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Nature of anisotropic fluctuation modes in ordered polymeric phases

An-Chang Shi* and Jaan Noolandi
Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, Ontario L5K 2L1, Canada

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The nature of anisotropic fluctuation modes in an ordered polymeric system is analysed using general symmetry arguments. It is shown that the anisotropic fluctuation modes in a periodic phase can be classified using a wave vector within the irreducible Brillouin zone and a band index. The spatial profiles of the fluctuation modes are described by Bloch functions which are plane waves modulated by periodic functions. These general statements enable the study of the stability and kinetic pathway of complex ordered polymeric structures. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: anisotropic fluctuations; stability of ordered phases; band structure)

INTRODUCTION

In the history of physics, great progress and/or deep insight into a new problem were often obtained by making an analogy with known problems. Examples in polymer physics include the genesis of the now widely used Edwards model[1], which has its roots in quantum electrodynamics[2]; and the relationship between polymer statistics and critical phenomena[3], which allows the application of the renormalization principles and techniques to polymers. Great progress has also been obtained by using the analogy between ideal polymer chain statistics under external potentials and a quantum mechanical problem[3]. In this paper, anisotropic fluctuation modes in ordered polymeric phases are analysed by exploiting an analogy with solid state physics[4] of an electron in a crystalline solid. It is well known that, due to the translational symmetry of the crystal structures, the electronic energy forms a band structure[4]. It will be shown that, for a polymeric ordered periodic structure, the anisotropic fluctuation modes form a band structure due to the translational symmetry. The fluctuation modes can be classified using a wave vector within the irreducible Brillouin zone and a band index. This cataloguing of fluctuation modes using symmetry provides a powerful tool to study the fluctuations and instability of ordered polymeric structures. Applications of this method to diblock copolymer melts have led to many interesting results[5–9].

In the theory of anisotropic fluctuations in block copolymer ordered phases[6], the derivation of a band structure for the fluctuation modes exploits the analogy between a polymer chain in a periodic potential and an electron in a crystalline solid, *viz.* both systems are described by a Schrödinger equation with a periodic potential. This development may lead to the wrong impression that the band structure in the fluctuation modes is a result of this particular quantum mechanics analogy. However, it must be emphasized that the formation of the band structure is a consequence of the discrete translational symmetry of the ordered periodic structure. Therefore the application of this powerful method is much more general. In this paper the spectrum of Gaussian fluctuations around an ordered phase is analysed using the symmetry argument, leading to the band structure description of the fluctuation modes.

SYMMETRIES AND ANISOTROPIC FLUCTUATIONS

Gaussian fluctuations

In order to study the stability of an ordered structure, it is necessary to consider thermal fluctuations around the ordered phase. In the spirit of density functional theory, the phase behaviour of a polymeric system can be described by a free energy functional $\mathcal{F}(\{\phi\})$ which depends on a set of order parameters $\phi_\alpha(\mathbf{r})$. For an ordered phase, the density profiles $\phi_\alpha^{(0)}$ are periodic functions which are determined by extremizing the free energy functional, leading to the mean-field equations

$$\left.\frac{\partial\mathcal{F}}{\partial\phi_\alpha(\mathbf{r})}\right|_{\phi_\alpha^{(0)}}=0 \tag{1}$$

It should be noted that the derivative operators ∂ stand for functional derivatives. The fluctuations around the mean-field ordered state can be described by expanding the order parameters

$$\phi_\alpha(\mathbf{r})=\phi_\alpha^{(0)}(\mathbf{r})+\delta\phi_\alpha(\mathbf{r}) \tag{2}$$

The free energy functional can be expanded around the mean-field solution

$$\mathcal{F}=\mathcal{F}^{(0)}+\delta\mathcal{F}^{(1)}+\delta\mathcal{F}^{(2)}+\ldots \tag{3}$$

where the zeroth order term $\mathcal{F}^{(0)}=\mathcal{F}(\{\phi^{(0)}\})$ is the mean-field free energy, the first-order contribution vanishes $\delta\mathcal{F}^{(1)}=0$ since $\phi_\alpha^{(0)}(\mathbf{r})$ extremizes $\mathcal{F}$, and the higher order contributions are given by functional derivatives of $\mathcal{F}$ evaluated at the mean-field solution

$$\delta\mathcal{F}^{(n)}=\sum_{\alpha_1\ldots\alpha_n}\frac{1}{n!}\int d\mathbf{r}_1\ldots d\mathbf{r}_n\left.\frac{\partial^n\mathcal{F}}{\partial\phi_{\alpha_1}(\mathbf{r}_1)\ldots\partial\phi_{\alpha_n}(\mathbf{r}_n)}\right|_{\phi_\alpha^{(0)}}\times\delta\phi_{\alpha_1}(\mathbf{r}_1)\ldots\delta\phi_{\alpha_n}(\mathbf{r}_n) \tag{4}$$

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* To whom correspondence should be addressed

For the study of the stability of the ordered phases, it is useful to consider the second-order (Gaussian fluctuation) contributions, which quantify the free energy cost of fluctuations at this order. In particular, if this free energy cost is positive, then the ordered phase is stable. The condition that $\mathcal{F}^{(2)} = 0$ determines the spinodal point of the ordered phase.

The Gaussian fluctuations in an ordered phase are formally described by a two-point operator $\hat{C}$

$$\mathcal{F}^{(2)} = \frac{1}{2}\langle \delta\phi, \hat{C}\delta\phi \rangle \equiv \frac{1}{2}\sum_{\alpha\beta}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\hat{C}_{\alpha\beta}(\mathbf{r},\mathbf{r}')\delta\phi_{\alpha}(\mathbf{r})\delta\phi_{\beta}(\mathbf{r}') \tag{5}$$

where the bracket denotes the usual scalar product, $\delta\phi$ denotes a vector with components $\delta\phi_{\alpha}(\mathbf{r})$. For a set of real order parameters, $\hat{C}$ is a linear real symmetric operator with components $\hat{C}_{\alpha\beta}(\mathbf{r},\mathbf{r}')$. If the order parameters are complex, $\hat{C}$ is a linear Hermitian operator because the free energy of the system must be real. The components of $\hat{C}$ are given by the second-order functional derivatives of the free energy functional evaluated at the mean-field solution

$$\hat{C}_{\alpha\beta}(\mathbf{r},\mathbf{r}') = \left.\frac{\partial^2\mathcal{F}}{\partial\phi_{\alpha}(\mathbf{r})\partial\phi_{\beta}(\mathbf{r}')}\right|_{\phi^{(0)}} \tag{6}$$

The fluctuations can now be expressed as a linear combination of eigenfunctions of $\hat{C}$

$$\sum_{\beta}\int \mathrm{d}\mathbf{r}'\hat{C}_{\alpha\beta}(\mathbf{r},\mathbf{r}')\psi_{\lambda}^{\beta}(\mathbf{r}) = \lambda\psi_{\lambda}^{\alpha}(\mathbf{r}) \tag{7}$$

where λ denotes the eigenvalues of $\hat{C}$. Because $\hat{C}$ is in general Hermitian, the eigenvalues λ are real, and the eigenfunctions are orthogonal and normalized $\langle\psi_{\lambda},\psi_{\lambda'}\rangle = \delta_{\lambda,\lambda'}$. Using the eigenfunctions $\psi_{\lambda}(\mathbf{r})$ as the basis functions, the fluctuations $\delta\phi$ can be written

$$\delta\phi_{\alpha}(\mathbf{r}) = \sum_{\lambda}\delta\phi_{\lambda}\psi_{\lambda}^{\alpha}(\mathbf{r}) \tag{8}$$

The Gaussian fluctuation contribution to the free energy can then be expressed using the eigenvalues and eigenfunctions of $\hat{C}$

$$\mathcal{F}^{(2)} = \frac{1}{2}\langle\delta\phi, \hat{C}\delta\phi\rangle = \frac{1}{2}\sum_{\lambda}\lambda|\delta\phi_{\lambda}|^2 \tag{9}$$

The anisotropic fluctuation modes can, therefore, be classified according to eigenfunctions of the operator $\hat{C}$. In particular, the free energy cost of the Gaussian fluctuations is quantified by the eigenvalues of $\hat{C}$. The most important fluctuation mode is the one with the lowest eigenvalue λ_0. The condition $\lambda_0 = 0$ determines the spinodal point (or the instability point) of the ordered phase, and the corresponding eigenfunction ψ_{λ_0} characterizes the spatial profile of the most unstable mode.

From the above derivations, it is obvious that the stability analysis of an ordered polymeric phase using Gaussian fluctuations follows three simple steps: (1) identification of the appropriate order parameters and derivation of the free energy functional; (2) construction of the phase diagram by solving the mean-field equations; (3) construction of the Gaussian fluctuation operator and identification of its eigenvalues and eigenfunctions. These steps are conceptually simple. However, a brute force approach to the problem is usually not efficient because of the complexity of the structure. It is therefore desirable to simplify the problem. In what follows it will be shown that the application of a symmetry argument to the problem provides a powerful method to classify the fluctuation modes.

Using symmetries to classify fluctuation modes

One of the great lessons of classical and quantum mechanics is that the symmetries of a system allow one to make a general statement about the system's behaviour. Because of the mathematical structure developed above, it is not too surprising that symmetry also helps to determine the properties of the anisotropic fluctuation modes in ordered polymeric structures.

In order to study the fluctuation modes in an ordered structure, the eigenvalue problem, $\hat{C}\psi_{\lambda} = \lambda\psi_{\lambda}$, has to be solved. For a general ordered phase, the structure can be quite complex so that it would be hard to solve the eigenvalue problem explicitly. However, it is important to notice that for an ordered structure, the system has certain symmetries. These symmetries can be exploited to give a powerful method for the description of the anisotropic fluctuation modes.

It is helpful to place the above notion in a formal setting using group theory arguments. For an ordered structure, the system is invariant under certain symmetry operations such as translation, rotation, and inversion. The application of these operations on the order parameters is formally described by an operator $\hat{O}$. If a particular symmetric operation is a symmetry of the ordered structure under consideration, then it should not matter whether one operates with $\hat{C}$, or one first performs the symmetric operation, then operates with $\hat{C}$, and then changes them back. Mathematically, this statement can be written as $\hat{C} = \hat{O}^{-1}\hat{C}\hat{O}$. This equation can be rearranged as $[\hat{O},\hat{C}] = \hat{O}\hat{C} - \hat{C}\hat{O} = 0$, where $[\mathcal{A},\mathcal{B}] \equiv \mathcal{A}\mathcal{B} - \mathcal{B}\mathcal{A}$ is defined as the commutator of the two operators $\mathcal{A}$ and $\mathcal{B}$. Therefore if the ordered phase is symmetric under a particular symmetry operation then that symmetry operator commutes with $\hat{C}$, i.e. $[\hat{O},\hat{C}] = 0$. The operation of this commutator on any eigenfunction ψ_{λ} of $\hat{C}$ leads to $[\hat{O},\hat{C}]\psi_{\lambda} = \hat{O}(\hat{C}\psi_{\lambda}) - \hat{C}(\hat{O}\psi_{\lambda}) = 0$, which can be rewritten as

$$\hat{C}(\hat{O}\psi_{\lambda}) = \hat{O}(\hat{C}\psi_{\lambda}) = \lambda(\hat{O}\psi_{\lambda}) \tag{10}$$

Therefore if ψ_{λ} is an eigenfunction of $\hat{C}$ with eigenvalue λ, then $\hat{O}\psi_{\lambda}$ is also an eigenfunction of $\hat{C}$ with the same eigenvalue λ. If there is no degeneracy, then there can only be one eigenfunction with eigenvalue λ, so that ψ_{λ} and $\hat{O}\psi_{\lambda}$ can be different only by a multiplicative factor η

$$\hat{O}\psi_{\lambda} = \eta\psi_{\lambda} \tag{11}$$

However, this equation is just the eigenvalue equation for the operator $\hat{O}$. Therefore, the eigenfunctions ψ_{λ} can be catalogued using the eigenvalues η of the symmetry operator $\hat{O}$. In the case of degenerate modes, it is always possible to form linear combinations of the degenerate modes to make eigenfunctions of the symmetry operator $\hat{O}$. Generally speaking, whenever two operators commute, one can construct simultaneous eigenfunctions of both operators. This is very convenient, since eigenfunctions and eigenvalues of simple symmetry operators are easily determined, whereas those for $\hat{C}$ are not. But if $\hat{C}$ commutes with a symmetry operator $\hat{O}$, we can construct and catalogue the eigenfunctions of $\hat{C}$ using their $\hat{O}$ properties. In the rest of this section the application of this approach using the space group symmetries of an ordered phase will be considered.

Continuous translation symmetry. One symmetry that a polymeric system can have is continuous translation symmetry, *viz.* a homogeneous disordered phase. This phase is unchanged if everything is translated through the same distance in a certain direction. Given this information, the functional form of the fluctuation modes can be determined. It is noted that the disordered phase has the highest possible symmetry for a polymeric system. The ordered structures are obtained by breaking the symmetry of the disordered phase.

A structure with translational symmetry is unchanged by a translation through a displacement **d**. For each **d**, a translational operator $\hat{\mathcal{T}}_{\mathbf{d}}$ can be defined. When operating on a function $f(\mathbf{r})$, $\hat{\mathcal{T}}_{\mathbf{d}}$ shifts the argument by **d**, $\hat{\mathcal{T}}_{\mathbf{d}} f(\mathbf{r}) = f(\mathbf{r}+\mathbf{d})$. If the structure under consideration has continuous translational symmetry, then $\hat{\mathcal{T}}_{\mathbf{d}}$ commutes with $\hat{\mathcal{C}}$, $[\hat{\mathcal{T}}_{\mathbf{d}}, \hat{\mathcal{C}}] = 0$. The fluctuation modes of $\hat{\mathcal{C}}$ can now be classified according to how they behave under $\hat{\mathcal{T}}_{\mathbf{d}}$. In order to proceed, the eigenfunctions of the translational operator $\hat{\mathcal{T}}_{\mathbf{d}}$ have to be obtained. It is easy to prove that the plane waves $\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}}$ are eigenfunctions of any translational operator

$$\hat{\mathcal{T}}_{\mathbf{d}} \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}} = \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot(\mathbf{r}+\mathbf{d})} = (\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{d}})\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}} \tag{12}$$

The corresponding eigenvalues are $\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{d}}$. The fluctuation modes of the homogeneous system must be eigenfunctions of all the $\hat{\mathcal{T}}_{\mathbf{d}}$s, so they should have the plane wave form $\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}}$. The fluctuation modes in the homogeneous phase can therefore be classified by plane waves with particular values for **q**, the wave vector.

Discrete translation symmetry. For an ordered polymeric phase, the system does not have continuous translational symmetry. Instead, the ordered structure has discrete translational symmetry. That is, it is not invariant under translation of any distance, and it is only invariant under translations of distances that are multiples of some fixed step lengths. The basic step lengths are the lattice constant a_i (i = 1,2,3), and the basic step vectors ($\mathbf{a}_1$,$\mathbf{a}_2$,$\mathbf{a}_3$) are the primitive lattice vectors. Because of the symmetry, the free energy functional of the system satisfies $\mathcal{F}(\mathbf{r}) = \mathcal{F}(\mathbf{r} + \mathbf{a}_i)$. By preparing this translation it can be shown that $\mathcal{F}(\mathbf{r}) = \mathcal{F}(\mathbf{r} + \mathbf{R})$, for any lattice vector **R** that is an integral multiple of $\mathbf{a}_i$, i.e. $\mathbf{R} = l\mathbf{a}_1 + m\mathbf{a}_2 + n\mathbf{a}_3$ where *l*, *m*, *n* are the integers. The repeating unit of the periodic structure is known as the unit cell.

Because of the discrete translational symmetries, the operator $\hat{\mathcal{C}}$ must commute with all of the translation operators defined by the lattice vectors **R**. With this knowledge, the Gaussian fluctuation modes (eigenmodes of $\hat{\mathcal{C}}$) can be identified as simultaneous eigenfunctions of the translation operator $\hat{\mathcal{T}}_{\mathbf{R}}$. As in the homogenous case, these eigenfunctions are plane waves

$$\hat{\mathcal{T}}_{\mathbf{R}} \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}} = \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot(\mathbf{r}+\mathbf{R})} = (\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{R}})\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}} \tag{13}$$

with the corresponding eigenvalues $\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{R}}$. The fluctuation modes can therefore be classified by specifying the wave vector **q**. However, an important difference between the continuous translation symmetry and the discrete translation symmetry is that not all values of **q** yield different eigenvalues. In order to proceed, it is convenient to define reciprocal lattice vectors. The three primitive lattice vectors ($\mathbf{a}_1$,$\mathbf{a}_2$,$\mathbf{a}_3$) give rise to three primitive reciprocal lattice vectors ($\mathbf{b}_1$,$\mathbf{b}_2$,$\mathbf{b}_3$) defined so that $\mathbf{a_i}\cdot\mathbf{b_j} = 2\pi\delta_{\mathbf{ij}}$. A general reciprocal lattice vector is then specified by $\mathbf{G} = l'\mathbf{b}_1 + m'\mathbf{b}_2 + n'\mathbf{b}_3$ where l', m', n' are integers. Considering two modes, one with wave vector **q** and the other with wave vector **q** + **G**, it is obvious that these two modes have the same eigenvalue $\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{R}}$ because $\mathbf{G}\cdot\mathbf{R} = (ll' + mm' + nn')2\pi$ by definition. In fact, all the modes with wave vectors of the form **q** + **G** have the same eigenvalue, therefore they form a degenerate set. Because any linear combination of these degenerate eigenfunctions is itself an eigenfunction with the same eigenvalue, linear combinations of the original modes can be used to construct eigenfunctions of the form

$$\begin{aligned} \psi_{\mathbf{q}}(\mathbf{r}) &= \sum_{\mathbf{G}} c(\mathbf{G})\mathrm{e}^{\mathrm{i}(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \\ &= \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}} \sum_{\mathbf{G}} c(\mathbf{G})\mathrm{e}^{\mathrm{i}\mathbf{G}\cdot\mathbf{r}} = \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}} u_{\mathbf{q}}(\mathbf{r}) \end{aligned} \tag{14}$$

where $c(\mathbf{G})$ are expansion coefficients to be determined by explicit solution, and $u_{\mathbf{q}}(\mathbf{r})$ is a (by construction) periodic function $u_{\mathbf{q}}(\mathbf{r}) = u_{\mathbf{q}}(\mathbf{r} + \mathbf{R})$. The discrete periodicity in the ordered structure leads to an eigenfunction which is simply the product of a plane wave with a periodic function. This result is commonly known as Bloch's theorem[4], and the form of the eigenfunction is known as a Bloch function. One key fact about the Bloch functions is that the Bloch function with wave vector **q** and the Bloch function with wave vector **q** + **G** are identical. The **q**s that differ by a reciprocal lattice vector **G** are not different from a physical point of view. Furthermore, the eigenvalues of the fluctuation modes must also be periodic in **q**: $\lambda(\mathbf{q}) = \lambda(\mathbf{q} + \mathbf{G})$. Therefore there is a lot of redundancy in the label **q**. Because of the periodicity in **q**, attention can be restricted to a finite zone in the reciprocal space in which one cannot get from one part of the volume to another by adding any reciprocal lattice vectors **G**. All values of **q** that lie outside this zone, by definition, can be reached from within the zone by adding a reciprocal lattice vector **G**, and therefore are redundant labels. This zone is known as the Brillouin zone. The Gaussian fluctuation modes in a three-dimensional periodic structure are Bloch functions that can be labelled by a wave vector, $\mathbf{k} = k_1\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3$, which lies in the Brillouin zone. Each value of the wave vector inside the Brillouin zone identifies an eigenfunction of $\hat{\mathcal{C}}$ with eigenvalue $\lambda(\mathbf{k})$ and an eigenfunction of the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) \tag{15}$$

where $u_{\mathbf{k}}(\mathbf{r})$ is a periodic function of the lattice $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R})$ for all lattice vectors **R**.

From very general symmetry principles, we arrive at the conclusion that the fluctuation modes in an ordered polymeric structure with discrete periodicity in three dimensions can be written as Bloch functions. All of the information about such a mode is given by the wave vector within the Brillouin zone and the periodic function $u_{\mathbf{k}}(\mathbf{r})$. The periodic function $u_{\mathbf{k}}(\mathbf{r})$ is obtained by solving for the original eigenvalue problem

$$\sum_{\beta} \int \mathrm{d}\mathbf{r}' \mathrm{e}^{-\mathbf{k}\cdot\mathbf{r}} \hat{\mathcal{C}}_{\alpha\beta}(\mathbf{r},\mathbf{r}') \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}'} u^{\beta}_{\mathbf{k}}(\mathbf{r}') = \lambda(\mathbf{k}) u^{\alpha}_{\mathbf{k}}(\mathbf{r}) \tag{16}$$

subjected to periodic condition $u^{\alpha}_{\mathbf{k}}(\mathbf{r}) = u^{\alpha}_{\mathbf{k}}(\mathbf{r} + \mathbf{R})$. The function $u_{\mathbf{k}}(\mathbf{r})$, and therefore the eigenmode profiles, are determined by the above eigenvalue problem. because of the periodic condition, the eigenvalue problem can be regarded as restricted to a single unit cell of the periodic structure. As a general mathematical observation, restricting an eigenvalue problem to a finite volume leads to a discrete spectrum of eigenvalues. For each value of **k**, the eigenvalues $\lambda(\mathbf{k})$ are, therefore, expected to form an infinite set with discretely spaced eigenvalues, which can be labelled with the band index n, $\lambda(\mathbf{k}) = \lambda_n(\mathbf{k})$. Since $\mathbf{k}$ enters only as a parameter in the eigenvalue problem, the eigenvalue of each band, for given n, varies continuously as $\mathbf{k}$ varies. Therefore, the fluctuation modes of an ordered polymeric system are described by a family of continuous functions, $\lambda_n(\mathbf{k})$, indexed in order of increasing value by the band number. The information contained in these functions forms the band structure description of the anisotropic fluctuations in an order polymeric phase.

Point group symmetry and the irreducible Brillouin zone. An ordered polymeric phase may have symmetries other than discrete translations. A given periodic structure may also be invariant under other symmetry operations such as rotations, mirror reflections, or inversions. This particular set of symmetry operations forms the point group of the periodic structure. The symmetry of an ordered phase is completely specified by the point group symmetry and the translation symmetry, i.e. by specifying its space group. A few conclusions can be drawn about the fluctuation modes of a system with rotational symmetry. Suppose the operator $\mathcal{R} = \mathcal{R}(\hat{\mathbf{n}}, \theta)$ rotates vectors by an angle θ about the $\hat{\mathbf{n}}$ axis. The operator $\hat{O}_{\mathcal{R}}$ on a scalar function $f(\mathbf{r})$ is defined by $\hat{O}_{\mathcal{R}} f(\mathbf{r}) = f(\mathcal{R}^{-1}\mathbf{r})$. If rotation by $\mathcal{R}$ leaves the system invariant, the operator $\hat{C}$ must commute with $\hat{O}_{\mathcal{R}}$, i.e. $[\hat{C}, \hat{O}_{\mathcal{R}}] = 0$. This immediately leads to

$$\hat{C}(\hat{O}_{\mathcal{R}}\psi_{n\mathbf{k}}(\mathbf{r})) = \hat{O}_{\mathcal{R}}(\hat{C}\psi_{n\mathbf{k}}(\mathbf{r})) = \lambda_n(\mathbf{k})(\hat{O}_{\mathcal{R}}\psi_{n\mathbf{k}}(\mathbf{r})) \qquad (17)$$

Therefore the function $(\hat{O}_{\mathcal{R}}\psi_{n\mathbf{k}}(\mathbf{r}))$ also satisfies the eigenvalue problem with the same eigenvalue $\lambda_n(\mathbf{k})$ as $\psi_{n\mathbf{k}}(\mathbf{r})$. This means that the rotated mode is also an eigenmode with the same eigenvalue. It can further be shown that the state $(\hat{O}_{\mathcal{R}}\psi_{n\mathbf{k}}(\mathbf{r}))$ is the Bloch state with wave vector $\mathcal{R}\mathbf{k}$ by applying $\hat{\mathcal{T}}_{\mathbf{R}}$[4]. Since $(\hat{O}_{\mathcal{R}}\psi_{n\mathbf{k}}(\mathbf{r}))$ is the Bloch function with wave vector $\mathcal{R}\mathbf{k}$ and has the same eigenvalue as $\psi_{n\mathbf{k}}(\mathbf{r})$, it follows that the eigenvalue $\lambda_n(\mathbf{k})$ has the rotational symmetry $\lambda_n(\mathcal{R}\mathbf{k}) = \lambda_n(\mathbf{k})$. It can then be concluded that when there is rotational symmetry in the ordered structure, the eigenvalue band $\lambda_n(\mathbf{k})$ has additional redundancies within the Brillouin zone. Similarly, whenever an ordered phase has point group symmetries (rotations, mirror reflections, or inversions), the eigenvalue bands have those symmetries as well. Since $\lambda_n(\mathbf{k})$ possesses the full symmetry of the point group, it is not necessary to consider them at every $\mathbf{k}$-point in the Brillouin zone. The smallest region within the Brillouin zone for which the $\lambda_n(\mathbf{k})$ are not related by symmetry is called the irreducible Brillouin zone.

In summary, the Gaussian fluctuations in an ordered polymeric phase are described by a linear Hermitian operator $\hat{C}$ whose components are given by the second-order functional derivatives of the free energy functional evaluated at the mean-field solution. The space group symmetries of the ordered phases ensure that the eigenvalues of this operator $\hat{C}$ can be labelled by a wave vector within the irreducible Brillouin zone and a band index n. The eigenfunctions of this operator have the form of Bloch functions

$$\psi^{\alpha}_{n\mathbf{k}}(\mathbf{r}) = \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \qquad (18)$$

where $u_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R})$ is a periodic function. Explicit solutions of the eigenvalues and eigenfunctions are obtained by solving the eigenvalue problem

$$\sum_{\beta} \int \mathrm{d}\mathbf{r}' \hat{C}_{\alpha\beta}(\mathbf{r}, \mathbf{r}')\psi^{\beta}_{n\mathbf{k}}(\mathbf{r}') = \lambda_n(\mathbf{k})\psi^{\alpha}_{n\mathbf{k}}(\mathbf{r}) \qquad (19)$$

where $\lambda_n(\mathbf{k})$ denotes the eigenvalues of $\hat{C}$, and they form a band structure. The eigenfunctions are orthogonal and normalized

$$\langle \psi_{n\mathbf{k}}, \psi_{n\mathbf{k}'} \rangle = \delta_{n,n'}\delta(\mathbf{k} - \mathbf{k}') \qquad (20)$$

so that the fluctuations $\delta\phi$ can be expanded using these eigenmodes

$$\delta\phi_{\alpha}(\mathbf{r}) = \sum_{n\mathbf{k}} \delta\phi_{n\mathbf{k}}\psi^{\alpha}_{n\mathbf{k}}(\mathbf{r}) \qquad (21)$$

The Gaussian fluctuation contribution to the free energy can then be expressed using the eigenvalues of $\hat{C}$

$$\mathcal{F}^{(2)} = \frac{1}{2}\sum_{n\mathbf{k}} \lambda_n(\mathbf{k})|\delta\phi_{n\mathbf{k}}|^2$$

The anisotropic fluctuations are therefore quantified by the eigenvalue band $\lambda_n(\mathbf{k})$. The smallest eigenvalue $\lambda_0(\mathbf{k}_0)$ determines the stability of the ordered phase: if $\lambda_0(\mathbf{k}_0) > 0$, the ordered phase is stable; and if $\lambda_0(\mathbf{k}_0) < 0$, the ordered phase is unstable. The condition that $\lambda_0(\mathbf{k}_0) = 0$ defines the spinodal point of the system. The profiles of the fluctuation modes are characterized by the eigenfunctions $\psi^{\alpha}_{n\mathbf{k}}(\mathbf{r})$. In particular, the most unstable mode, $\psi^{\alpha}_{0\mathbf{k}_0}(\mathbf{r})$, corresponding to the smallest eigenvalues, characterizes the initial kinetics of the order–order phase transitions. The application of the stability analysis to diblock copolymer ordered phases have been carried out[5–9].

LANDAU–BRAZOVSKII THEORY: A SIMPLE EXAMPLE

Because the above derivations are based on general symmetry arguments, the conclusions concerning the nature of anisotropic fluctuation modes are applicable to all systems with periodic structures. In this section, the utility of the theory is illustrated by considering a simple example, the Landau–Brazovskii (LB) theory for weak crystallization. This theory is a general framework for systems undergoing a phase transition driven by a short wavelength instability between the disordered liquid and ordered crystalline phases. Therefore this theory can be applied to thermotropic and lyotropic liquid crystals, as well as diblock copolymers[10]. Within mean-field approximation, it has been shown that the LB theory can account for many ordered structures such as the lamellar, cylindrical, and spherical phases[10]. In what follows the stability analysis of the ordered structures is outlined and applied to simple lamellar phase. A complete stability analysis of the different ordered phases with LB theory is beyond the scope of this paper and will be presented in future publications. The LB free energy functional is written

$$\mathcal{F}(\{\phi\}) = \int \mathrm{d}\mathbf{r} \left\{ \frac{\xi_0^2}{8q_0^2}[(\nabla^2 + q_0^2)\phi(\mathbf{r})]^2 + \frac{\tau}{2}[\phi(\mathbf{r})]^2 - \frac{\gamma}{3!}[\phi(\mathbf{r})]^3 + \frac{\mu}{4!}[\phi(\mathbf{r})]^4 \right\} \qquad (22)$$

where $\phi(\mathbf{r})$ is the order parameter characterizing the composition profiles, τ is the reduced temperature, q_0 is the critical wavelength, ξ_0 is the bare correlation length, and γ and μ are phenomenological constants $\mu > 0$.

We now follow the recipe outlined above to study the stability of the ordered phases within the LB theory. The first step of the study is to determine the mean-field solutions. The mean-field equation for the system can be derived easily by requiring $\mathcal{F}^{(1)} = 0$

$$\frac{\xi_0^2}{4q_0^4}(\nabla^2 + q_0^2)^2\phi_0(\mathbf{r}) + \tau\phi_0(\mathbf{r}) - \frac{\gamma}{2}[\phi_0(\mathbf{r})]^2 + \frac{\mu}{3!}[\phi_0(\mathbf{r})]^3 = 0 \tag{23}$$

In general, the mean-field solution is specified by a set of reciprocal space lattice vectors $\{\mathbf{G}\}$ and the corresponding plane wave amplitudes $\phi_0(\mathbf{G})$, $\phi_0(\mathbf{r}) = \sum_{\{\mathbf{G}\}}\phi_0(\mathbf{G})\mathrm{e}^{\mathrm{i}\mathbf{G}\cdot\mathbf{r}}$, which are obtained by solving the mean-field equation. The corresponding mean-field free energy is given by

$$\mathcal{F}^{(0)} = \int \mathrm{d}\mathbf{r} \left\{ \frac{\xi_0^2}{8q_0^2}[(\nabla^2 + q_0^2)\phi_0(\mathbf{r})]^2 + \frac{\tau}{2}[\phi_0(\mathbf{r})]^2 - \frac{\gamma}{3!}[\phi_0(\mathbf{r})]^3 + \frac{\mu}{4!}[\phi_0(\mathbf{r})]^4 \right\} \tag{24}$$

The mean-field free energy must be minimized with respect to the periodicity of the structure to obtain the equilibrium lattice spacing. Mean-field solutions for different ordered structures have been obtained[10]. In general, the mean-field equations have to be solved numerically.

The second step of the study is to construct the two-point correlation operator $\hat{C}(\mathbf{r}, \mathbf{r}')$ using the mean-field solution. For the LB theory, it is easy to show that the operator $\hat{C}(\mathbf{r}, \mathbf{r}')$ has the form $\hat{C}(\mathbf{r}, \mathbf{r}') = \hat{C}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')$, where

$$\hat{C}(\mathbf{r}) = \frac{\xi_0^2}{4q_0^2}(\nabla^2 + q_0^2)^2 + \tau + V(\mathbf{r}) \tag{25}$$

where $V(\mathbf{r}) \equiv -\gamma\phi_0(\mathbf{r}) + 0.5\mu[\phi_0(\mathbf{r})]^2 = \sum_{\{\mathbf{G}\}}V(\mathbf{G})\mathrm{e}^{\mathrm{i}\mathbf{G}\cdot\mathbf{r}}$ is a periodic function determined by the mean-field solution. It should be noted that, in general, the $\hat{C}$ operator has a dimension determined by the set of reciprocal lattice vectors used in the analysis.

The third step of the study is to obtain the eigenvalue band $\lambda_n(\mathbf{k})$ and eigenfunctions $\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}\mathbf{u}_\mathrm{n}}\mathbf{k}(\mathbf{r})$ of the operator $\hat{C}(\mathbf{r})$ by solving

$$\left[\frac{\xi_0^2}{4q_0^2}(\nabla^2 + q_0^2)^2 + \tau + V(\mathbf{r})\right]\psi_{n\mathbf{k}}(\mathbf{r}) = \lambda_n(\mathbf{k})\psi_{n\mathbf{k}}(\mathbf{r}) \tag{26}$$

This eigenvalue problem can be simplified by using the fact that the eigenfunctions must be Bloch functions $\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\{\mathbf{G}\}}u_{n\mathbf{k}}(\mathbf{G})\mathrm{e}^{\mathrm{i}(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$. The eigenvalue problem can now be cast into a linear eigenvalue problem

$$\left[\frac{\xi_0^2}{4q_0^2}((\mathbf{k} + \mathbf{G})^2 - q_0^2)^2 + \tau - \lambda_n(\mathbf{k})\right]u_{n\mathbf{k}}(\mathbf{G}) + \sum_{\{\mathbf{G}'\}}V(\mathbf{G}')u_{n\mathbf{k}}(\mathbf{G} - \mathbf{G}') = 0 \tag{27}$$

The stability line of the ordered structure can now be determined by the condition $\lambda_0(\mathbf{k}) = 0$. The corresponding most unstable modes can then be used to identify kinetic pathways of the order–order phase transitions.

In general, the eigenvalue problem defined above has to be solved numerically to obtain eigenvalues $\lambda_n(\mathbf{k})$ and the eigenfunctions $u_{n\mathbf{k}}(\mathbf{G})$. However, for weakly ordered structures, the potential $V(\mathbf{r})$ is small and it is possible to calculate the eigenvalue and eigenfunctions using perturbation theory[6]. For a homogeneous phase, the order parameter vanishes so that $V(\mathbf{r}) = 0$. The eigenvalue of the two-point correlation operator is easily found for the disordered phase

$$\lambda^{(0)}(\mathbf{k}) = \frac{\xi_0^2}{4q_0^2}(\mathbf{k}^2 - q_0^2)^2 + \tau$$

The smallest eigenvalue occurs at a spherical shell specified by $k = q_0$ for the homogeneous phase. For a weakly ordered structure, there are two types of contributions from the periodic potential $V(\mathbf{r}) = \sum_{\{\mathbf{G}\}}V(\mathbf{G})\mathrm{e}^{\mathrm{i}\mathbf{G}\cdot\mathbf{r}}$. When the zeroth order eigenvalue $\lambda^{(0)}(\mathbf{k})$ is non-degenerate, the correction from the periodic potential is of the order of $|V(\mathbf{G})|^2$. However, when the zeroth order eigenvalue is degenerate, the correction becomes of the order of $|V(\mathbf{G})|$, and, more importantly, a gap appears at the degenerate point. The degeneracy occurs at the Brillouin zone boundaries. Specifically, when the wave vector $\mathbf{k}$ lies on a Bragg plane defined by $\mathbf{k}^2 = (\mathbf{k} - \mathbf{G})^2$, the eigenvalue of $\hat{C}$ has the form $\lambda^{(0)}(\mathbf{k}) \pm |V(\mathbf{G})|$. The periodic potential has two effects on the eigenvalues, the eigenvalue spectrum becomes anisotropic and the smallest eigenvalue now occurs at the points specified by the conditions $k = q_0$ and $\mathbf{k}^2 = (\mathbf{k} - \mathbf{G})^2$, where $\mathbf{G}$ corresponds to the largest value of $|V(\mathbf{G})|$.

It is informative to apply the above results to a specific example, the weakly ordered lamellar phase in which the largest potential component occurs at the first harmonics defined by $\mathbf{G} = (0,0, \pm q_0)$. The zone boundary is then defined by the condition $k_z = \pm q_0/2$. The smallest eigenvalue $\lambda_0(\mathbf{k})$ occurs at the point defined by $k_x^2 + k_y^2 = 0.75q_0^2$. Therefore the most unstable modes occur at two rings defined by $k_x^2 + k_y^2 = 0.75q_0^2$ and $k_z = \pm q_0/2$. These predictions have been confirmed in the exact numerical calculations[5]. It should be noted that the most unstable fluctuation modes for the lamellar phase are infinitely degenerate. This feature of the fluctuation modes has been used to explain the occurrence of the modulated layered structure[7–9].

CONCLUSIONS AND DISCUSSION

Using general symmetry arguments, it has been shown that for an ordered polymeric structure, the anisotropic fluctuation modes can be catalogued by a wave vector $\mathbf{k}$ within the irreducible Brillouin zone and band index n. The eigenvalues of the Gaussian fluctuation operator form a band structure, similar to the electronic energy band structure in crystalline solids. The fluctuation modes are described by the Bloch functions, which are plane waves modulated by periodic functions. What is emerging from these general statements is a powerful technique of classifying the anisotropic fluctuation modes in an ordered polymeric phase. The stability and kinetic pathways of the polymeric ordered phases can be analysed using the Gaussian fluctuation modes.

The band structure description of the fluctuation modes is obtained from the observation that the eigenfunctions of the Gaussian fluctuation operator $\hat{C}$ are also eigenfunctions of the space group symmetry operator $\hat{O}$. However, this observation only provides a method to classify the eigenfunctions of $\hat{C}$, i.e. it states that the eigenfunctions must assume the form of a Bloch function. In order to obtain explicit eigenvalues and eigenfunctions the eigenvalue equations have to be solved. Although the symmetry arguments do not solve the eigenvalue problem completely, the solution of the eigenvalue problem is greatly simplified. The band structure description of the anisotropic Gaussian fluctuation modes provides a powerful method to catalogue the fluctuation modes, as demonstrated in the stability analysis of diblock copolymer ordered phases[7,8].

It should be emphasized that the symmetry arguments are not restricted to polymeric systems. The same general statements on the nature of anisotropic fluctuation modes can be applied to any ordered systems. In particular, the application is expected of the fluctuation mode analysis to the structural relationships between different ordered phases in other self-assembling amphiphilic systems[11] such as the non-ionic surfactant system[12].

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