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1999 J. Phys.: Condens. Matter 11 10183

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## Nature of anisotropic fluctuation modes in ordered systems

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Received 11 August 1999

**Abstract.** The nature of anisotropic fluctuation modes in an ordered 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. These general features enable a study of the stability and kinetic pathway of complex ordered polymeric structures to be carried out. The utility of the theory is illustrated using the Landau–Brazovskii theory of weak crystallization.

### 1. Introduction

A wide variety of physical–chemical systems display ordered structures, ranging from classical crystalline solids to self-assembling soft materials. In soft materials such as block copolymers, surfactant solutions, and colloidal suspensions, structural order over many length scales can be formed, providing a versatile means to create nanostructures with potential applications in biomaterials, optics, and microelectronics. These materials form ordered structures on scales from a few to hundreds of nanometres. Monodisperse, charged colloidal suspensions can assemble three-dimensional crystals [1]. Surfactant systems form a variety of morphologies and can be used as templates to prepare nanostructured solid materials [2]. Block copolymers display a fascinating array of nanostructures [3]. These soft-matter systems have the desirable feature that their morphology can be systematically controlled by changing the molecular parameters. For example, diblock copolymers can form cubic arrays of spheres, hexagonal arrays of cylinders, bicontinuous cubic phases, or lamellae, depending on the relative block lengths [3]. In order to control the formation of the different ordered structures, it is essential to understand their stabilities and structural relations. Traditionally, the structure and phase transitions are studied using mean-field theory, which ignores thermal fluctuations. The stability of the ordered structure is, however, determined by fluctuations around the mean-field theory. In particular, the Gaussian fluctuation spectrum determines the spinodal of the ordered structure. It is therefore desirable to develop theoretical methods beyond the mean-field approximation for the study of anisotropic fluctuations in ordered phases. As will be shown below, the theoretical formulation of Gaussian fluctuations in an ordered phase is straightforward. However, a brute force approach to the problem is not efficient because of the complexity of the ordered structure. It is therefore desirable to understand the origin and nature of the anisotropic fluctuation modes. In what follows, an anisotropic fluctuation theory is developed by exploiting the analogy of thermal fluctuations in a periodic potential and electronic energy bands in solid-state physics.

In the history of physics, great progress and/or deep insight to a new problem were often obtained by making analogies with known problems. Examples in polymer physics include the genesis of the now widely used Edwards model [4], which has its root in quantum electrodynamics [5]; and the relationship between polymer statistics and critical phenomena [6], 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 [6]. In this paper, anisotropic fluctuation modes in ordered phases are analysed by exploiting an analogy with the solid-state physics [7] 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 [7]. It will be shown that, for an 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 for studying the fluctuations and instability of ordered structures. Applications of this method to diblock copolymer melts have led to many interesting results [8–12]. In particular, the anisotropic fluctuation theory allows calculations of the spinodal lines, the most unstable modes, and the scattering functions of the ordered phases. For diblock copolymer melts, it has been found that the one-phase regions of the lamellar, cylindrical, and spherical phases are within their corresponding stability regions. On the other hand, the hexagonally perforated lamellar phase is found to be unstable along the lamellar–cylindrical phase boundary. The most unstable fluctuation modes are identified and used to infer the kinetic pathways of the order–order phase transitions. The scattering functions of all of the diblock copolymer phases are calculated. The theoretical phase behaviour, scattering functions, kinetic pathways of the phase transitions, and the epitaxial relations between the ordered phases are in agreement with comprehensive experimental studies on a variety of diblock copolymer systems [13].

In the theory of anisotropic fluctuation in block copolymer ordered phases [9], 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—that is, 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. The utility of the anisotropic fluctuation theory is demonstrated using a simple example, the Landau–Brazovskii theory of weak crystallization. An account of the general theoretical development is given in [14].

## 2. Symmetries and anisotropic fluctuations

### 2.1. Gaussian fluctuations

In order to study the stability of an ordered structure, it is necessary to consider thermal fluctuations around the ordered phase. In general, the phase behaviour of a statistical mechanics 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

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

The fluctuations around the mean-field ordered state can be described by expanding the order parameters  $\phi_\alpha(\mathbf{r}) = \phi_\alpha^{(0)}(\mathbf{r}) + \delta\phi_\alpha(\mathbf{r})$ . The free-energy functional can be expanded around the mean-field solution  $\mathcal{F} = \mathcal{F}^{(0)} + \delta\mathcal{F}^{(1)} + \delta\mathcal{F}^{(2)} + \dots$ , 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:

$$\delta\mathcal{F}^{(n)} = \sum_{\alpha_1, \dots, \alpha_n} \frac{1}{n!} \int d\mathbf{r}_1 \cdots d\mathbf{r}_n \left. \frac{\delta^n \mathcal{F}}{\delta \phi_{\alpha_1}(\mathbf{r}_1) \cdots \delta \phi_{\alpha_n}(\mathbf{r}_n)} \right|_{\phi^{(0)}} \delta\phi_{\alpha_1}(\mathbf{r}_1) \cdots \delta\phi_{\alpha_n}(\mathbf{r}_n). \quad (2)$$

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, corresponding to a free-energy minimum. 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  $\hat{\mathcal{C}}$  defined through the relation

$$\mathcal{F}^{(2)} = \frac{1}{2} \langle \delta\phi, \hat{\mathcal{C}} \delta\phi \rangle \equiv \frac{1}{2} \sum_{\alpha\beta} \int d\mathbf{r} d\mathbf{r}' \hat{\mathcal{C}}_{\alpha\beta}(\mathbf{r}, \mathbf{r}') \delta\phi_\alpha(\mathbf{r}) \delta\phi_\beta(\mathbf{r}') \quad (3)$$

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

$$\hat{\mathcal{C}}_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \left. \frac{\delta^2 \mathcal{F}}{\delta \phi_\alpha(\mathbf{r}) \delta \phi_\beta(\mathbf{r}')} \right|_{\phi^{(0)}}. \quad (4)$$

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

$$\sum_{\beta} \int d\mathbf{r}' \hat{\mathcal{C}}_{\alpha\beta}(\mathbf{r}, \mathbf{r}') \psi_{\lambda}^{\beta}(\mathbf{r}') = \lambda \psi_{\lambda}^{\alpha}(\mathbf{r}) \quad (5)$$

where  $\lambda$  denotes the eigenvalues of  $\hat{\mathcal{C}}$ . Because  $\hat{\mathcal{C}}$  is in general Hermitian, the eigenvalues  $\lambda$  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 as

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

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

$$\mathcal{F}^{(2)} = \frac{1}{2} \langle \delta\phi, \hat{\mathcal{C}} \delta\phi \rangle = \frac{1}{2} \sum_{\lambda} \lambda |\delta\phi_{\lambda}|^2. \quad (6)$$

The anisotropic fluctuation modes can, therefore, be classified according to eigenfunctions of the operator  $\hat{\mathcal{C}}$ . In particular, the free-energy cost of the Gaussian fluctuations is quantified by the eigenvalues of  $\hat{\mathcal{C}}$ . The most important fluctuation mode is the one with the lowest eigenvalue  $\lambda_0$ . The condition  $\lambda_0 = 0$  determines the spinodal point (or the instability point)

of the ordered phase, and the corresponding eigenfunction  $\psi_{\lambda_0}$  characterizes the spatial profile of the most unstable mode.

From the above derivations, it is obvious that the stability analysis of an ordered 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 symmetry arguments to the problem provides a powerful method for classifying the fluctuation modes.

## 2.2. 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 general statements about the system's behaviour. Because of the mathematical structure developed above, it is not too surprising that symmetry also helps in determining the properties of the anisotropic fluctuation modes in ordered 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 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 to 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  $[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$  is defined as the commutator of the two operators  $\hat{A}$  and  $\hat{B}$ . Therefore the ordered phase is symmetric under a particular symmetry operation only if that symmetry operator commutes with  $\hat{C}$ , i.e.,  $[\hat{O}, \hat{C}] = 0$ . The operation of this commutator on any eigenfunction  $\psi_\lambda$  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  $\hat{C}(\hat{O}\psi_\lambda) = \hat{O}(\hat{C}\psi_\lambda) = \lambda(\hat{O}\psi_\lambda)$ . Therefore if  $\psi_\lambda$  is an eigenfunction of  $\hat{C}$  with eigenvalue  $\lambda$ , then  $\hat{O}\psi_\lambda$  is also an eigenfunction of  $\hat{C}$  with the same eigenvalue  $\lambda$ . If there is no degeneracy, then there can only be one eigenfunction with eigenvalue  $\lambda$ , so  $\psi_\lambda$  and  $\hat{O}\psi_\lambda$  can be different only by a multiplicative factor  $\eta$ ,  $\hat{O}\psi_\lambda = \eta\psi_\lambda$ . However, this relation is just the eigenvalue equation for the operator  $\hat{O}$ . Therefore, the eigenfunction  $\psi_\lambda$  is simultaneously the eigenfunction of the symmetry operator  $\hat{O}$  with eigenvalue  $\eta$ . In the case of degenerate modes, it is always possible to form linear combinations of the degenerate modes to make eigenfunction of the symmetry operator  $\hat{O}$ . Generally speaking, whenever two operators commute, one can construct simultaneous eigenfunctions of the two operators. This is very convenient, since eigenfunctions and eigenvalues of simple symmetry operators are easily determined, whereas those for  $\hat{C}$  are not. 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.

*2.2.1. Continuous translation symmetry.* One symmetry that a condensed matter system can have is continuous translation symmetry, for 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 condensed matter 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  $\mathbf{d}$ . For each  $\mathbf{d}$ , a translational operator  $\hat{T}_{\mathbf{d}}$  can be defined. When operating on a function  $f(\mathbf{r})$ ,  $\hat{T}_{\mathbf{d}}$  shifts the argument by  $\mathbf{d}$ ,  $\hat{T}_{\mathbf{d}}f(\mathbf{r}) = f(\mathbf{r} + \mathbf{d})$ . If the structure under consideration has continuous translational symmetry, then  $\hat{T}_{\mathbf{d}}$  commutes with  $\hat{C}$ ,  $[\hat{T}_{\mathbf{d}}, \hat{C}] = 0$ . The fluctuation modes of  $\hat{C}$  can now be classified according to how they behave under  $\hat{T}_{\mathbf{d}}$ . In order to proceed, the eigenfunctions of the translational operator  $\hat{T}_{\mathbf{d}}$  have to be obtained. It is well known and easy to prove that the plane waves  $e^{i\mathbf{q}\cdot\mathbf{r}}$  are eigenfunctions of any translational operator,  $\hat{T}_{\mathbf{d}}e^{i\mathbf{q}\cdot\mathbf{r}} = e^{i\mathbf{q}\cdot(\mathbf{r}+\mathbf{d})} = (e^{i\mathbf{q}\cdot\mathbf{d}})e^{i\mathbf{q}\cdot\mathbf{r}}$ , with corresponding eigenvalues  $e^{i\mathbf{q}\cdot\mathbf{d}}$ . The fluctuation modes of the homogeneous system must be eigenfunctions of all the  $\hat{T}_{\mathbf{d}}$ s, so they should have the plane-wave form  $e^{i\mathbf{q}\cdot\mathbf{r}}$ . The fluctuation modes in the homogeneous phase can therefore be classified by plane waves with particular values for  $\mathbf{q}$ , the wave vector.

*2.2.2. Discrete translation symmetry.* For an ordered 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 over arbitrary distances. The system is only invariant under translations over distances that are multiples of some fixed step lengths. The basic step lengths are the lattice constants  $a_i$  ( $i = 1, 2, 3$ ), 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 repeating this translation it can be shown that  $\mathcal{F}(\mathbf{r}) = \mathcal{F}(\mathbf{r} + \mathbf{R})$ , for any lattice vector  $\mathbf{R}$  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 integers. The repeating unit of the periodic structure is known as the unit cell.

Because of the discrete translational symmetries, the operator  $\hat{C}$  must commute with all of the translation operators defined by the lattice vectors  $\mathbf{R}$ . With this knowledge, the Gaussian fluctuation modes (eigenmodes of  $\hat{C}$ ) can be identified as simultaneous eigenfunctions of the translation operator  $\hat{T}_{\mathbf{R}}$ . As in the homogeneous case, these eigenfunctions are plane waves:  $\hat{T}_{\mathbf{R}}e^{i\mathbf{q}\cdot\mathbf{r}} = e^{i\mathbf{q}\cdot(\mathbf{r}+\mathbf{R})} = (e^{i\mathbf{q}\cdot\mathbf{R}})e^{i\mathbf{q}\cdot\mathbf{r}}$ , with the corresponding eigenvalues  $e^{i\mathbf{q}\cdot\mathbf{R}}$ . The fluctuation modes can therefore be classified by specifying the wave vector  $\mathbf{q}$ . However, an important difference between the continuous translation symmetry and the discrete translation symmetry is that not all values of  $\mathbf{q}$  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 such that  $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$ . 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  $\mathbf{q}$  and the other with wave vector  $\mathbf{q} + \mathbf{G}$ , it is obvious that these two modes have the same eigenvalue  $e^{i\mathbf{q}\cdot\mathbf{R}}$  because  $\mathbf{G} \cdot \mathbf{R} = (l'l' + mm' + nn')2\pi$  by definition. In fact, all of the modes with wave vectors of the form  $\mathbf{q} + \mathbf{G}$  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

$$\psi_{\mathbf{q}}(\mathbf{r}) = \sum_{\mathbf{G}} c(\mathbf{G}) e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} = e^{i\mathbf{q}\cdot\mathbf{r}} \sum_{\mathbf{G}} c(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} = e^{i\mathbf{q}\cdot\mathbf{r}} u_{\mathbf{q}}(\mathbf{r}) \quad (7)$$

where the  $c(\mathbf{G})$  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 in solid-state physics [7], and the form of the eigenfunction is known as the Bloch function. One key fact about Bloch functions is that the Bloch function with wave vector  $\mathbf{q}$  and the Bloch function with wave vector  $\mathbf{q} + \mathbf{G}$  are identical. The  $\mathbf{q}$ s that differ by a reciprocal-lattice vector  $\mathbf{G}$  are not different from a physical point of view. Furthermore, the eigenvalues of the fluctuation modes must also be periodic in  $\mathbf{q}$ :  $\lambda(\mathbf{q}) = \lambda(\mathbf{q} + \mathbf{G})$ . Therefore there is a lot of redundancy in the label  $\mathbf{q}$ . Because of the periodicity in  $\mathbf{q}$ , 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  $\mathbf{G}$ . All values of  $\mathbf{q}$  that lie outside of this zone, by definition, can be reached from within the zone by adding a reciprocal-lattice vector  $\mathbf{G}$ , 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  $\hat{C}$  with eigenvalue  $\lambda(\mathbf{k})$  and an eigenfunction of the form,  $\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$ , where  $u_{\mathbf{k}}(\mathbf{r})$  is a periodic function on the lattice  $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R})$  for all lattice vectors  $\mathbf{R}$ .

From very general symmetry principles, we have arrived at the conclusion that the fluctuation modes in an ordered 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 original eigenvalue problem

$$\sum_{\beta} \int d\mathbf{r}' e^{-i\mathbf{k}\cdot\mathbf{r}} \hat{C}_{\alpha\beta}(\mathbf{r}, \mathbf{r}') e^{i\mathbf{k}\cdot\mathbf{r}'} u_{\mathbf{k}}^{\beta}(\mathbf{r}') = \lambda(\mathbf{k}) u_{\mathbf{k}}^{\alpha}(\mathbf{r}) \quad (8)$$

subject to the periodicity condition  $u_{\mathbf{k}}^{\alpha}(\mathbf{r}) = u_{\mathbf{k}}^{\alpha}(\mathbf{r} + \mathbf{R})$ . The functions  $u_{\mathbf{k}}(\mathbf{r})$ , and therefore the eigenmode profiles, are determined by the above eigenvalue problem. Because of the periodicity 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  $\mathbf{k}$ , the eigenvalues  $\lambda(\mathbf{k})$  are, therefore, expected to form an infinite set with discretely spaced eigenvalues, which can then 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 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 ordered phase.

**2.2.3. Point group symmetry and the irreducible Brillouin zone.** An ordered 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  $\mathcal{R} = \mathcal{R}(\hat{n}, \theta)$  rotates vectors by an angle  $\theta$  about the  $\hat{n}$ -axis. The operator  $\hat{\mathcal{O}}_{\mathcal{R}}$  acting on a scalar function  $f(\mathbf{r})$  is defined by  $\hat{\mathcal{O}}_{\mathcal{R}}f(\mathbf{r}) = f(\mathcal{R}^{-1}\mathbf{r})$ . If rotation under  $\mathcal{R}$  leaves the system invariant, the operator  $\hat{\mathcal{C}}$  must commute with  $\hat{\mathcal{O}}_{\mathcal{R}}$ , i.e.,  $[\hat{\mathcal{C}}, \hat{\mathcal{O}}_{\mathcal{R}}] = 0$ . This immediately leads to the relation

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

Therefore the function  $\hat{\mathcal{O}}_{\mathcal{R}}\psi_{n\mathbf{k}}(\mathbf{r})$  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 be further shown that the state  $\hat{\mathcal{O}}_{\mathcal{R}}\psi_{n\mathbf{k}}(\mathbf{r})$  is the Bloch state with wave vector  $\mathcal{R}\mathbf{k}$  by applying  $\hat{\mathcal{T}}_{\mathcal{R}}$  [7]. Since  $\hat{\mathcal{O}}_{\mathcal{R}}\psi_{n\mathbf{k}}(\mathbf{r})$  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 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 has those symmetries as well. Since the  $\lambda_n(\mathbf{k})$  possess 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 fluctuation modes in an ordered phase are described by a linear Hermitian operator  $\hat{\mathcal{C}}$  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  $\hat{\mathcal{C}}$  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:

$$\psi_{n\mathbf{k}}^{\alpha}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r}) \quad (9)$$

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

$$\sum_{\beta} \int d\mathbf{r}' \hat{\mathcal{C}}_{\alpha\beta}(\mathbf{r}, \mathbf{r}')\psi_{n\mathbf{k}}^{\beta}(\mathbf{r}') = \lambda_n(\mathbf{k})\psi_{n\mathbf{k}}^{\alpha}(\mathbf{r}) \quad (10)$$

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

$$\langle \psi_{n\mathbf{k}}, \psi_{n\mathbf{k}'} \rangle = \delta_{n,n'}\delta(\mathbf{k} - \mathbf{k}') \quad (11)$$

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

$$\delta\phi_{\alpha}(\mathbf{r}) = \sum_{n\mathbf{k}} \delta\phi_{n\mathbf{k}} \psi_{n\mathbf{k}}^{\alpha}(\mathbf{r}). \quad (12)$$

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

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

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  $\psi_{n\mathbf{k}}^{\alpha}(\mathbf{r})$ . In particular, the most unstable mode,  $\psi_{0\mathbf{k}_0}^{\alpha}(\mathbf{r})$ , corresponding to



the smallest eigenvalues, characterizes the initial kinetics of the order–order phase transitions. Application of the stability analysis to diblock copolymer ordered phases has been carried out [8–12]. In the next section, the utility of the anisotropic fluctuation theory is demonstrated using a simple example, the Landau–Brazovskii theory of weak crystallization.

### 3. Landau–Brazovskii theory: a simple example

Because the above derivations are based on general symmetry arguments, the conclusions concerning the nature of the anisotropic fluctuation modes are applicable to all statistical mechanics 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 [15]. Therefore this theory can be applied to thermotropic and lyotropic liquid crystals [15], as well as diblock copolymers [16]. Within the 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 [16]. In what follows, the stability analysis of the ordered structures is presented.

The LB free-energy functional is defined by [15]

$$\mathcal{F}(\{\phi\}) = \int d\mathbf{r} \left\{ \frac{\xi_0^2}{8q_0^2} [(\nabla^2 + q_0^2)\phi(\mathbf{r})]^2 + \frac{\tau}{2} [\phi(\mathbf{r})]^2 - \frac{\gamma}{3!} [\phi(\mathbf{r})]^3 + \frac{\lambda}{4!} [\phi(\mathbf{r})]^4 \right\} \quad (13)$$

where  $\phi(\mathbf{r})$  is the order parameter characterizing the composition fluctuations,  $\tau$  is the reduced temperature,  $q_0$  is the critical wavelength,  $\xi_0$  is the bare correlation length,  $\gamma$  and  $\lambda > 0$  are phenomenological constants. There are five parameters in the LB theory, i.e.,  $\xi_0$ ,  $q_0$ ,  $\tau$ ,  $\gamma$ , and  $\lambda$ . In order to simplify the formulation, we can use  $1/q_0$  as the length scale ( $\tilde{x} = q_0x$ ), and  $\lambda$  as the free-energy scale. The scaled quantities are then defined by

$$\begin{aligned} \tilde{\mathcal{F}} &= q_0^3 \mathcal{F} / \lambda & \tilde{\xi} &= (q_0 \xi_0)^2 / (4\lambda) \\ \tilde{\tau} &= \tau / \lambda & \tilde{\gamma} &= \gamma / \lambda. \end{aligned}$$

For fixed values of  $\tilde{\xi}$ , the phase behaviour of the system is controlled by the two parameters  $\tilde{\tau}$  and  $\tilde{\gamma}$ . In what follows we will neglect the tilde and write the free-energy functional in the form

$$\mathcal{F} = \int d\mathbf{r} \left\{ \frac{\xi^2}{2} [(\nabla^2 + 1)\phi(\mathbf{r})]^2 + \frac{\tau}{2} [\phi(\mathbf{r})]^2 - \frac{\gamma}{3!} [\phi(\mathbf{r})]^3 + \frac{1}{4!} [\phi(\mathbf{r})]^4 \right\}. \quad (14)$$

In order to study fluctuations, we expand the order parameter around a known profile  $\phi_0(\mathbf{r})$ ,  $\phi(\mathbf{r}) = \phi_0(\mathbf{r}) + \delta\phi(\mathbf{r})$ . The free-energy functional can then be expanded in the form  $\mathcal{F} = \mathcal{F}^{(0)} + \mathcal{F}^{(1)} + \mathcal{F}^{(2)} + \dots$ , where the zeroth-order contribution is the mean-field free energy

$$\mathcal{F}^{(0)} = \int d\mathbf{r} \left\{ \frac{\xi^2}{2} [(\nabla^2 + 1)\phi_0(\mathbf{r})]^2 + \frac{\tau}{2} [\phi_0(\mathbf{r})]^2 - \frac{\gamma}{3!} [\phi_0(\mathbf{r})]^3 + \frac{1}{4!} [\phi_0(\mathbf{r})]^4 \right\}. \quad (15)$$

The first-order contribution to the free energy has the form

$$\mathcal{F}^{(1)} = \int d\mathbf{r} \left\{ [\xi^2(\nabla^2 + 1)^2 + \tau] \phi_0(\mathbf{r}) - \frac{\gamma}{2} [\phi_0(\mathbf{r})]^2 + \frac{1}{3!} [\phi_0(\mathbf{r})]^3 \right\} \delta\phi(\mathbf{r}). \quad (16)$$

The second-order contribution (Gaussian fluctuation) to the free-energy functional is

$$\begin{aligned} \mathcal{F}^{(2)} &= \frac{1}{2} \int d\mathbf{r} \delta\phi(\mathbf{r}) \left\{ \xi^2(\nabla^2 + 1)^2 + \tau - \gamma\phi^{(0)}(\mathbf{r}) + \frac{1}{2} [\phi^{(0)}(\mathbf{r})]^2 \right\} \delta\phi(\mathbf{r}) \\ &= \frac{1}{2} \int d\mathbf{r} \delta\phi(\mathbf{r}) \hat{\mathcal{C}}(\mathbf{r}) \delta\phi(\mathbf{r}) \end{aligned} \quad (17)$$

where the Gaussian fluctuation operator  $\hat{C}(\mathbf{r})$  is defined by

$$\hat{C}(\mathbf{r}) = \xi^2(\nabla^2 + 1)^2 + \tau + V(\mathbf{r}).$$

The potential  $V(\mathbf{r})$  is given in terms of the mean-field solution

$$V(\mathbf{r}) = -\gamma\phi^{(0)}(\mathbf{r}) + \frac{1}{2}[\phi^{(0)}(\mathbf{r})]^2.$$

For an ordered structure, the mean-field solution is a periodic function, so the potential  $V(\mathbf{r})$  is also a periodic function.

In order to study the phase behaviour of the system, the mean-field equation has to be solved first to obtain the ordered structure. A stability analysis of the ordered structure can then be carried out by using the eigenfunctions of the operator  $\hat{C}(\mathbf{r})$ .

### 3.1. The mean-field phase diagram

The first step of the study is to determine the mean-field solutions. The mean-field equation is obtained by setting  $\mathcal{F}^{(1)} = 0$ , leading to the following expression:

$$[\xi^2(\nabla^2 + 1)^2 + \tau]\phi_0(\mathbf{r}) - \frac{\gamma}{2}[\phi_0(\mathbf{r})]^2 + \frac{1}{3!}[\phi_0(\mathbf{r})]^3 = 0. \quad (18)$$

For an ordered structure, it is convenient to cast the theory in the reciprocal space. For an ordered structure with a given set of reciprocal-lattice vectors  $\{\mathbf{G}\}$ , the mean-field order parameter is specified as

$$\phi^{(0)}(\mathbf{r}) = \sum_{\{\mathbf{G}\}} \phi_0(\mathbf{G})e^{i\mathbf{G}\cdot\mathbf{r}}.$$

For the cases where the order parameters are real (density modulations), the Fourier components satisfy  $\phi_0(-\mathbf{G}) = \phi_0^*(\mathbf{G})$ . The mean-field free-energy density  $f_0 = \mathcal{F}^{(0)}/V$  can be written in terms of the reciprocal-space order parameters  $\phi_0(\mathbf{G})$  as

$$f_0 = \frac{1}{2} \sum_{\mathbf{G}} [\xi^2(\mathbf{G}^2 - 1)^2 + \tau] \phi_0(\mathbf{G})\phi_0(-\mathbf{G}) - \frac{\gamma}{3!} \sum_{\mathbf{G}_1, \mathbf{G}_2} \phi_0(\mathbf{G}_1)\phi_0(\mathbf{G}_2)\phi_0(-\mathbf{G}_1 - \mathbf{G}_2) + \frac{1}{4!} \sum_{\mathbf{G}_1, \mathbf{G}_2, \mathbf{G}_3} \phi_0(\mathbf{G}_1)\phi_0(\mathbf{G}_2)\phi_0(\mathbf{G}_3)\phi_0(-\mathbf{G}_1 - \mathbf{G}_2 - \mathbf{G}_3). \quad (19)$$

The corresponding mean-field equation has the form

$$[\xi^2(\mathbf{G}^2 - 1) + \tau]\phi_0(\mathbf{G}) - \frac{\gamma}{2} \sum_{\mathbf{G}'} \phi_0(\mathbf{G} - \mathbf{G}')\phi_0(\mathbf{G}') + \frac{1}{3!} \sum_{\mathbf{G}', \mathbf{G}''} \phi_0(\mathbf{G} - \mathbf{G}' - \mathbf{G}'')\phi_0(\mathbf{G}')\phi_0(\mathbf{G}'') = 0. \quad (20)$$

The mean-field solutions are obtained by solving the mean-field equations for different ordered structures.

The mean-field theory can be simplified by using the symmetry of the system. Because the ordered structure is symmetric under the operation of the point group, the Fourier coefficients  $\phi_0(\mathbf{G})$  are not independent if the reciprocal-lattice vectors  $\mathbf{G}$  are related by the point group symmetry. The point group symmetry of an ordered structure makes it possible to simplify the mean-field equation. For a given star of  $N_n$  reciprocal wave vectors  $\{\mathbf{G}_i^n\}$ , the coefficients are not independent:

$$\phi_0(\mathbf{G}_i^n) = S_i^n \phi_0(\mathbf{G}_1^n) = \frac{S_i^n}{\sqrt{N_n}} A_n$$

where the sign  $S_i^n = \pm 1$  is determined by the symmetry of the structure, and  $|\mathbf{G}_i^n|^2 = \lambda_n$  is the same for the  $N_n$  wave vectors. The Fourier expansion of the order parameter becomes

$$\phi^{(0)}(\mathbf{r}) = \sum_n \phi_0(\mathbf{G}_1^n) \left( \sum_{i \in n} S_i^n e^{i\mathbf{G}_i^n \cdot \mathbf{r}} \right) = \sum_n A_n f_n(\mathbf{r})$$

where the new basis functions  $f_n(\mathbf{r})$  are linear combinations of the plane waves defined for the  $n$ th star by

$$f_n(\mathbf{r}) = \frac{1}{\sqrt{N_n}} \sum_{i \in n} S_i^n e^{i\mathbf{G}_i^n \cdot \mathbf{r}}. \quad (21)$$

These new basis functions satisfy the relations  $\nabla^2 f_n(\mathbf{r}) = -\lambda_n f_n(\mathbf{r})$  and are orthogonal:

$$\frac{1}{V} \int d\mathbf{r} f_n(\mathbf{r}) f_m(\mathbf{r}) = \delta_{n,m}.$$

For convenience, the basis functions  $f_n(\mathbf{r})$  are ordered according to the eigenvalues  $\lambda_n = |\mathbf{G}_i^n|^2$ . In particular, the first basis function is  $f_1(\mathbf{r}) = 1$  with  $\lambda_1 = 0$ . The inversion symmetry of the phases ensures that the  $f_n(\mathbf{r})$  are real functions, and the coefficients  $A_n$  can be taken as real numbers. The mean-field free-energy density can now be written in terms of the coefficients  $A_n$  as

$$f_0 = \frac{1}{2} \sum_n [\xi^2 (\lambda_n - 1)^2 + \tau] A_n^2 - \frac{\gamma}{3!} \sum_{n,m,l} \Gamma_{1nml}^{(4)} A_n A_m A_l + \frac{1}{4!} \sum_{n,m,h,l} \Gamma_{nmhl}^{(4)} A_n A_m A_h A_l \quad (22)$$

where the coefficients  $\Gamma_{ijkl}^{(4)}$  are defined by

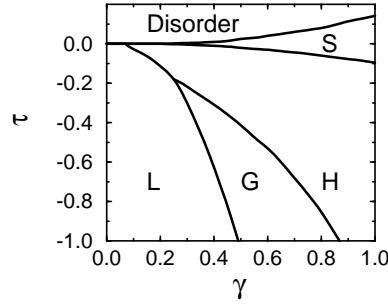
$$\begin{aligned} \Gamma_{nmhl}^{(4)} &= \int d\mathbf{r} f_n(\mathbf{r}) f_m(\mathbf{r}) f_h(\mathbf{r}) f_l(\mathbf{r}) \\ &= \frac{1}{\sqrt{N_n N_m N_h N_l}} \sum_{i \in n} \sum_{j \in m} \sum_{s \in h} \sum_{k \in l} S_i^n S_j^m S_s^h S_k^l \delta_{\mathbf{G}_i^n + \mathbf{G}_j^m + \mathbf{G}_s^h + \mathbf{G}_k^l, \mathbf{0}}. \end{aligned} \quad (23)$$

The corresponding mean-field equation has the form

$$[\xi^2 (\lambda_n - 1) + \tau] A_n - \frac{\gamma}{2} \sum_{m,l} \Gamma_{1nml}^{(4)} A_m A_l + \frac{1}{3!} \sum_{m,h,l} \Gamma_{nmhl}^{(4)} A_m A_h A_l = 0. \quad (24)$$

In most of the cases, the order parameter  $\phi(\mathbf{r})$  is defined as the fluctuation above the homogeneous phase so that  $\int d\mathbf{r} \phi(\mathbf{r}) = 0$ . Because the first basis function  $f_1 = 1$ , we have  $A_1 = 0$ . In principle there are an infinite number of coefficients  $A_n$ ; in practice the number of basis functions has to be finite. Choosing  $N + 1$  basis functions, the mean-field equation becomes a set of  $N$  non-linear equations, which can be solved using a standard algorithm.

In mean-field theory the phase diagram is constructed by comparing the free-energy densities of the different ordered structures. Besides the disordered phase, four ordered structures are considered in this study: lamellar, cylindrical, spherical, and a bicontinuous phase with space group  $Ia3d$  (gyroid). Each of these ordered structures is specified by its space group symmetry. The mean-field free energy must be minimized with respect to the periodicity of the structure to obtain the equilibrium lattice spacing. The number of basis functions is determined by the convergence of the free-energy density. The resulting mean-field phase diagram is shown in figure 1 for  $\xi = 1$ . It should be noticed that the phase diagram is controlled by the parameters  $\tau$  and  $\gamma$ . Phase transitions are driven by both the temperature-like parameter  $\tau$  and the symmetry parameter  $\gamma$ . An approximate mean-field phase diagram for the LB theory has been obtained [16] using a limited number of basis functions. The exact mean-field phase diagram presented in figure 1 is in qualitative agreement with previous results.



**Figure 1.** The mean-field phase diagram of the theory for  $\xi = 1$ . The structures are as follows: disordered phase (Disorder), lamellar phase (L), hexagonally packed cylinders (H), body-centred-cubic spheres (S), and gyroid phase with space group  $Ia3d$  (G).

### 3.2. The Gaussian fluctuation spectrum

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 the Gaussian fluctuation operator  $\hat{C}(\mathbf{r})$  is specified above. For an ordered structure, the mean-field solution is a periodic function, so the potential  $V(\mathbf{r})$  is also a periodic function. For a given ordered structure,  $V(\mathbf{r})$  can be written in the form  $V(\mathbf{r}) = \sum_n V_n f_n(\mathbf{r})$  where the expansion coefficients  $V_n$  are given by

$$V_n = -\gamma A_n + \frac{1}{2} \sum_{m,l} \Gamma_{lnml}^{(4)} A_m A_l. \quad (25)$$

Using the expression for the basis functions, the Fourier coefficients of  $V(\mathbf{r})$  are given by  $V(\mathbf{G}_i^n) = (S_i^n / \sqrt{N_n}) V_n$ . Because the potential  $V(\mathbf{r})$  is a periodic function, we can use the Bloch theorem to specify the form of the eigenfunctions

$$\psi_{nk}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\{\mathbf{G}\}} u_{nk}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

where  $\mathbf{k}$  is a wave vector within the first irreducible BZ and  $n$  labels the set of eigenvalues for a given  $\mathbf{k}$ . In this representation the Gaussian fluctuation operator becomes a symmetric matrix indexed by the reciprocal-lattice vectors, and whose matrix elements are given by

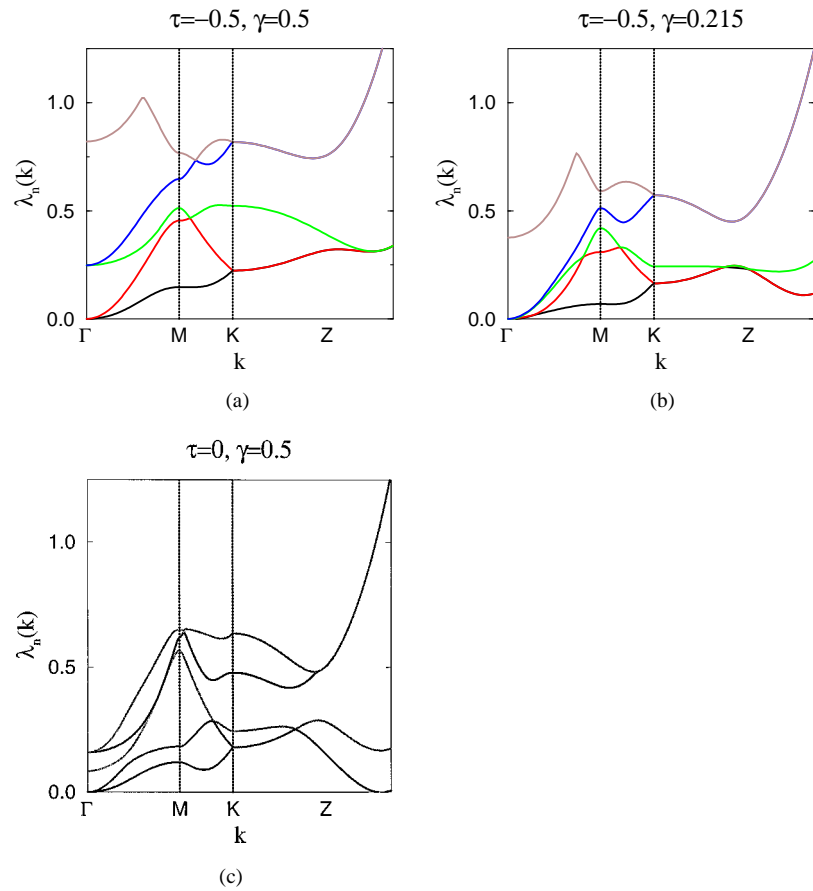
$$\hat{C}(\mathbf{G}, \mathbf{G}') = (\xi^2 [(\mathbf{k} + \mathbf{G})^2 - 1]^2 + \tau) \delta_{\mathbf{G}, \mathbf{G}'} + V(\mathbf{G} - \mathbf{G}'). \quad (26)$$

The eigenvalue problem becomes an eigenvalue problem with a real symmetric matrix:

$$\sum_{\{\mathbf{G}'\}} \hat{C}(\mathbf{G}, \mathbf{G}') u_{nk}(\mathbf{G}') = \lambda_n(\mathbf{k}) u_{nk}(\mathbf{G}). \quad (27)$$

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 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.

For a given structure, the mean-field solution is used to construct the Gaussian fluctuation operator. The eigenvalue and eigenfunction of the fluctuation operator are then obtained by solving the eigenproblem numerically for the wavevectors within the first Brillouin zone. Typical fluctuation eigenvalue bands are given in figure 2 for the hexagonal-packed cylinders. The existence of soft modes at  $\mathbf{k} = 0$  (Goldstone modes) is evident in these fluctuation spectra. It should also be noticed that the most unstable modes occur at different points  $\mathbf{k}_0$  for different

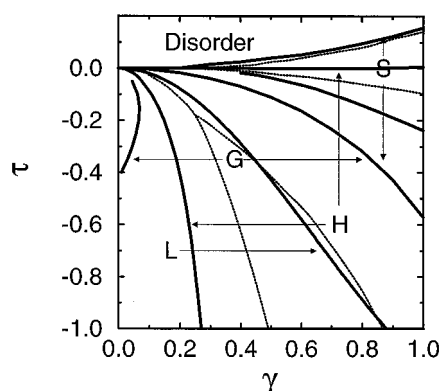


**Figure 2.** Band structure of Gaussian fluctuation modes in the hexagonal phase. The first Brillouin zone of the structure is a hexagonal prism. The plot is along the paths defined by the special points in the reciprocal space:  $\Gamma$  (0, 0, 0), M (0,  $1/\sqrt{3}$ , 0), K ( $1/3$ ,  $1/\sqrt{3}$ , 0), Z ( $1/3$ ,  $1/\sqrt{3}$ , z). The parameters are: (a)  $\tau = -0.5$ ,  $\gamma = 0.5$ , corresponding to a stable cylindrical phase; (b)  $\tau = -0.5$ ,  $\gamma = 0.215$ , in which the hexagonal phase is unstable against a lamellar phase; and (c)  $\tau = 0$ ,  $\gamma = 0.5$ , in which the hexagonal phase is unstable against a spherical phase. The most unstable modes are at (a) (0, 0, 0), (b) (0, 0, 0), and (c) ( $1/3$ ,  $1/\sqrt{3}$ ,  $2\sqrt{2}/3$ ). The real-space representations of the most unstable modes for (b) and (c) are given in figure 4.

(This figure can be viewed in colour in the electronic version of the article; see [www.iop.org](http://www.iop.org))

controlling parameters. The spinodal lines of the ordered structures are determined by the condition  $\lambda_0(\mathbf{k}_0) = 0$ . Figure 3 shows the calculated spinodal lines for the four ordered structures. Each phase is enveloped by two spinodal lines. The ordered structure becomes absolutely unstable at the points beyond the spinodal lines.

The most unstable modes can be used to get information about the kinetic pathway of the order–order phase transitions. The effects of the most unstable modes can be studied by considering the function  $\phi(\mathbf{r}) = \phi_0(\mathbf{r}) + a\psi_{1\mathbf{k}_0}(\mathbf{r})$ , where  $a$  is a coefficient and  $\psi_{1\mathbf{k}_0}(\mathbf{r})$  is the eigenfunction with the lowest eigenvalue. A contour plot of this function provides the location of the interfaces in the system. It is obvious that the structural relationships between the different ordered phases are determined by the most unstable modes. Furthermore, the kinetic pathway of the order–order phase transitions can be obtained from the most unstable modes.



**Figure 3.** The phase diagram and spinodal lines of the different structures for  $\xi = 1$ . The dotted lines are the mean-field phase boundaries. The spinodal lines of the different phases are indicated by the arrows.

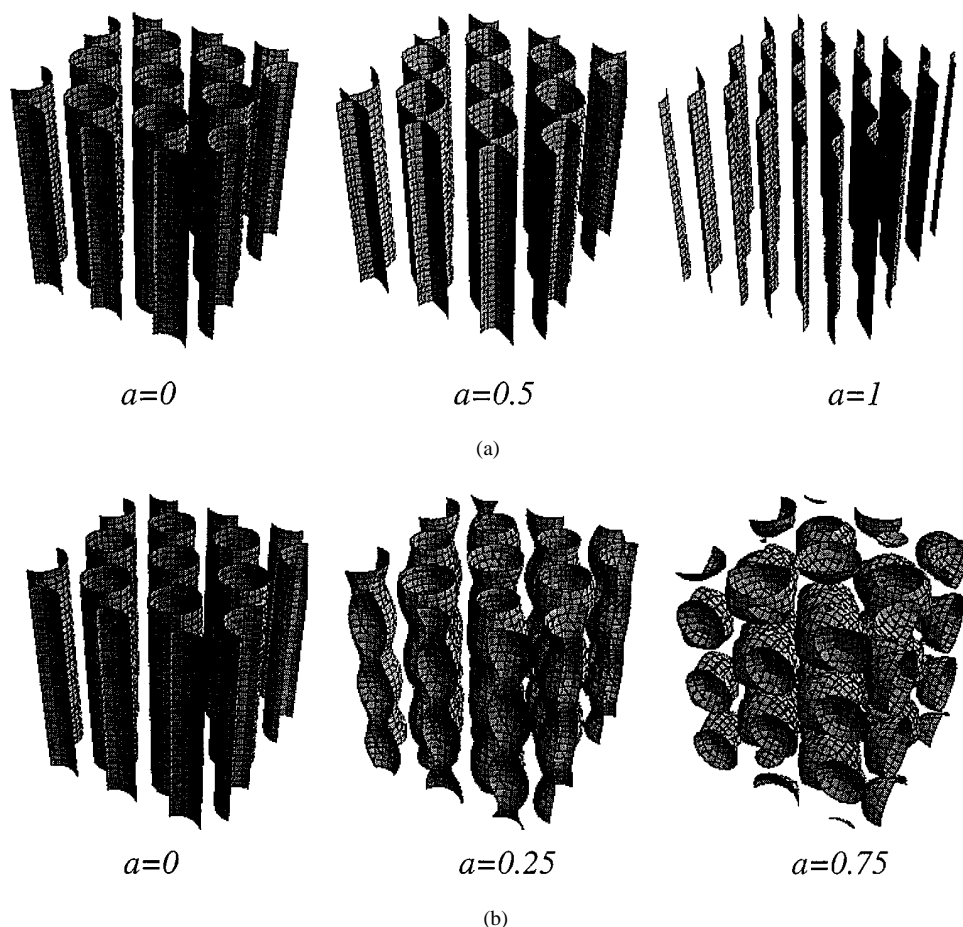
For the particular example given in figure 4, it can be concluded that (a) the transition from the cylindrical phase to the lamellar phase occurs through the deformation of the cylinders, and (b) the transition from the cylindrical phase to the spherical phase occurs through the undulation of the cylinders. It is interesting to notice that the most unstable modes, structural relationships, and kinetic pathways obtained for the LB theory are in qualitative agreement with the ones obtained for block copolymers.

#### 4. Conclusions and discussion

Using general symmetry arguments, it has been shown that for an ordered 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 emerges from these general statements is a powerful technique for classifying the anisotropic fluctuation modes in an ordered phase. The stability and kinetic pathways of the 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 for classifying 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 for cataloguing the fluctuation modes, as demonstrated in the stability analysis of diblock copolymer ordered phases [10, 11], and the Landau–Brazovskii theory of weak crystallization.

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, it is expected that the application of the fluctuation mode analysis to the structural relationships between different ordered phases in



**Figure 4.** Real-space representations of the most unstable modes for the parameters: (a)  $\tau = -0.5$ ,  $\gamma = 0.215$ , in which the hexagonal phase is unstable against a lamellar phase; and (b)  $\tau = 0$ ,  $\gamma = 0.5$ , in which the hexagonal phase is unstable against a spherical phase. The plots are generated as the contours defined by  $\phi(\mathbf{r}) = \phi_0(\mathbf{r}) + a\psi_{1k_0}(\mathbf{r}) = 0$  for different values of  $a$ . Structural relationships between different ordered phases can be obtained from these plots.

other self-assembling amphiphilic systems [2], such as the non-ionic surfactant system [17], and colloidal suspensions [1], will be proven valuable.

### Acknowledgments

I would like to acknowledge Drs C Yeung, M Laradji, R C Desai, and especially J Noolandi for a fruitful collaboration on the study of anisotropic fluctuations in block copolymer systems.

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