2\cdot\bar{\mathbf{x}}_2)}G^{(2)}(\mathbf{r}_1,\mathbf{r}_2) \quad (49)$$

Carrying out some Gaussian integrals leads to the two-point correlation function:

$$\tilde{G}^{(2)}(\bar{\mathbf{k}}_1,\bar{\mathbf{k}}_2,z_1,z_2) = (2\pi)^2\delta^2(\bar{\mathbf{k}}_1+\bar{\mathbf{k}}_2) \times \Bigg[\int_{\max\{z_1,z_2\}}^{h}\mathrm{d}z_V\frac{\mathrm{d}\sigma}{\mathrm{d}z_V}\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z_1}\right)_{z_V}\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z_2}\right)_{z_V} e^{-k_1^2|\upsilon(z_1;z_V)-\upsilon(z_2;z_V)|/2a} - \frac{1}{\sigma}\int_{z_1}^{h}\mathrm{d}z_V\frac{\mathrm{d}\sigma}{\mathrm{d}z_V}\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z_1}\right)_{z_V} e^{-k_1^2\upsilon(z_1;z_V)/2a} \times \int_{z_2}^{h}\mathrm{d}z'_V\frac{\mathrm{d}\sigma}{\mathrm{d}z'_V}\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z_2}\right)_{z'_V} e^{-k_2^2\upsilon(z_2;z'_V)/2a}\Bigg] \quad (50)$$

If we change variables $z \rightarrow z/h$, $\bar{\mathbf{x}} \rightarrow \bar{\mathbf{x}}/(V/a)^{1/2}$, $\bar{\mathbf{k}} \rightarrow \bar{\mathbf{k}}(V/a)^{1/2}$, and $\upsilon \rightarrow \upsilon/V$, thus measuring heights as fractions of the total layer height, $x - y$ distances in units on the order of the free radius of a chain, and distances along the chain in fractions of the total chain length, we can write the correlations in the form

$$\tilde{G}^{(2)}(\bar{\mathbf{k}}_1,\bar{\mathbf{k}}_2,z_1,z_2) = (2\pi)^2\delta^2(\bar{\mathbf{k}}_1+\bar{\mathbf{k}}_2)\,\frac{V}{a\sigma}\left(\frac{V\sigma}{h}\right)^2\tilde{\Gamma}(k_1,z_1,z_2) \quad (51)$$

where $\tilde{\Gamma}$ is the dimensionless function

$$\tilde{\Gamma}(k,z,z') = \int_{\max\{z,z'\}}^{1}\mathrm{d}z_V\,\frac{\mathrm{d}s}{\mathrm{d}z_V}\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_{z_V}\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z'}\right)_{z_V} e^{-k^2|\upsilon(z;z_V)-\upsilon(z';z_V)|/2} - \int_{z}^{1}\mathrm{d}z_V\,\frac{\mathrm{d}s}{\mathrm{d}z_V}\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z}\right)_{z_V} e^{-k^2\upsilon(z;z_V)/2} \times \int_{z'}^{1}\mathrm{d}z'_V\,\frac{\mathrm{d}s}{\mathrm{d}z'_V}\left(\frac{\mathrm{d}\upsilon}{\mathrm{d}z'}\right)_{z'_V} e^{-k^2\upsilon(z';z'_V)/2} \quad (52)$$

where now we have introduced dimensionless chain trajectories

$$\upsilon(z;z_V) \equiv \frac{2}{\pi}\sin^{-1} z/z_V \quad (53)$$

and dimensionless free-end distributions for the melt and solvent cases:

$$\left.\frac{\mathrm{d}s}{\mathrm{d}z}\right|_{\text{melt}} \equiv z(1 - z^2)^{-1/2}$$

$$\left.\frac{\mathrm{d}s}{\mathrm{d}z}\right|_{\text{solv}} \equiv 3z(1 - z^2)^{1/2} \quad (54)$$

We note that $\tilde{\Gamma}(k{=}0,z,z')$ is equal to the classical correlation function (eq 33) integrated over x_2 and y_2, i.e., that the z-dependent correlations at the scale of the layer thickness are consistent in the two cases.

The function $\tilde{\Gamma}$ is useful, since from it the real-space correlation function

$$\Gamma(|\bar{\mathbf{x}}|,z,z') = \int\frac{\mathrm{d}^2k}{(2\pi)^2}\, e^{-i\bar{\mathbf{k}}\cdot\bar{\mathbf{x}}}\tilde{\Gamma}(k,z,z') \quad (55)$$

or the scattering function

$$S(k,k_z) = \int_0^1\mathrm{d}z\int_0^1\mathrm{d}z'\, e^{ik_z(z-z')}\tilde{\Gamma}(k,z,z') \quad (56)$$

may be easily computed. The scattering function is particularly interesting since it is proportional to the radiation scattered from A–B fluctuations in the layer as a function of the momentum transfer k in the x–y plane and k_z in the z-direction.[20]

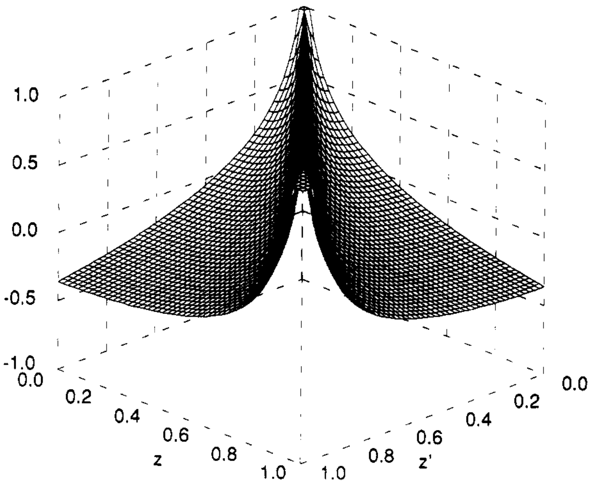

Figure 1. Height-height correlations $g(z,z')$ for the grafted melt layer in the classical limit. The heights z and z' are measured in units of the total layer height h. Note the logarithmic divergence for $z = z'$. The function is truncated at $g = 1$.

IV. Results for the Melt Layer

We now present explicit computations for the two-point correlations in a grafted polymer layer under melt conditions, following the formulation presented in section III. The simplest result is the classical limit of the correlation function (eq 33), where conformational fluctuations in the x–y plane are ignored. In this limit, the results of section II allow explicit calculation of the correlation function, which has the form of a product of x and y δ functions and a nontrivial function g of the z coordinates:

$$G^{(2)}(\mathbf{r},\mathbf{r}') = \frac{\delta(x-x')\,\delta(y-y')}{\sigma}g(z,z') \quad (57)$$

The normalization of the $x - y$ term reflects the fact that there is one chain per area σ^{-1}.

The function g for the melt is readily computed by inserting the contour function (eq 30) and the end distribution (eq 9) into the expression eq 33 and integrating:

$$g(z,z') = \frac{4}{\pi^2(1 - z_<^2)^{1/2}}F\left(\frac{1 - z_>^2}{1 - z_<^2}\right)^{1/2} - 1 \quad (58)$$

Here, $z_> = \max(z,z')$, $z_< = \min(z,z')$, $F(k) = \int_0^{\pi/2}\mathrm{d}\theta\,(1 - k^2\sin^2\theta)^{-1/2}$ is a complete elliptic integral, and all heights z are measured in units of the total layer height h (and are thus between 0 and 1). In Figure 1, we display the function $g(z,z')$. The heights z are measured in units of the total layer height h. The function is symmetric under the interchange of z and z' and is singular along the line $z = z'$. This logarithmic divergence reflects that if one monomer of a chain is at height z', it is almost certain that there are monomers of the same chain at z near to z'. If z is either above or below z', the correlations drop off in strength.

The three parts of Figure 2 show the full real-space correlation function $G^{(2)}(\mathbf{r},\mathbf{r}')$, following the calculation presented in section III.B. This function depends on z and z' and also on the in-plane radial coordinate $r = [(x - x')^2 + (y - y')^2]$. We display the two-point function as a function of z and r, for z' set to 0.2, 0.5, and 0.8 in parts a–c of the figure, respectively. Thus, the plots represent

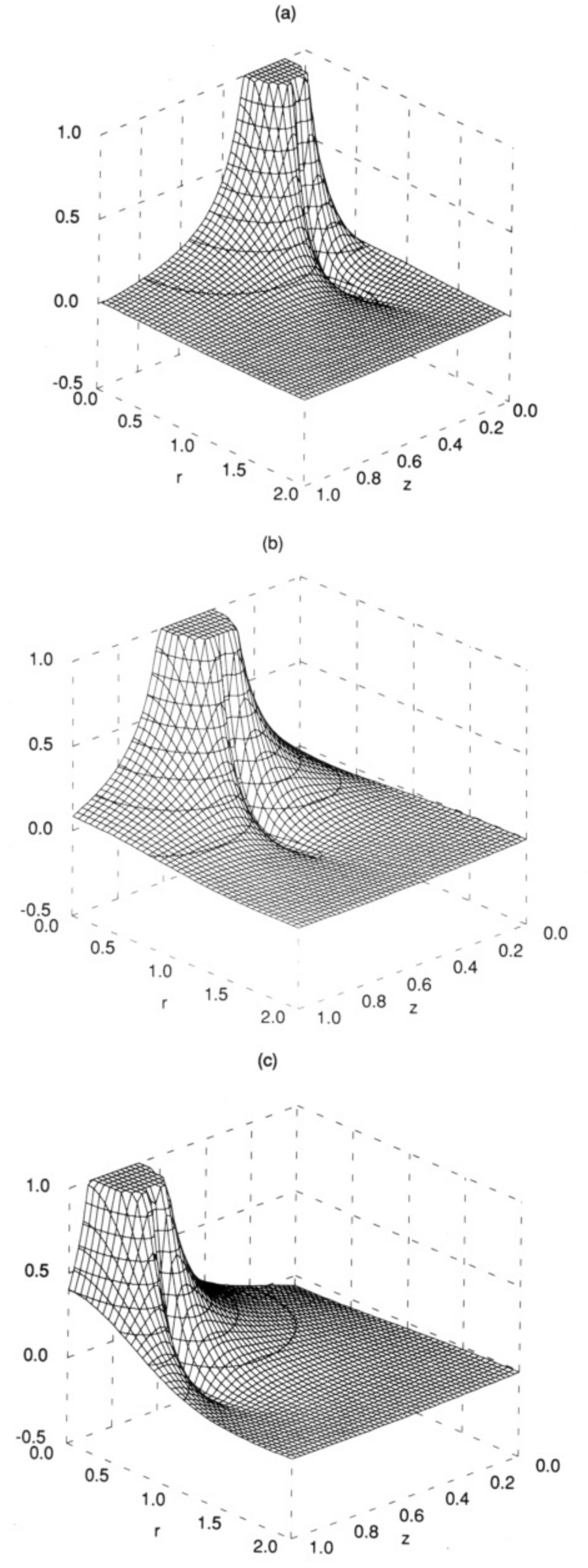

Figure 2. Two-point correlation function $G^{(2)}(\mathbf{r},\mathbf{r}')$ for the grafted melt layer, for fixed z'. Parts a–c correspond to $z' = 0.2$, 0.5, and 0.8, respectively. The correlations are shown as a function of $r = [(x - x')^2 + (y - y')^2]^{1/2}$, measured in units of $(V/a)^{1/2}$, and z, measured in units of the layer height h. Note that, in the strongly stretched limit, $h \gg (V/a)^{1/2}$, so that the response function is strongly anisotropic. The correlations diverge for $r = 0$ and $z = z'$, but now we can resolve the decay in the x–y plane. Note the depletion zone for $z = z'$ and $r \approx (V/a)^{1/2}$. In all the plots, the correlation function is truncated at $G^{(2)} = 1$.

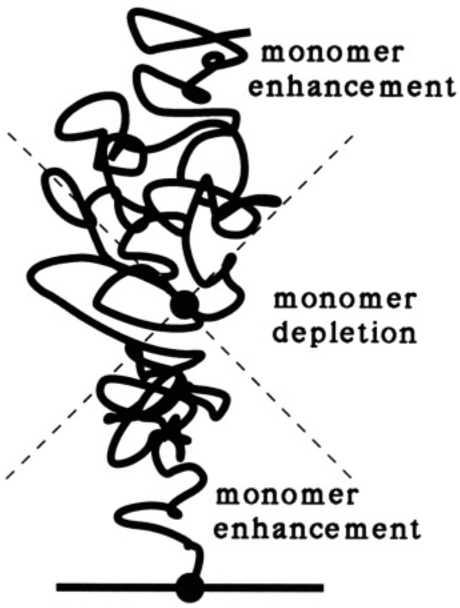

Figure 3. Extended conformations and the connectedness of the chains gives rise to an enhancement in two-point correlations along the chain trajectory and a depletion of monomer perpendicular to the trajectory.

the probability of observing monomers of the same chain at z and z' along the z-axis and a distance r apart in the x–y plane. In the figure, the $x - y$ distance is measured in units of $(V/a)^{1/2}$, and z distances are in units of the layer height h.

The dominant feature in parts a–c of Figure 2 is the divergence at $z = z'$ and $r = 0$. As in the classical limit (Figure 1), this divergence is due to the connectivity of the polymer chains: it is very likely to see monomers of the same chain at nearby points in space. The correlations simply die away as we look at z either above or below z' for $r = 0$ (the classical limit is obtained from the full $G^{(2)}$ by integrating over the x and y variables). In the strong-stretching limit ($V \rightarrow \infty$) the scales for the correlations to decay over in the z and r directions are very different: in the z direction, there are nontrivial correlations over distances of the layer height $h = \sigma V$, while in the radial direction r, the correlations decay over distances of order $(V/a)^{1/2}$.

Our full calculation of the correlations allows us to look at the structure in the correlations as a function of $x - y$ displacements on the order of a few radii of gyration. We note that, for $z = z'$, the correlations as a function of r have minima at $r \approx 1$. This depletion of the correlation is due to the "directedness" of the polymer conformations and is cartooned in Figure 3. We are more likely to observe monomers of a chain above and below a monomer at our test point at $(\bar{0},z')$ than at the same z and r of a few units of $(V/a)^{1/2}$ (off to the side of the test point) since the chains are stretched at scales of more than $(V/a)^{1/2}$.

We note that, although the correlation function displayed in Figure 2b ($z = {}^1/_2$) appears to be symmetric under $z \rightarrow {}^1/_2 - z$, this is not a symmetry of the system. We see no reason for this approximate symmetry, especially when we consider that the individual polymer conformations are quite asymmetrical, being much more stretched near the grafted end than near the free end.

In Figure 4 we display the scattering function (eq 56) for the grafted melt. The wave number in the z direction, k_z, is presented in units of $2\pi/h$, while that in the $x - y$ plane, k, is in units of $(a/V)^{1/2}$. We note that there are peaks at $k_z = \pm 2\pi/h$ along $k = 0$; these peaks reflect the

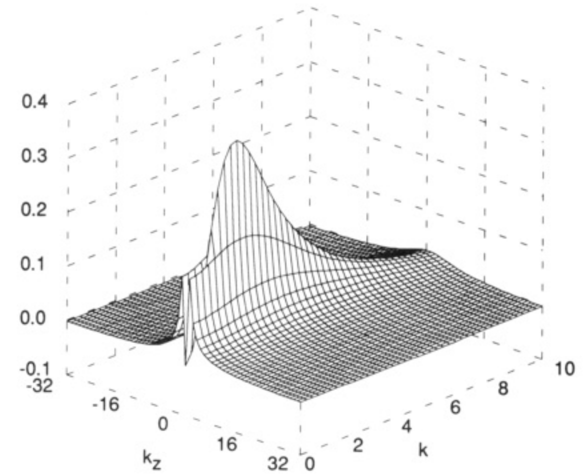

Figure 4. Scattering function for the grafted melt layer. The intensity of scattering from A–B concentration fluctuations is indicated as a function of momentum transfer k in the x–y plane, in units of $(a/V)^{1/2}$, and momentum transfer k_z along the z-axis, in units of $2\pi/h$. We note that the largest peak is at $k \approx 2(a/V)^{1/2}$, corresponding to scattering from the random-walk conformational fluctuations.

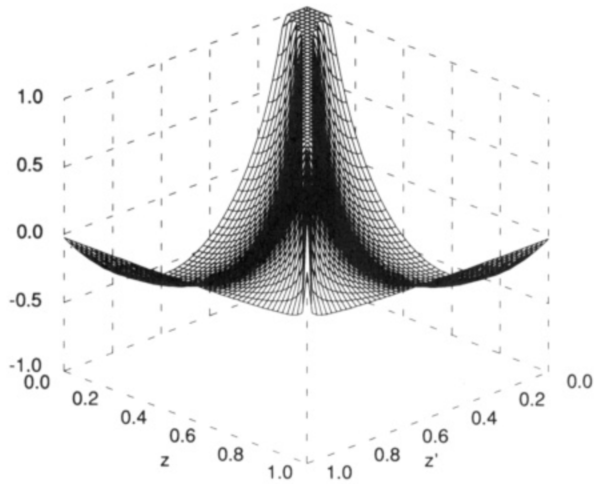

Figure 5. Height–height correlations $g(z,z')$ for the solvent-swollen layer in the classical limit. As in Figure 1, z and z' are measured in units of the layer height. Again, monomer–monomer correlations diverge for $z = z'$, but now they tend to zero at the top of the layer for $z \neq z'$ due to the monomer density being zero there. The figure is truncated at $g = 1$.

fact that, in the z-direction, the correlations decay over a length h.

An important piece of physics is that, at $k_z = k = 0$, the scattering function goes to zero. Remembering that our correlation function describes concentration fluctuations of a two-component brush with evenly mixed grafts, we realize that the scattering at zero momentum must be zero since long-wavelength concentration fluctuations are prevented by the grafting. Arbitrarily, large regions of the layer that have any excess of one component are prevented by the stretching energy of the chains and the mixing of the grafts. Conversely, if the grafts were permitted to slide around on the surface, such fluctuations would indeed occur, leading to a nonzero scattering amplitude at zero momentum. We note the long-wavelength behavior of scattering from diblock copolymers:[13] in that case (as in the mixed-graft layer) the scattering function goes to zero since the two components are chemically joined to one another.

An alternate interpretation of the zero of the scattering function follows from the fact that our correlation function is the two-point cumulant correlation function for a single grafted chain in a layer: the zero-momentum piece of such a correlation function vanishes. The scattering is not zero along the entire line $k = 0$: this, of course, is due to the fact that fluctuations with arbitrarily small k *can* occur, so long as they have $k_z \neq 0$. These fluctuations are "layering" fluctuations[18] and correspond to chains of one component contributing monomer to the top of the layer and the other component contributing to the bottom, as might occur if the free ends were similarly segregated. We shall have more to say about tendencies toward such ordering below.

It is clear from Figure 4 that the dominant peak in the scattering is due to fluctuations with $k \approx (a/V)^{1/2}$ and $k_z = 0$. This peak is roughly double the height of the peaks along $k = 0$ discussed above, thus the characteristic chain length (or demixing interaction strength) at which this peak becomes important is about half of that for which the $k = 0$ peaks become important. This strong peak is due to the "diffusive" or random-walk fluctuations in the x–y plane. These fluctuations will tend to demix the layer on a scale of $(V/a)^{1/2}$, producing "stripes" or "ripples" in concentration in the x–y plane.[19] This is of course a purely diffusive effect and cannot be understood in the classical approximation.

V. Results for the Solvent-Swollen Layer

The classical correlation function in the case of the layer in solvent takes the form eq 57, with a different function $g(z,z')$. The calculation leading to g is the same as that for the melt, except that the end distribution for the solvent-swollen layer (eq 10) is used. The integrals lead to

$$g(z,z') = \left(\frac{\sigma V}{h}\right)^2 \left[\frac{12(1-z_<^2)^{1/2}}{\pi^2} \left\{ F\left(\frac{1-z_>^2}{1-z_<^2}\right)^{1/2} - E\left(\frac{1-z_>^2}{1-z_<^2}\right)^{1/2} \right\} - \frac{9(1-z^2)(1-z'^2)}{4} \right] \qquad (59)$$

where $E(k) = \int_0^{\pi/2} \mathrm{d}\theta\, (1 - k^2 \sin^2\theta)^{1/2}$ is another complete elliptic integral and where again all heights z are measured in units of the total layer height h.

The first feature of this function is that it carries an overall factor of $(\sigma V/h)^2$, which for the solvent-swollen layer, can be very much less than unity (in the melt case, this factor reduces to exactly 1 from space-filling considerations). The number $\sigma V/h$ is of course the overall monomer volume fraction of the layer and appears squared since $G^{(2)}$ is the two-point monomer correlation function. The obvious consequence of this factor is that the strength (or characteristic temperature scale) of monomer concentration fluctuations is greatly reduced in the solvent case (compared to the melt) by purely geometric effects. This factor also appears in the full $G^{(2)}$ in the solvent case; for the remainder of this discussion we will omit this factor.

In Figure 5 we display the function g for the solvent-swollen layer. The classical correlations are quite similar in structure to those for the melt layer, having a logarithmic divergence at $z = z'$ and dying off on the scale of the layer height. However, we note the important difference in the solvent case: that, except for $z = z' = 0$, the correlations along $z = 0$ and $z' = 0$ are zero. This is due to the fact that the monomer density goes to zero at the top of the layer. We note also that the divergences for $z = z' \approx 0$ are stronger than those at $z = z' \approx 1$: this is due to the high concentration of monomer at the bottom of the layer in the solvent case.

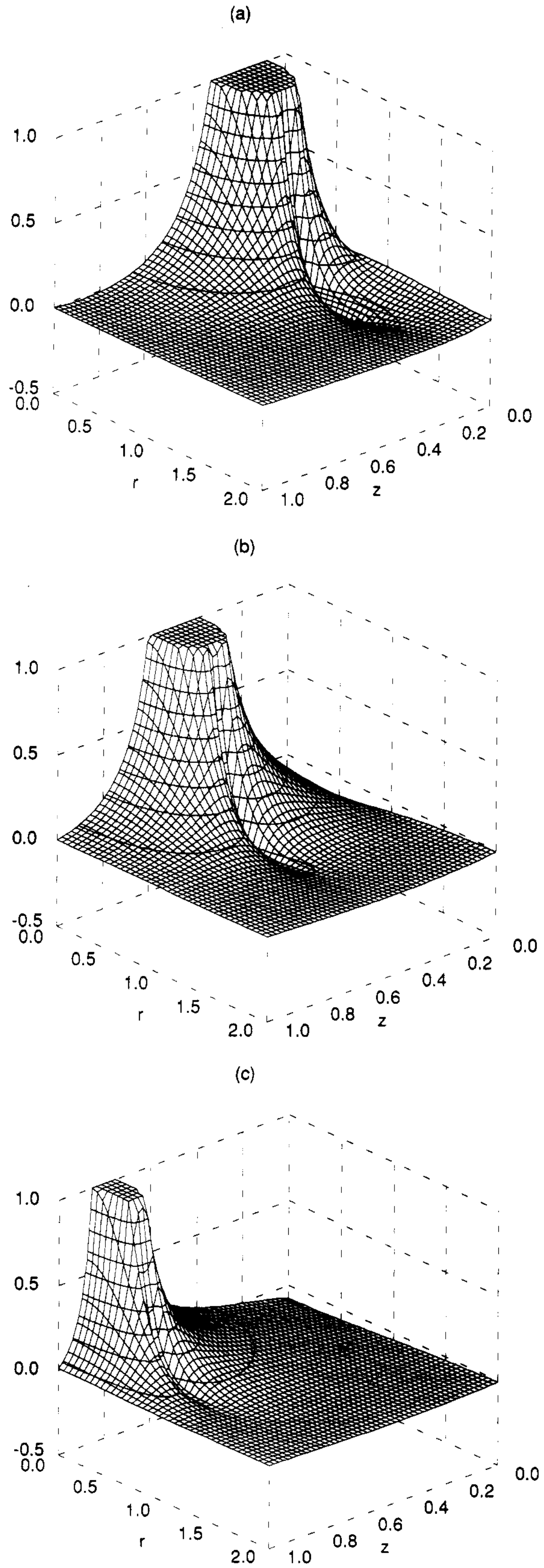

Figure 6. Two-point correlation function $G^{(2)}(\mathbf{r},\mathbf{r}')$ of the solvent-swollen layer for fixed z'. As in Figure 2, parts a–c display correlations versus r and z for $z' = 0.2$, 0.5, and 0.5, respectively. The depletion zone is present in this case. The correlations are truncated at $G^{(2)} = 1$.

Parts a–c of Figure 6 show the solvent case real-space two-point monomer correlation function $G^{(2)}(\mathbf{r},\mathbf{r}')$ as a function of r and z for $z' = 0.2$, 0.5, and 0.8, respectively. Figure 6 is quite similar to Figure 2: for each of the cases, the divergences at $r = 0$ and $z = z'$ and the depletion zones around $z = z'$ are similar to those in the melt case.

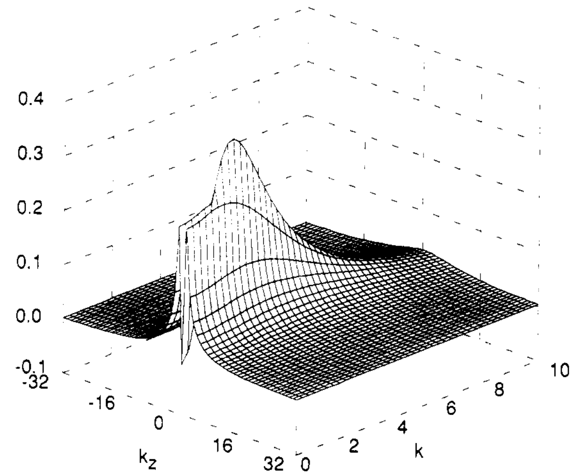

Figure 7. Scattering function for a solvent-swollen grafted layer. Axes are as in Figure 4. Note that the peak at $k \approx 2(a/V)^{1/2}$ is still larger than those at $k = 0$ but that they are closer to one another in size than in the melt case.

Figure 7 shows the scattering function obtained from the real-space correlations. Compared to the melt case (Figure 4), we see that the peaks along $k = 0$ for the solvent-swollen layer are a larger fraction of the peak at $k \approx (a/V)^{1/2}$. In the solvent case, there are stronger concentration fluctuations in the z-direction because ends are distributed throughout the layer (in the melt case, ends are concentrated near the top of the layer). However, the diffusive peak still gives rise to the strongest scattering, and thus fluctuations toward rippling will be stronger than those toward layering in the solvent case.

VI. Effects of Demixing Interactions

The results of this paper have been derived under the assumption that the A and B components of the layer are identical except in their coupling to the external field. This is relevant to scattering experiments done on two-component polymer layers under melt conditions where the chemical differences between the two components do not lead to any appreciable demixing tendency. In experiments done on solvent-swollen layers, it is likely that any demixing interactions will be predominantly screened out by the solvent and that the results of section V will apply. However, for long chains, and particularly under melt conditions, demixing interactions cannot be ignored. Ultimately, there may be rather novel demixing phase transitions.[17] In this section we calculate the compositional response function in the presence of demixing interactions.

We again consider the "symmetric" melt case where $f_A = f_B = {}^1/_2$ and where the A and B grafts are evenly mixed at the grafting surface. Fluctuations of the monomer volume fraction away from $\phi_A(\mathbf{r}) = \phi_B(\mathbf{r}) = {}^1/_2$ may be described by nonzero values of the order parameter $\phi(\mathbf{r}) = \phi_A(\mathbf{r}) - \phi_B(\mathbf{r})$. The effects of such fluctuations can be studied using a mixing energy of the Flory–Huggins form[14]

$$S_{\text{int}} = \Lambda \int d^3r\, \phi_A(\mathbf{r})\, \phi_B(\mathbf{r}) = -\frac{\Lambda}{4} \int d^3r\, \phi^2(\mathbf{r}) + \text{constant} \tag{60}$$

The coupling constant Λ has the dimensions of an inverse volume and is related to the Flory χ-parameter[14] by $\Lambda V = \chi N$, where N is the polymerization index of the chains, and V is the chain volume. In mean-field theory, we expect a continuous phase transition, since the system is symmetric under interchange of the A and B chains. It therefore suffices to consider infinitesimal fluctuations of ϕ.

A recent theory[21] cautions that there can be significant differences between the true mixing energy and the "ideal" mixing energy (eq 60). However, for small fluctuations away from a uniform state ($\phi(\mathbf{r}) \ll 1$) we may adopt the form of the ideal mixing energy along with the assumption that $\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) = 1$ if we define $\Lambda v \phi$ to be the free energy reduction realized by moving a small volume v of A chain from a region with a volume fraction with $\phi_A = {}^1/_2$ to a region with $\phi_A = (1 + \phi)/2$. This definition leads to conventional bulk phase separation[14] of a blend for $\Lambda V = 2$, giving a simple calibration for our results.

If $\langle \phi(\mathbf{r}) \rangle \neq 0$, we may consider the interaction to be a shift in the chemical potential $\mu(\mathbf{r})$:

$$\mu(\mathbf{r}) \rightarrow \mu(\mathbf{r}) - \left\langle \frac{\delta S_{\text{int}}}{\delta \phi(\mathbf{r})} \right\rangle = \mu(\mathbf{r}) + \frac{\Lambda}{2} \langle \phi(\mathbf{r}) \rangle \tag{61}$$

The linear-response relation (eq 16) becomes

$$\langle \phi(\mathbf{r}_1) \rangle = \int \mathrm{d}^3 r_2 \, G^{(2)}(\mathbf{r}_1,\mathbf{r}_2) \left[\mu(\mathbf{r}_2) + \frac{\Lambda}{2} \langle \phi(\mathbf{r}_2) \rangle \right] \tag{62}$$

This equation implicitly gives the response function $G_\Lambda{}^{(2)}$ in the presence of interactions since by definition

$$\langle \phi(\mathbf{r}_1) \rangle = \int \mathrm{d}^3 r_2 \, G_\Lambda{}^{(2)}(\mathbf{r}_1,\mathbf{r}_2) \, \mu(\mathbf{r}_2) \tag{63}$$

to linear order in μ. Substituting for $\langle \phi(\mathbf{r}) \rangle$ on both sides of eq 62 yields an integral equation for $G_\Lambda{}^{(2)}$:

$$G_\Lambda{}^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = G^{(2)}(\mathbf{r}_1,\mathbf{r}_2) + \frac{\Lambda}{2} \int \mathrm{d}^3 r_3 \, G^{(2)}(\mathbf{r}_1,\mathbf{r}_3) \, G_\Lambda{}^{(2)}(\mathbf{r}_3,\mathbf{r}_2) \tag{64}$$

This integral equation may be written more compactly by defining the matrix inverse $[X]^{-1}$ of a two-point function X:

$$\int \mathrm{d}^3 r'' \, X(\mathbf{r},\mathbf{r}'') \, [X]^{-1}(\mathbf{r}'',\mathbf{r}') = \delta^3(\mathbf{r}-\mathbf{r}') \tag{65}$$

Matrix multiplying eq 64 from the left and right by $[G^{(2)}]^{-1}$ and $[G_\Lambda{}^{(2)}]^{-1}$, respectively, yields

$$[G_\Lambda{}^{(2)}]^{-1}(\mathbf{r},\mathbf{r}') = [G^{(2)}]^{-1}(\mathbf{r},\mathbf{r}') - \frac{\Lambda}{2} \delta^3(\mathbf{r}-\mathbf{r}') \tag{66}$$

This is the counterpart for our inhomogeneous grafted system of the well-known result for the scattering structure factor $S_\Lambda(q)$ for polymer blends[13]

$$\frac{1}{S_\Lambda(q)} = \frac{1}{S(q)} - \frac{\Lambda}{2} \tag{67}$$

where the structure factor in the absence of interactions $S(q)$ is a combination of single-chain scattering functions.

The interacting system correlation function (eq 66) may be alternatively calculated by examining the free energy of the system. We presume that $\langle \phi(\mathbf{r}) \rangle = 0$ for an external field $\mu(\mathbf{r}) = 0$ and that ϕ is a fluctuating field in thermal equilibrium. The change in the thermodynamical potential $W = -\log Z$ for a small μ defines the two-point correlation function:[22]

$$\Delta W[\mu] = -\frac{1}{2} \int \mathrm{d}^3 r \, \mathrm{d}^3 r' \, \mu(\mathbf{r}) \, G^{(2)}(\mathbf{r},\mathbf{r}') \, \mu(\mathbf{r}') + \mathcal{O}(\mu^3) \tag{68}$$

If we wish to consider the ensemble with ϕ (rather than μ) fixed, we must Legendre transform the grand potential to obtain the Helmholtz free energy F:

$$F = W + \int \mathrm{d}^3 r \, \mu(\mathbf{r}) \, \phi(\mathbf{r}) \tag{69}$$

The Helmholtz free energy cost of a slight inhomogeneity may thus be written in terms of $\phi(\mathbf{r})$:

$$\Delta F[\phi(\mathbf{r})] = \frac{1}{2} \int \mathrm{d}^3 r \, \mathrm{d}^3 r' \, \phi(\mathbf{r}) \, [G^{(2)}]^{-1}(\mathbf{r},\mathbf{r}') \, \phi(\mathbf{r}') + \mathcal{O}(\phi^3) \tag{70}$$

One can take the demixing interactions into account simply by adding their contribution to the free energy: $\Delta F_\Lambda = \Delta F_{\Lambda=0} + S_{\text{int}}$. Some algebra yields

$$G_\Lambda{}^{(2)}(\mathbf{r},\mathbf{r}') = \left[[G^{(2)}]^{-1}(\mathbf{r},\mathbf{r}') - \frac{\Lambda}{2} \delta^3(\mathbf{r}-\mathbf{r}') \right]^{-1} \tag{71}$$

which is equivalent to eq 66.

The induced $\langle \phi \rangle$ of eq 66 becomes larger as Λ increases. Ultimately, at a critical value Λ_c there is a response with vanishingly small μ and eq 62 becomes an eigenvalue equation:

$$\langle \phi(\mathbf{r}_1) \rangle = \frac{\Lambda_c}{2} \int \mathrm{d}^3 r_2 \, G^{(2)}(\mathbf{r}_1,\mathbf{r}_2) \, \langle \phi(\mathbf{r}_2) \rangle \tag{72}$$

The critical coupling Λ_c is thus $2/\epsilon_{\max}$, where $\epsilon_{\max}$ is the largest eigenvalue of $G^{(2)}$. This condition corresponds to the limit of stability of the linear theory and occurs at the mean-field phase transition.

The function $G^{(2)}$ is real and symmetric in its arguments and may be written in terms of normalized eigenfunctions and corresponding real eigenvalues. A suitable eigenbasis for the x–y dependence is plane waves, due to the translational symmetry of the noninteracting system in the x–y plane. In the z-direction we cannot guess the eigenfunctions, but the finite extent of the layer quantizes the spectrum. As a result, we are able to write

$$G^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = V \int \frac{\mathrm{d}^2 k}{(2\pi)^2} e^{i\bar{\mathbf{k}}\cdot(\mathbf{x}_1-\mathbf{x}_2)} \sum_{n=1}^{\infty} \epsilon_n(k) \, \eta_n^*(k,z_1) \, \eta_n(k,z_2) \tag{73}$$

Here, the eigenvalues $\epsilon_n(k)$ depend only on the magnitude of the in-plane momentum, and, for each k, the functions $\{\eta\}$ are an orthonormal set:

$$\int_0^h \mathrm{d}z \, \eta_m^*(k,z) \, \eta_n(k,z) = \delta_{mn} \tag{74}$$

The overall factor of V above makes the eigenvalues ϵ dimensionless and of order unity and indicates that the relevant coupling constant is $\Lambda V = \chi N$. In Figure 8 we plot the first few eigenvalues: we plot $2/\epsilon_n(k)$ versus in-plane momentum k. This plot allows us to read off the first mode that will become unstable in the Gaussian theory. The lowest mode has $k \approx 1.841(a/V)^{1/2}$, and it becomes unstable for $\Lambda V \approx 4.549$. By comparison, a $k = 0$ mode does not become unstable until $\Lambda V \approx 8$. All of these properties are identical with those presented in ref 17.

The fact that the instability is at $k \neq 0$ tells us an important fact: any demixing phase transition that occurs in a symmetric two-component polymer layer will involve a mesoscopic in-plane wavelength or ripples in concentration in the x–y plane. Such a transition should be preceded by strong in-plane concentration fluctuations and should be observed if one constructs a grafted layer out of chains that are about 2.3 times as long as the critical chain length at which a bulk blend would demix. We shall discuss these phase transitions in much more detail in a future publication.

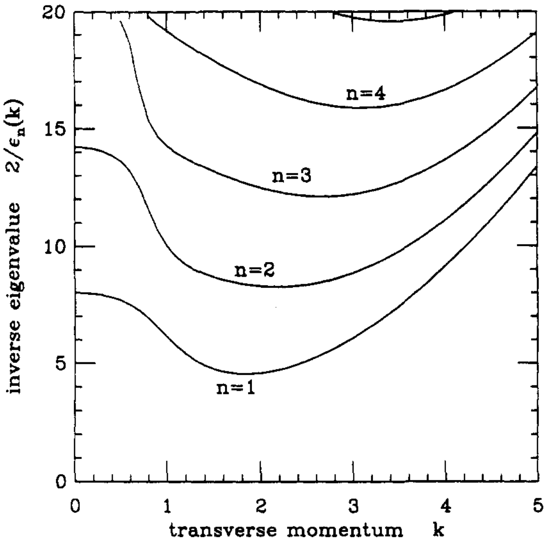

Figure 8. Inverse eigenvalues of the two-point correlations for a two-component melt layer. We show the lowest four "bands". The minimum of the lowest band is about 4.549, achieved for an in-plane momentum of $k \approx 1.841(a/V)^{1/2}$. The lowest inverse eigenvalue at $k = 0$ is at 8. Plotted is $2/\epsilon_n(k)$, corresponding to the value of ΛV for which a phase transition occurs in the mean-field theory.

VII. Discussion

In the grafted polymer systems that we have examined in this paper, interchain interactions lead to strong stretching of the polymers. The chains are extended over much larger distances than they would be in a free melt. However, over short distances, the chains look as if they are Gaussian random coils. In particular, the conformational fluctuations in the x–y plane are purely diffusive (assuming no demixing tendencies in the two-component models discussed above). We have presented calculational methods that can be used to obtain the monomer–monomer correlation functions for grafted polymer layers. The essential approximation is the mean-field assumption that the chains are statistically independent. Since in the strong-stretching regime the volume pervaded by a chain under grafted melt conditions is even larger than that in a free melt, we expect this to be a good approximation.

Our most basic results ignore the diffusive fluctuations of chain conformations around the most likely ones. The classical correlations thus obtained indicate what one might expect: the extended conformations lead to monomer–monomer correlations that extend throughout the layer in the z-direction. The correlation length in the z-direction is arbitrarily large, scaling with the molecular weight for either the melt or solvent-swollen layers.

The central result of this paper is the extension of this picture to take into account diffusive fluctuations of the stretched-coil conformations. These fluctuations do not change our picture of the correlations in the z-direction, but in the x–y direction, we no longer have δ-function correlations. The Gaussian fluctuations give rise to correlations decaying over mesoscopic distances in the x–y plane. This in-plane correlation length scales with the square root of the molecular weight and thus is arbitrarily far from either the monomer size or the layer thickness. Somewhat surprising is the fact that these diffusive fluctuations are dominant: they are more important than the correlations in the z-direction imposed by the extended conformations of the chains. In a scattering experiment, the strongest scattering is observed for in-plane momentum transfers on the order of the inverse of the mesoscopic scale.

The experimental means for testing our predictions by neutron scattering have been developed[23] and tested.[24,25] The interpretation of these experiments is complicated by the effects of incomplete contrast matching; only partial data on the radii of gyration of lamellar diblocks is available to date.[24,25] This experiment shows an apparent small *shrinkage* in the lateral radius of gyration relative to the unperturbed radius. Our theory predicts that there should be no such shrinkage in a well-oriented, monodisperse sample in its equilibrium state.

The correlations treated here imply distinctive nonlocal response properties for the two-component layer. An example is the behavior of small impurity molecules in the layer. If an impurity molecule at $\mathbf{r}$ has a preferential interaction with, say, the A chains, a second impurity at $\mathbf{r}'$ must experience an induced nonlocal attractive interaction proportional to $G^{(2)}(\mathbf{r},\mathbf{r}')$. Because of the form of this interaction (Figures 2 and 6), the impurities would tend to condense into columns perpendicular to the grafting surface.

In section VI, we have sketched some results concerning the effects of interactions between the A and B chains. In a future paper, we will elaborate these results into a more complete theory for concentration fluctuations in multicomponent grafted layers. Of particular interest is the calculation of higher order terms that stabilize the theory beyond phase transitions. These terms are essential in order to study the effects of fluctuations on the ordered phases.

We have seen that, for a two-component layer, where the two types of chains are uniformly grafted, there is a tendency toward a "rippled" phase-separated state. Another possibility mentioned above is a transition to a state with no in-plane structure but layered in the z-direction. The relative stability of these two types of ordered phases is determined by the "free" ($\Lambda = 0$) system two-point correlation function. We hope to tune this relative stability by changing the architecture of the grafted chains.

As an example of this tuning, one might graft diblock copolymer chains composed of half A and half B monomers. If there were an equal number of A and B ends grafted, the system would be symmetric under A ↔ B interchange, and we would expect any phase transition to be second order (in mean-field theory). However, we would expect there to be stronger composition fluctuations in the z-direction in this case since for a single chain, if there are monomers of one type at the top of the layer, not only do we expect there to be fewer monomers of that type at the bottom but also we expect an enhanced number of monomers of the opposite type due to the chain architecture. This may well promote fluctuations toward layering. The extension of our calculations to such exotic molecular architectures is straightforward.

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