Stress in Self-Consistent-Field Theory

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ABSTRACT: We develop a perturbation theory to efficiently calculate derivatives of the free energy with respect to changes in the parameters of the unit cell in the self-consistent-field theory (SCFT) of block copolymer crystals, thus determining the state of mechanical stress in any nonequilibrium unit cell. By requiring that the stress thus calculated vanish, we are able to find the unit cell that minimizes the free energy simultaneously with the solution of the SCFT equations, at little added computational effort.

1. Introduction

Self-consistent-field theory (SCFT) has become a standard tool for understanding and predicting self-assembled structures formed by block copolymers. The SCFT equations for complex three-dimensional structures can now be solved for intermediate segregation strengths without further approximation by either the spectral method of Matsen and Schick[1] or real-space methods.[2,3] A necessary part of the calculation of the equilibrium free energy of a periodic structure is the identification of the size and shape of the unit cell that minimizes the free energy and that, correspondingly, yields a stress-free crystal. For phases whose unit cell is characterized by a single domain size, such as the lamellar, hexagonal, and cubic phases found for diblock copolymers, the required one-dimensional minimization is a relatively simple and inexpensive operation. The search for an optimum unit cell becomes more complex, however, when one must minimize with respect to several unit cell parameters simultaneously, as for any noncubic three-dimensional crystal. The recent discovery of a noncubic phase in triblock copolymers,[4] which is believed to have an orthorhombic unit cell, has prompted us to develop an efficient method of equilibrating the unit cell of an arbitrary crystal.

We have developed a perturbation theory to efficiently calculate derivatives of the SCFT free energy with respect to changes in unit cell parameters, thus calculating the state of stress of a nonequilibrium unit cell. A more general perturbation theory describing arbitrary, inhomogeneous perturbations of the chemical potential and density fields has been developed by Shi et al.[5] We have also developed an iteration algorithm that uses the perturbatively calculated stress to simultaneously equilibrate the unit cell and solve the SCFT equations

2. Self-Consistent-Field Theory

We consider a melt of multiblock copolymers, each of N monomers and B blocks, with monomers labeled by an index $0 < s < N$ and blocks labeled by $\alpha = 1, ..., B$. Monomers with $s_{\alpha-1} < s < s_\alpha$ are in block α and have a statistical segment length b_α. The melt is incompressible: each monomer occupies a volume v_0 independent of species. In SCFT, this system is characterized by calculating the constrained single-chain partition functions $q(\mathbf{r},s)$ and $q^\dagger(\mathbf{r},s)$. The quantity $q(\mathbf{r},s)$ is the partition function of a Gaussian subchain containing monomers 0 to s, with monomer s constrained at $\mathbf{r}$, in a self-consistently determined chemical potential, while $q^\dagger(\mathbf{r},s)$ is the constrained partition function containing monomers N to s. The function $q(\mathbf{r},s)$ satisfies a modified Schroedinger or diffusion equation, which we express in Dirac notation as

$$\frac{\partial}{\partial s}|q(s)\rangle = -\hat{H}_{\alpha(s)}|q(s)\rangle \tag{1}$$

where $q(\mathbf{r},s) = \langle \mathbf{r}|q(s)\rangle$, with an initial condition $q(\mathbf{r},s=0) = 1$, while $q^\dagger(\mathbf{r},s)$ satisfies eq 1 with the right-hand side multiplied by -1, with an initial condition $q^\dagger(\mathbf{r},s=N) = 1$. Here, $\hat{H}_{\alpha(s)}$ is a linear operator for monomers of type $\alpha(s)$, where $\alpha(s)$ is the block index for monomer s. The operator $\hat{H}_\alpha$ is given, in a coordinate-space representation, as

$$\hat{H}_\alpha = -\frac{b_\alpha{}^2}{6}\nabla^2 + \omega_\alpha(\mathbf{r}) \tag{2}$$

The volume fraction of monomers of type α (i.e., the number of α monomers per unit volume times v_0) is given by

$$\phi_\alpha(\mathbf{r}) = \frac{1}{NQ}\int_{s_{\alpha-1}}^{s_\alpha} \mathrm{d}s\; q(\mathbf{r},s)\, q^\dagger(\mathbf{r},s) \tag{3}$$

where for a system of volume V

$$Q \equiv \frac{1}{V}\int \mathrm{d}\mathbf{r}\; q(\mathbf{r},N) \tag{4}$$

We use the Flory−Huggins form for the chemical potential

$$\omega_\alpha(\mathbf{r}) = \chi_{\alpha\beta}\phi_\beta(\mathbf{r}) + \xi(\mathbf{r}) \tag{5}$$

where $\chi_{\alpha\beta}$ is the Flory−Huggins interaction parameter for monomers α and β, and $\xi(\mathbf{r})$ is a Lagrange field chosen to satisfy the incompressibility constraint

$$\sum_{\alpha=1}^{B}\phi_\alpha(\mathbf{r}) = 1 \tag{6}$$

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In eq 5, and hereafter, summation over repeated block indices α or β is implicit. The free energy per chain is

$$\frac{F}{kT} = -\ln Q - \frac{N}{V}\int \mathrm{d}\mathbf{r}\left[\omega_\alpha(\mathbf{r})\,\phi_\alpha(\mathbf{r}) - \frac{1}{2}\chi_{\alpha\beta}\phi_\alpha(\mathbf{r})\,\phi_\beta(\mathbf{r})\right] \tag{7}$$

We use SCFT to compare the free energy of competing periodic structures in block copolymer melts. The unit cell for each type of crystal can be characterized by a set of parameters θ_i, where the number of parameters depends on the crystal system, e.g., the length of any one edge of a cubic crystal, the lengths of the three orthogonal edges of an orthorhombic crystal, or the three angles and three lengths of a triclinic crystal. The equilibrium parameters are those which minimize the free energy or, equivalently, those for which the stress vanishes at equilibrium. A solution of the SCFT in an equilibrium unit cell must thus satisfy the condition

$$\frac{\mathrm{d}F}{\mathrm{d}\theta_i} = 0 \tag{8}$$

for each of the unit cell parameters in addition to eqs 5 and 6. The elements of the stress tensor for a crystal with a nonequilibrium unit cell are linear combinations of the derivatives $\mathrm{d}F/\mathrm{d}\theta_i$, and so we refer to these derivatives, somewhat loosely, as stresses.

3. Stress in SCFT

In this section, we derive a general expression for stress in SCFT. We consider the free energy to be a function of the unit cell parameters θ_i and a functional of the chemical potential fields ω, in which the density fields are determined by eq 3. To describe simultaneous variations of ω and θ_i, we find it useful to consider the ω fields to be functions of a dimensionless position $\tilde{\mathbf{r}} \equiv (\tilde{r}_1, \tilde{r}_2, \tilde{r}_3)$, defined such that

$$\mathbf{r} = \sum_{\mu=1}^{3} \tilde{r}_\mu \mathbf{a}_\mu \tag{9}$$

where the $\mathbf{a}_\mu$, with $\mu = 1, 2, 3$, are Bravais lattice vectors whose magnitudes and relative orientations are functions of the unit cell parameters. Simultaneous variations of the chemical potential $\omega(\tilde{\mathbf{r}})$ at fixed $\tilde{\mathbf{r}}$ and of the unit cell parameters θ_i thus correspond to variations of the chemical potential relative to that produced by an affine deformation of the ω fields.

The total derivative of the free energy per chain with respect to a unit cell parameter θ_i is

$$\frac{\mathrm{d}F}{\mathrm{d}\theta_i} = \frac{\partial F}{\partial \theta_i} + \int \mathrm{d}\tilde{\mathbf{r}}\,\frac{\delta F}{\delta \omega_\gamma(\tilde{\mathbf{r}})}\frac{\mathrm{d}\omega_\gamma(\tilde{\mathbf{r}})}{\mathrm{d}\theta_i} \tag{10}$$

where $\partial F/\partial\theta_i$ denotes a derivative with respect to a unit cell parameter at fixed $\omega(\tilde{\mathbf{r}})$, corresponding to an affine deformation, and $\delta F/\delta\omega_\gamma(\tilde{\mathbf{r}})$ denotes a functional derivative in a fixed unit cell. The derivatives with respect to θ_i and ω_γ, from eq 7, are

$$\frac{1}{kT}\frac{\partial F}{\partial \theta_i} = -\frac{\partial \ln Q}{\partial \theta_i} - N\int \mathrm{d}\tilde{\mathbf{r}}\,[\omega_\alpha(\tilde{\mathbf{r}}) - \chi_{\alpha\beta}\phi_\beta(\tilde{\mathbf{r}})]\frac{\partial \phi_\alpha(\tilde{\mathbf{r}})}{\partial \theta_i} \tag{11}$$

$$\frac{1}{kT}\frac{\delta F}{\delta \omega_\gamma(\tilde{\mathbf{r}})} = -\frac{\delta \ln Q}{\delta \omega_\gamma(\tilde{\mathbf{r}})} - N\phi_\gamma(\tilde{\mathbf{r}}) - N\int \mathrm{d}\tilde{\mathbf{r}}'\,[\omega_\alpha(\tilde{\mathbf{r}}') - \chi_{\alpha\beta}\phi_\beta(\tilde{\mathbf{r}}')]\frac{\delta \phi_\alpha(\tilde{\mathbf{r}}')}{\delta \omega_\gamma(\tilde{\mathbf{r}})} \tag{12}$$

where we have used the identity $\int \mathrm{d}\mathbf{r}/V = \int \mathrm{d}\tilde{\mathbf{r}}$ to rewrite the integrals. To further simplify eq 12, we use the fact that

$$-\frac{\delta \ln Q}{\delta \omega_\gamma(\tilde{\mathbf{r}})} = N\phi_\gamma(\tilde{\mathbf{r}}) \tag{13}$$

giving

$$\frac{1}{kT}\frac{\delta F}{\delta \omega_\gamma(\tilde{\mathbf{r}})} = -N\int \mathrm{d}\tilde{\mathbf{r}}'\,[\omega_\alpha(\tilde{\mathbf{r}}') - \chi_{\alpha\beta}\phi_\beta(\tilde{\mathbf{r}}')]\frac{\delta \phi_\alpha(\tilde{\mathbf{r}}')}{\delta \omega_\gamma(\tilde{\mathbf{r}})} \tag{14}$$

For any set of ω fields that satisfy the self-consistency condition of eq 5, we may rewrite the integrals in eqs 11 and 14 in terms of $\xi(\tilde{\mathbf{r}})$, giving

$$\frac{1}{kT}\frac{\partial F}{\partial \theta_i} = -\frac{\partial \ln Q}{\partial \theta_i} - N\int \mathrm{d}\tilde{\mathbf{r}}\,\xi(\tilde{\mathbf{r}})\sum_\alpha \frac{\partial \phi_\alpha(\tilde{\mathbf{r}})}{\partial \theta_i} \tag{15}$$

$$\frac{1}{kT}\frac{\delta F}{\delta \omega_\gamma(\tilde{\mathbf{r}})} = -N\int \mathrm{d}\tilde{\mathbf{r}}'\,\xi(\tilde{\mathbf{r}}')\sum_\alpha \frac{\delta \phi_\alpha(\tilde{\mathbf{r}}')}{\delta \omega_\gamma(\tilde{\mathbf{r}})} \tag{16}$$

Substituting eqs 15 and 16 into eq 10, while recognizing that the total derivative of volume fraction with respect to the unit cell parameter θ_i is given by

$$\frac{\mathrm{d}\phi_\alpha(\tilde{\mathbf{r}})}{\mathrm{d}\theta_i} = \frac{\partial \phi_\alpha(\tilde{\mathbf{r}})}{\partial \theta_i} + \int \mathrm{d}\tilde{\mathbf{r}}'\,\frac{\delta \phi_\alpha(\tilde{\mathbf{r}})}{\delta \omega_\gamma(\tilde{\mathbf{r}}')}\frac{\mathrm{d}\omega_\gamma(\tilde{\mathbf{r}}')}{\mathrm{d}\theta_i} \tag{17}$$

yields a total derivative

$$\frac{1}{kT}\frac{\mathrm{d}F}{\mathrm{d}\theta_i} = -\frac{\partial \ln Q}{\partial \theta_i} - N\int \mathrm{d}\tilde{\mathbf{r}}\,\xi(\tilde{\mathbf{r}})\frac{\mathrm{d}}{\mathrm{d}\theta_i}\sum_\alpha \phi_\alpha(\tilde{\mathbf{r}}) \tag{18}$$

where we have interchanged the sum and derivative in the integrand. Because the melt is incompressible, the total derivative of $\sum_\alpha \phi_\alpha(\tilde{\mathbf{r}})$ with respect to θ_i must vanish, leaving

$$\frac{\mathrm{d}F}{\mathrm{d}\theta_i} = -kT\frac{\partial \ln Q}{\partial \theta_i} \tag{19}$$

The stress associated with a solution to the SCFT equations in a nonequilibrium unit cell is thus proportional to the variation of ln Q induced by an affine deformation of the ω fields.

4. Perturbation Theory for Stress

We now construct a perturbation theory for the changes in Q induced by such an affine deformation. This is most conveniently treated by describing the periodic functions ω, q, and $q^\dagger$ as functions of the

dimensionless coordinate $\tilde{\mathbf{r}}$. The Laplacian that appears in eq 2 for $\hat{H}_\alpha$ may be expressed in this system of coordinates as a sum

$$\nabla^2 = \sum_{\mu,\nu=1}^{3} \frac{\mathbf{b}_\mu \cdot \mathbf{b}_\nu}{(2\pi)^2} \frac{\partial}{\partial \tilde{r}_\mu} \frac{\partial}{\partial \tilde{r}_\nu} \tag{20}$$

where $\mathbf{b}_\mu$, with $\mu = 1, 2, 3$, is a reciprocal lattice basis vector, for which $\mathbf{a}_\mu \cdot \mathbf{b}_\nu = 2\pi\delta_{\mu\nu}$. In this system of coordinates, an affine deformation leaves the function $\omega_\alpha(\tilde{\mathbf{r}})$ unchanged, but induces a change $\delta\nabla^2$ in the representation of ∇^2, due to changes in the factors of $\mathbf{b}_\mu \cdot \mathbf{b}_\nu$ in eq 20, causing a corresponding perturbation in the representation of $\hat{H}_\alpha$

$$\delta\hat{H}_\alpha = -\frac{b_\alpha^2}{6}\delta\nabla^2 \tag{21}$$

We focus here upon the spectral representation of SCFT, in which all spatially varying functions are expanded in a set of orthonormal periodic basis functions $f_i(\tilde{\mathbf{r}})$ with the space group symmetry of the phase of interest, and that are also eigenfunctions of ∇^2, so that

$$-\nabla^2 f_i = \lambda_i f_i \tag{22}$$

In this representation, the perturbation $\delta\hat{H}_\alpha$ is a diagonal operator

$$\langle f_i|\delta H_\alpha|f_j\rangle = \frac{b_\alpha^2}{6}\delta\lambda_i\delta_{ij} \tag{23}$$

with eigenvalues proportional to the perturbations of the corresponding eigenvalues of the Laplacian, where $\langle f_i|f_j\rangle \equiv \int d\tilde{\mathbf{r}}\, f_i(\tilde{\mathbf{r}})\, f_j(\tilde{\mathbf{r}}) = \delta_{ij}$.

We construct a perturbation theory for Q by considering corresponding perturbations of the propagators, or Greens functions, for homopolymer subchains. The propagator $G_\alpha(\tilde{\mathbf{r}},\tilde{\mathbf{r}}';s)$ is proportional to the partition function of a Gaussian hompolymer subchain of type α with its ends constrained at $\tilde{\mathbf{r}}$ and $\tilde{\mathbf{r}}'$.[6] In Dirac notation, we represent the propagator as an operator $\hat{G}_\alpha(s)$, whose effect upon a function $g(\tilde{\mathbf{r}}) = \langle\tilde{\mathbf{r}}|g\rangle$ is defined by the convolution

$$\langle\tilde{\mathbf{r}}|\hat{G}_\alpha(s)|g\rangle \equiv \int d\tilde{\mathbf{r}}'\, G_\alpha(\tilde{\mathbf{r}}, \tilde{\mathbf{r}}';s)\, g(\tilde{\mathbf{r}}') \tag{24}$$

The propagator satisfies the modified wave equation

$$\left[\frac{\partial}{\partial s} + \hat{H}_\alpha\right]\hat{G}_\alpha(s) = 0 \tag{25}$$

for $s > 0$ with the initial condition $\hat{G}(s{=}0) = \tilde{I}$, or equivalently, $G(\tilde{\mathbf{r}},\tilde{\mathbf{r}}';s{=}0) = \delta(\tilde{\mathbf{r}} - \tilde{\mathbf{r}}')$. The propagator may be expanded in orthonormal solutions of the eigenvalue equation

$$\hat{H}_\alpha|\psi_j^\alpha\rangle = E_j^\alpha|\psi_j^\alpha\rangle \tag{26}$$

as

$$\hat{G}_\alpha(s) = |\psi_j^\alpha\rangle e^{-sE_j^\alpha}\langle\psi_j^\alpha| \tag{27}$$

We may express the singly constrained partition functions $|q(s_\alpha)\rangle$ and $|q^\dagger(s_\alpha)\rangle$ at the junction of blocks α and $\alpha + 1$ as products of propagators:

$$|q(s_\alpha)\rangle = \hat{G}_\alpha(N_\alpha)\,\hat{G}_{\alpha-1}(N_{\alpha-1})\cdots\hat{G}_2(N_2)\,\hat{G}_1(N_1)|0\rangle$$

$$|q^\dagger(s_\alpha)\rangle = \hat{G}_{\alpha+1}(N_{\alpha+1})\cdots\hat{G}_{B-1}(N_{B-1})\,\hat{G}_B(N_B)|0\rangle \tag{28}$$

where $|0\rangle$ represents the spatially uniform initial condition, for which $\langle\mathbf{r}|0\rangle = 1$ for all $\mathbf{r}$, and $N_\alpha \equiv s_\alpha - s_{\alpha-1}$ is the length of block α. Similarly

$$Q = \langle 0|q(N)\rangle = \langle 0|\hat{G}_B(N_B)\,\hat{G}_{B-1}(N_{B-1})\ldots\hat{G}_2(N_2)\,\hat{G}_1(N_1)|0\rangle \tag{29}$$

Using the above expressions for Q, $|q\rangle$, and $|q^\dagger\rangle$, the perturbation of Q caused by an arbitrary perturbation of the propagators $\hat{G}_\alpha(N_\alpha)$ may be expressed as a sum

$$\delta Q = \sum_{\alpha=1}^{B}\langle q^\dagger(s_\alpha)|\delta\hat{G}_\alpha(N_\alpha)|q(s_{\alpha-1})\rangle \tag{30}$$

for $\alpha = 1, \ldots, B$, where $\langle q^\dagger(s_\alpha)|$ and $|q(s_{\alpha-1})\rangle$ are evaluated in the unperturbed state.

The perturbation of $\hat{G}_\alpha(s)$ caused by an infinitesimal perturbation $\hat{H}_\alpha \rightarrow \hat{H}_\alpha + \delta\hat{H}_\alpha$ satisfies

$$\left[\frac{\partial}{\partial s} + \hat{H}_\alpha\right]\delta\hat{G}_\alpha = -\delta\hat{H}_\alpha\hat{G}_\alpha \tag{31}$$

where $\hat{G}_\alpha(s)$ is the unperturbed propagator. This yields a perturbation

$$\delta\hat{G}_\alpha(s) = -\int_0^s ds'\, \hat{G}_\alpha(s - s')\delta\hat{H}_\alpha\hat{G}_\alpha(s') \tag{32}$$

with matrix elements

$$\langle\psi_i^\alpha|\delta\hat{G}_\alpha(s)|\psi_j^\alpha\rangle = -\langle\psi_i^\alpha|\delta\hat{H}_\alpha|\psi_j^\alpha\rangle\int_0^s ds'\, e^{-E_i^\alpha(s-s')}e^{-E_j^\alpha s'} \tag{33}$$

$$= -\langle\psi_i^\alpha|\delta\hat{H}_\alpha|\psi_j^\alpha\rangle\frac{e^{-E_i^\alpha s} - e^{-E_j^\alpha s}}{E_j^\alpha - E_i^\alpha} \tag{34}$$

by analogy to the standard first-order perturbation theory for a quantum-mechanical system. The required matrix elements of $\delta\hat{H}_\alpha$ may be calculated from the sum

$$\langle\psi_i^\alpha|\delta\hat{H}|\psi_k^\alpha\rangle = \frac{b_\alpha^2}{6}\sum_j\langle\psi_i^\alpha|f_j\rangle\delta\lambda_j\langle f_j|\psi_k^\alpha\rangle \tag{35}$$

To calculate the perturbation of F/kT caused by a specified perturbation of the unit cell, within a spectral implementation of the SCFT, using a truncated basis of M basis functions, we must (i) calculate the corresponding perturbations of the eigenvalues λ_i of the Laplacian for all M spectral basis functions, (ii) calculate the M^2 matrix elements $\langle\psi_i|\delta\hat{H}|\psi_k\rangle$ from eq 35, and (iii) calculate the perturbation of Q from eqs 34 and 30. The required eigenvalues and eigenvectors of $\hat{H}_\alpha$ and the values of $|q(s_\alpha)\rangle$ at the junctions between blocks must already be calculated as part of the spectral solution of the SCFT equations, at a cost of $O(M^3)$ for each iteration of the ω fields. The additional cost of the calculation of the stress is dominated by the evaluation of the sum on the right-hand side of eq 35, which is the only additional procedure that requires $O(M^3)$ floating point operations. In our current implementation of the SCFT, in which we have taken care to optimize both the underlying SCFT calculation and stress calculation, the

time required to calculate the derivative $\partial \ln Q/\partial\theta_i$ for a single unit cell parameter θ_i is about 10% of that required to calculate the density and free energy for a specified set of ω fields.

We now briefly discuss a method of calculating deformation induced changes in the eigenvalues of $-\nabla^2$ for periodic basis functions. Periodic basis functions with a specified space group symmetry can be automatically generated as sums of plane waves of the form[7]

$$f(\mathbf{r}) = \sum_{k=1}^{K} c_k e^{i\mathbf{G}_k\cdot\mathbf{r}} \tag{36}$$

with complex coefficients of equal magnitude $|c_k| = 1/\sqrt{K}$, in which $\mathbf{G}_1$, ..., $\mathbf{G}_K$ is a set of K reciprocal lattice vectors, known as a star, that all have equal square magnitude $|\mathbf{G}_k|^2 = \lambda$ and that are all related by the corresponding set of point group symmetries. When expressed in terms of the dimensionless variable $\tilde{\mathbf{r}}$, the basis function $f(\tilde{\mathbf{r}})$ is independent of cell parameters. We consider the change in λ produced by an infinitesimal deformation of the unit cell that preserves the space group symmetry used to construct the basis function $f(\tilde{\mathbf{r}})$. For any such deformation, all of the wavevectors in a star retain equal magnitude, so that the change in λ is given by the change in $|\mathbf{G}_k|^2$ for any of the wavevectors in the star. An arbitrarily chosen wavevector in the star, denoted $\mathbf{G}$, may be expressed as a sum $\mathbf{G} = \sum_\mu \tilde{G}_\mu \mathbf{b}_\mu$, where the $\tilde{G}_\mu$'s are integer coefficients. The desired variation of λ is thus

$$\delta\lambda = \delta|\mathbf{G}|^2 = \sum_{\mu\nu} \tilde{G}_\mu \tilde{G}_\nu \delta(\mathbf{b}_\mu\cdot\mathbf{b}_\nu) \tag{37}$$

To calculate the variations $\delta\mathbf{b}_\mu$ of the reciprocal basis vectors for a known set of deformations $\delta\mathbf{a}_\mu$ of the Bravais lattice vectors, we substitute the expansion $\delta\mathbf{b}_\mu = \sum_\nu c_{\mu\nu}\mathbf{b}_\nu$, based on the completeness of the reciprocal lattice vectors, into the identity $0 = \delta(\mathbf{a}_\lambda\cdot\mathbf{b}_\mu) = \delta\mathbf{a}_\lambda\cdot\mathbf{b}_\mu + \mathbf{a}_\lambda\cdot\delta\mathbf{b}_\mu$ and solve for $c_{\mu\nu}$ to show that

$$\delta\mathbf{b}_\mu = -\frac{1}{2\pi}\sum_\nu \mathbf{b}_\mu\cdot\delta\mathbf{a}_\nu\mathbf{b}_\nu \tag{38}$$

Equations 38 and 37 together yield $\delta(\mathbf{b}_\mu\cdot\mathbf{b}_\nu) = \delta\mathbf{b}_\mu\cdot\mathbf{b}_\nu + \mathbf{b}_\mu\cdot\delta\mathbf{b}_\nu$ and $\delta\lambda$.

In Figure 1 we present calculations of the SCFT free energy per chain and its derivative with respect to a unit cell parameter c, calculated using the above perturbation theory, for a tetragonal crystal produced by deforming a body-centered-cubic (bcc) crystal. The calculations are for the free energy of a diblock copolymer melt, with a minority volume fraction $f = 0.25$, $\chi N = 20.0$, and $b_1 = b_2$, which, in equilibrium, forms a bcc crystal with a cubic unit cell size $c_0 = 4.54R_g$ (where $R_g^2 = Nb^2/6$). The cubic structure has been deformed by uniaxial extension into an $I4/mmm$ tetragonal crystal by varying the unit cell length c along one of three orthogonal axes while keeping the lengths along the other two axes equal to c_0. To calculate the derivative dF/dc for a deformation that breaks the cubic symmetry, we have solved the SCFT equations using basis functions with the symmetry of the tetragonal space group. The solid line through the free energy data and the dotted line through the stress data correspond to a fit of the free energy data to a fourth-order polynomial and the derivative of that polynomial, respectively. The

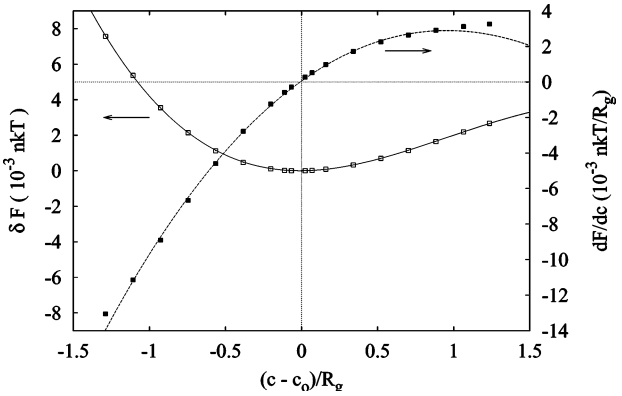

Figure 1. Calculated free energy per chain (open squares) and its perturbatively calculated derivative dF/dc (closed squares) vs the unit cell length c of a diblock copolymer tetragonal $I4/mmm$ crystal that is obtained by extending a body-centered $Im\bar{3}m$ equilibrium crystal along its c axis while keeping the cell lengths along the two perpendicular axes constant at the equilibrium value c_0, for a copolymer with equal statistical segment lengths, $f_a = 0.25$, $\chi N = 20.0$. The solid and dotted lines are a fourth-order polynomial fit to $F(c)$ and the derivative of this polynomial, respectively.

agreement of this fit with data for both F and dF/dc confirms the correctness of the perturbation theory for dF/dc.

Though we focus here on the spectral method, it is also possible to perturbatively calculate the stress using a finite-difference or finite-element spatial discretization of eq 1. Equation 19 for the stress is completely generic and independent of the method used to discretize the SCFT equations, as is eq 21 for the perturbation $\delta\hat{H}_\alpha$ induced by an affine change of coordinates. To calculate the desired change in Q within a spatial discretization, one could solve a discretization of

$$\left[\frac{\partial}{\partial s} + \hat{H}_{\alpha(s)}\right]|\delta q(s)\rangle = -\delta\hat{H}_{\alpha(s)}|q(s)\rangle \tag{39}$$

for the perturbation $|\delta q(s)\rangle$, using a solution of the corresponding homogeneous equation for the unperturbed solution $|q(s)\rangle$ and using eqs 20 and 21 to calculate the perturbation $\delta\hat{H}_\alpha$. In a discretization that uses a regular grid for the dimensionless variable $\tilde{\mathbf{r}}$, the operator $\delta\hat{H}_\alpha$ may also be calculated from the discretized equations by considering deformation-induced changes in the values of the coefficients needed to calculate a discretized Laplacian from the values of $q(\tilde{\mathbf{r}},s)$ at a set of nearby grid points. The time required to calculate $\delta q(\mathbf{r},N)$ by integrating the above would be very similar to that required to calculate the unperturbed $q(\tilde{\mathbf{r}},s)$ or about half that required to calculate both q and $q^\dagger$.

5. Equilibration of the Unit Cell

The calculation of the stress presented above may be used to accelerate a numerical search for a solution of the SCFT with an equilibrium unit cell. The simplest way to search for the equilibrium set of unit cell parameters is to repeatedly iterate the SCFT equations for the ω fields to convergence for a sequence of fixed unit cells, using some sort of minimization algorithm (e.g., a conjugate gradient method) to guide the choice of a sequence of trial unit cells. Implementation of the above perturbation theory would allow the use of a minimization algorithm that makes use of values of the derivatives of a function with respect to its arguments,

at little added computational cost per iteration, and thereby accelerate the search for a minimum.

Alternatively, one can carry out the search for an equilibrium unit cell simultaneously with the solution of the SCFT equations. We propose a fully coupled spectral algorithm in which the unknown coefficients of the ω fields in a spectral expansion and the unit cell parameters are iterated simultaneously to find a simultaneous solution of the self-consistency condition of eq 5, the incompressibility constraint of eq 6, and the mechanical equilibrium condition of eq 8. This may be accomplished by a Newton−Raphson (or quasi-Newton) iteration, in which the unit cell parameters θ_i are added to the coefficients of the ω fields as unknowns and in which the equations

$$\frac{\partial \ln Q}{\partial \theta_i} = 0 \tag{40}$$

for each of the unit cell parameters are added to the list of residual equations. The Jacobian for the resulting set of residuals may be calculated numerically, by calculating the changes in the residuals produced by changes in each of the unit cell parameters and changes in each of the coefficients of the ω fields, or evaluated in some approximate method, and the unknowns updated accordingly.

Initial calculations for noncubic crystals have provided encouraging results for the efficiency and robustness of this approach. We have simultaneously solved the SCFT equations and zero-stress condition for a network structure with an orthorhombic *Fddd* space group, a proposed structure for the noncubic networks observed in triblock copolymers.[4] As an example, we have considered a model system corresponding to poly(isoprene-*b*-styrene-*b*-ethylene oxide) (ISO), the system in which this noncubic network phase was initially observed, with volume fractions $f_I = 0.33$, $f_S = 0.49$, and $f_O = 0.18$, statistical segment lengths in the ratios $(b_I:b_S:b_O) = (1.00:0.90:1.28)$, and Flory−Huggins interaction parameters $\chi_{IS}N = 17$, $\chi_{IO}N = 43$, and $\chi_{SO}N = 13$. A detailed discussion of phase behavior in this parameter region will be given elsewhere. Here, we discuss only the equilibration of this proposed structure as a test of our algorithm. As an initial guess, we use a converged SCFT solution for the *Fddd* phase where the ratios of unit cell parameters are those in the structural model proposed by Bailey et al., $(a:b:c) = (1:\sqrt{3}:2\sqrt{3})$, with a length $a = 4.5R_g$ chosen to minimize the free energy subject to this constraint on the ratios of cell parameters. A calculation of the equilibrium orthorhombic cell by the method described above, in which all three cell dimensions are allowed to vary independently, then converged in six iterations to a unit cell with $(a:b:c) = (1.00:1.97:3.61)$ and $a = 4.7R_g$, causing changes of 5−20% in a, b, and c. The combined iteration of the ω fields and the unit cell parameters is generally found to converge in approximately the same number of iterations as that required to converge the ω fields in a fixed unit cell. We also find that the combined iteration is often more robust than the solution of the SCFT equations in a fixed nonequilibrium unit cell when using a converged solution for the ω fields in a slightly different unit cell as an initial guess: in the above example, quasi-Newton iteration of ω alone in a unit cell with equilibrium cell dimensions fails to converge from the same initial guess as that used in the combined iteration.

6. Conclusion

We have presented a perturbation theory to calculate the stress in SCFT by spectral methods. The time required to calculate the stress is significantly less than that required to calculate the density and free energy and also scales as the number of basis functions cubed. Perturbative calculation of the stress should provide a more efficient and accurate method of characterizing the elasticity of block copolymer crystals than that used in our previous work on this subject,[7] in which moduli were extracted from numerically calculated second derivatives of the free energy. By requiring that the stress vanish at equilibrium, we have constructed an algorithm for simultaneous iteration of the unit cell parameters and chemical potential fields, which allows us to find solutions with an equilibrated unit cell in a time comparable to that required to solve the SCFT equations for a fixed unit cell.

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References and Notes

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