

Strain-induced instabilities in hexagonal columnar phases

I. W. Hamley

Department of Physics, University of Durham, South Road, Durham DH1 3LE, United Kingdom

(Received 16 May 1994)

Structural instabilities in the hexagonal-packed cylinder phase of block copolymers subject to uniaxial tension orthogonal to the column axis are investigated theoretically. For small strains, a Landau elastic free energy density which is identical to that for hexagonal columnar liquid crystals can be used to determine the threshold and form of the instability, which can be of two types. In the first the distortion field is scalar and the columns or rods are modulated in thickness, while in the second the distortion field is a vector, resulting in saddle-splay curvature. A detailed theoretical analysis of the instability is presented for asymmetric diblock copolymers near the ordering transition. For these materials, the first-order phase transition to the hexagonal-packed rod phase is induced by composition fluctuations and belongs to the Brazovskii class. The coefficients in a series expansion of the Brazovskii free energy density are identified with the elastic constants in the elastic free energy density, enabling them to be calculated from a microscopic random phase approximation model. It is thus shown that small uniaxial strains should induce a transition from the hexagonal rod phase to a "modulated rod" structure above a critical strain.

PACS number(s): 61.25.Hq, 61.30.Cz, 61.41.+e, 62.20.Dc

I. INTRODUCTION

The mechanical properties of block copolymers are of both practical and fundamental importance. The elastomeric properties of block copolymers are utilized in polymer blend compatibilizing or hardness modification applications, for example [1]. At a more fundamental level, the effect of mechanical deformations on thermodynamic phase behavior has recently begun to be investigated using model block copolymer systems. For example, melting transitions induced by shear have recently been observed for the lamellar phase in diblock melts [2] and cubic micellar phases in triblock copolymer solutions [3].

When an amorphous block copolymer is cooled below its order-disorder transition (ODT) temperature, incompatible block components tend to microphase separate into structures with periods on the order of the polymer radius of gyration. Macrophase separation is prevented by the chemical connectivity of the blocks. In the classical picture, lamellar, hexagonal-packed cylinder, or body-centered-cubic (bcc) micelle phases form depending on the diblock composition, specified by f , the volume fraction of one component, and χN . Here, χ is the Flory-Huggins interaction parameter that accounts for local and nonlocal interactions between polymer segments and N is the degree of polymerization. Empirically, χ is inversely proportional to temperature.

The effect of symmetry-breaking mechanical fields on microphase-separated structures is of great interest for several reasons. First, in the context of recent work on diblock copolymers near the order-disorder transition, a variety of new structures such as hexagonal modulated lamellae, hexagonal perforated layers [5], and deformed cylinders [6] have been observed between the classical lamellar and hexagonal-packed cylinder phases. The nature of the deformations of the cylinders (modulations or

saddle splay) has not yet been ascertained, but small angle neutron scattering reveals an in-plane rhombic lattice [6]. These experiments have been performed on samples previously subject to reciprocating shear, and it is not clear what influence mechanical deformation has on the thermodynamic stability of lamellar and hexagonal-packed cylinder phases. Uniaxial tension is the simplest mechanical deformation that can be applied and structural instabilities that can result can be interpreted using quasistatic elastic theory.

Second, and related to the above, the relation between the thermodynamic and mechanical properties of thermotropic liquid crystals and block copolymers can be developed. The instability of the smectic (lamellar) phase in liquid crystals under uniaxial tension is an example of a Helfrich-Hurault instability [7]. When a monodomain lamellar phase is subject to a uniaxial strain orthogonal to the layers under the constraint of a fixed number of layers (a so-called quasistatic deformation), above a critical strain a buckled structure results. The critical strain depends on domain size and the lamellar compression and splay elastic constants [8,9]. The deformation results when the time scale for global rearrangements where the number of layers is changed by edge dislocation creation is long compared to the time scale of the strain experiment. Within certain time ranges the system can stay in a constrained metastable state with a fixed number of layers. This holds for smectic liquid crystals and should hold over a wider range for polymeric systems where the internal relaxation times are much longer [10,11]. The structure above the critical strain is initially square modulated lamellae. As the strain is increased, defects proliferate and a square array of "focal conic" defects results [7].

Previous studies have been concerned with quasistatic tensile deformations in lamellar phases. Kawasaki and

Ohta analyzed the mechanical properties of both weakly and strongly segregated lamellar block copolymers within mean field theory [12]. In addition, they considered the cylindrical and spherical morphologies in the strong-segregation limit. Mean field theory is not valid near the ordering transition for block copolymers of finite molecular weight; instead, composition fluctuations drive the first-order phase transitions to the disordered phase [13], placing block copolymers in the Brazovskii class [14]. The quasistatic properties of lamellar diblocks near the ordering transition have recently been treated theoretically [10,11] using fluctuation theory [15]. In Ref. [11], uniaxial tensile strains were considered, while applied stresses have additionally been considered [10].

In this paper the behavior of a hexagonal columnar phase subject to small uniaxial tensile strains is studied. An undulation instability for this phase in thermotropic liquid crystals has been observed [16,17]. However, the deformation was different to that considered here because samples with columns orthogonal to parallel plates were subject to a shear parallel to the plates, the resulting structure consisting of undulations normal to the column axis. The continuum elastic theory should apply equally for tensile deformations of hexagonal columnar (sometimes called discotic) liquid crystals or the hexagonal-packed cylinder phase in diblock copolymers, although it is the latter which are considered in detail here. Two types of deformation are possible where the deformation field is a scalar (giving a “modulated” cylinder structure) or a vector (giving “helicoidal”-type structures). First, the continuum elastic theory for columnar phases, and then compositional fluctuation theory for weakly segregated diblocks, are presented. This enables the elastic moduli for the hexagonal-packed cylinder phase in diblock copolymers to be calculated and the type of structure formed for small tensile deformations to be identified. Finally, we summarize and briefly discuss a possible connection between these structures and those recently observed on heating asymmetric diblock copolymers near the order-disorder transition, which were subject to reciprocating shear.

II. THEORY

A. Continuum elastic theory

We start from the free energy given by de Gennes and Prost for the hexagonal columnar phase formed by thermotropic liquid crystals [7]. Within a static limit the cylinder deformations are specified by the two-dimensional vector field

$$\mathbf{v}(\mathbf{r}) = (v_x(\mathbf{r}), v_y(\mathbf{r})),$$

where the axis system is defined in Fig. 1. The continuum free energy expanded to lowest order is [7]

$$\begin{aligned} F = & \frac{\bar{B}}{2} (\partial_x u_x + \partial_y u_y)^2 \\ & + \frac{C}{2} [(\partial_x u_x - \partial_y u_y)^2 + (\partial_y u_x + \partial_x u_y)^2] \\ & + \frac{K_3}{2} [(\partial_z^2 u_x)^2 + (\partial_z^2 u_y)^2]. \end{aligned} \quad (1)$$

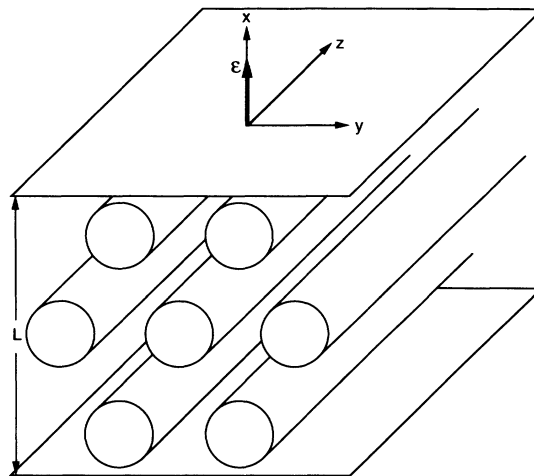


FIG. 1. Illustrating the deformation considered in this work, together with the axis system used.

Here \bar{B} is an elastic constant equal to the compressional modulus B for static phenomena. For dynamic processes where the time for reaching equilibrium density is large compared to the experimental time scale, $\bar{B} = B - D^2/A$, where the coefficients A and D are elastic constants related to the bulk dilatation θ [7]:

$$\begin{aligned} F = & \frac{A}{2} \theta^2 + \frac{\bar{B}}{2} (\partial_x v_x + \partial_y v_y)^2 \\ & + \frac{C}{2} [(\partial_x v_x - \partial_y v_y)^2 + (\partial_y v_x + \partial_x v_y)^2] \\ & + D\theta(\partial_x v_x + \partial_y v_y) + \frac{K_3}{2} [(\partial_z^2 v_x)^2 + (\partial_z^2 v_y)^2]. \end{aligned} \quad (2)$$

B is the elastic constant corresponding to homogeneous compression or dilatation of the columns, C is a saddle-splay constant for elliptical deformations of the columns (with constant average diameter), and K_3 is the column bending elastic constant. It is important to note that the $\mathbf{v}(\mathbf{r})$ are column displacement variables and not the local curvatures considered in Ref. [18], i.e., the saddle-splay modulus is not the same as that occurring in the Helfrich free energy for locally deformed layers [19]. The appropriate choice of variables for quasistatic deformations are the $\mathbf{v}(\mathbf{r})$ [7,20]. For small deformations the symmetry of the hexagonal phase leads to the requirement that $\partial_x v_y = -\partial_x v_x$ and $\partial_y v_x = \partial_y v_y$. Using these relations in Eq. (2) and rearranging gives

$$\begin{aligned} F = & \frac{1}{2} (\bar{B} + 2C) [(\partial_x v_x)^2 + (\partial_y v_y)^2] + 2\partial_x v_x \partial_y v_y (\frac{1}{2}\bar{B} - 2C) \\ & + \frac{K_3}{2} [(\partial_z^2 v_x)^2 + (\partial_z^2 v_y)^2]. \end{aligned} \quad (3)$$

Two types of deformation can be considered depending on the signs of $(\bar{B} - 2C)$ and $\partial_x v_x \partial_y v_y$, viz., (i) $\frac{1}{2}\bar{B} \leq C$, $\partial_x v_x \partial_y v_y \geq 0$ and (ii) $\frac{1}{2}\bar{B} > C$, $\partial_x v_x \partial_y v_y < 0$. Illustrations of possible types of deformations corresponding to these cases are presented in Fig. 2. Before describing these deformations further, we extend Eq. (3) to higher orders,

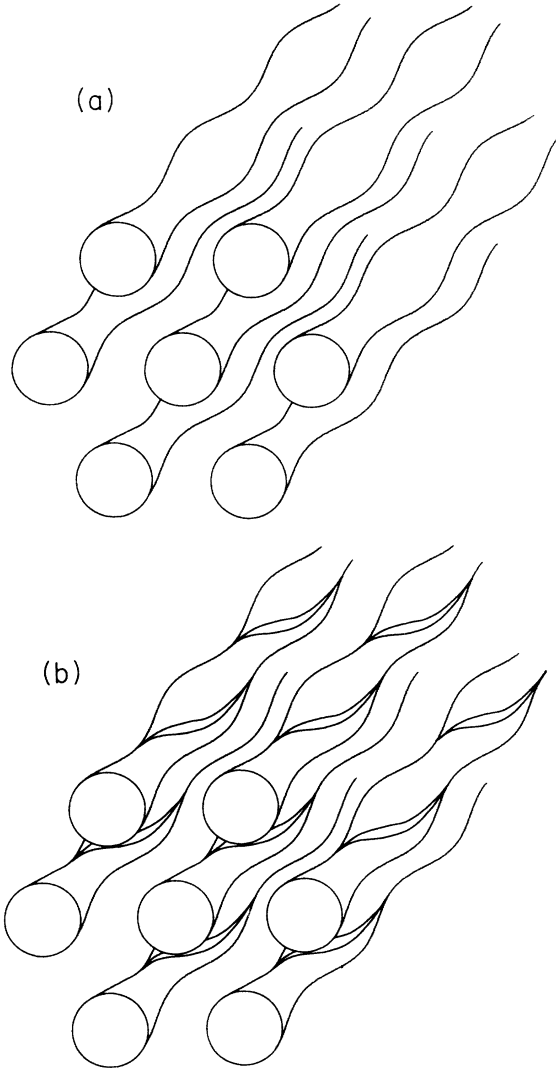


FIG. 2. (a) A "modulated" cylinder structure where the diameter varies sinusoidally along the length of the cylinder axis. This structure can be described by a scalar function $u(\mathbf{r})$. (b) A "twisted" cylinder structure in the hexagonal cylinder phase subject to a two-dimensional deformation field $\mathbf{u}(\mathbf{r})$, where there is an elliptical deformation (at constant average diameter) implying saddle-splay curvature.

which is necessary when calculating instabilities. The result is

$$\begin{aligned}
 F = & \frac{\bar{B}}{2} [\partial_x v_x + \partial_y v_y - \frac{1}{2}(\partial_1 v_x)^2 - \frac{1}{2}(\partial_1 v_y)^2]^2 \\
 & + \frac{C}{2} [(\partial_x v_x - \partial_y v_y - \frac{1}{2}(\partial_1 v_x)^2 + \frac{1}{2}(\partial_1 v_y)^2)^2] \\
 & + \frac{C}{2} [\partial_y v_x + \partial_x v_y]^2 + \frac{K_3}{2} [(\partial_z^2 v_x)^2 + (\partial_z^2 v_y)^2]. \quad (4)
 \end{aligned}$$

1. Case (i)

A deformation for which $\partial_x v_x \partial_y v_y \geq 0$ can always be reparametrized in terms of a scalar field $v(\mathbf{r})$. Then the

free energy reduces to the Landau-de Gennes free energy for the lamellar phase:

$$F = \frac{1}{2}(\bar{B} + C)[\partial_x v - \frac{1}{2}(\partial_1 v)^2]^2 + \frac{1}{2}K_3(\partial_z^2 v)^2. \quad (5)$$

The analysis of the strain-induced buckling instability is then identical to that for a lamellar phase, with the compressional modulus replaced by $(\bar{B} + C)$ for the hexagonal phase [7].

We introduce a uniform strain ϵ on a system of thickness L such that a uniaxial deformation orthogonal to the layers is specified by $v = \epsilon x + u(\mathbf{r})$ (note that the layers of cylinders are here normal to x). Considering the free energy per unit volume, V , substitution of v into Eq. (5) and integrating gives to lowest order [10]

$$\begin{aligned}
 f = & \frac{1}{2}(\bar{B} + C)\epsilon^2 + \bar{B}\epsilon \langle \partial_x u \rangle - \frac{1}{2} \langle (\partial_z u)^2 \rangle \\
 & + \frac{1}{2}\bar{B} \langle (\partial_x u)^2 \rangle + \frac{1}{2}K_3 \langle (\partial_z^2 u)^2 \rangle, \quad (6)
 \end{aligned}$$

where $\langle \rangle$ denotes a spatial average.

The critical strain can then be calculated adopting an ansatz for $u(\mathbf{r})$. For lamellae, Delrieu showed that above the critical strain a square modulated structure has the lowest free energy [21] and $u(\mathbf{r})$ can be parametrized as

$$u(\mathbf{r}) = \frac{u_0}{\sqrt{2}} \sin(\kappa x) [\cos(ky) + \cos(kz)], \quad (7)$$

where u_0 is the amplitude of the undulation of wave number k , and $\kappa = \pi/L$ ensures that u vanishes at the boundaries since L is the domain size [8]. The critical strain ϵ_c can then be shown to be given by

$$\epsilon_c = 2\kappa [K_3 / (\bar{B} + C)]^{1/2}, \quad (8)$$

with a wave vector $k = \sqrt{\kappa/\Lambda}$ where $\Lambda = \sqrt{k_3 / (\bar{B} + C)}$ [7]. Expressions for the strain free energy density beyond the critical strain and the stress (which can be obtained from the derivative of the free energy with respect to strain) have been given for a lamellar system by Wang [10]. Since equivalent results should hold for the hexagonal-packed cylinder phase which behaves as a layered system for deformations in the (xy) plane, we do not give details again here.

Representative calculations of density distributions in the square modulated structure are shown in Fig. 3 for three orthogonal planes. The compositional order parameter in these density plots was parametrized as

$$\begin{aligned}
 \bar{\psi}(\underline{r}) = & \cos[2q_x(x+u)] + \cos[q_x(x+u) + q_y y] \\
 & + \cos[-q_x(x+u) + q_y y]. \quad (9)
 \end{aligned}$$

Here $q_x = q/2$, $q_y = \sqrt{3}q/2$, with $q = 2\pi/d$. The undulation term $u(\mathbf{r})$ was represented by Eq. (7) with $u_0 = 0.07$, and κ and k were chosen to be $\pi/2d$ and $q/2$, respectively. The hexagonal ordering of cylinders (distorted away from $x=0$ due to the boundary conditions) is clear in the (x,y) plane (at $z=0$). The modulations of the cylinders are clearly evident in the (x,z) plane at $y=0$, while the square symmetry of the modulations is illustrated in the density plot in the (y,z) plane (at $x=d/4$).

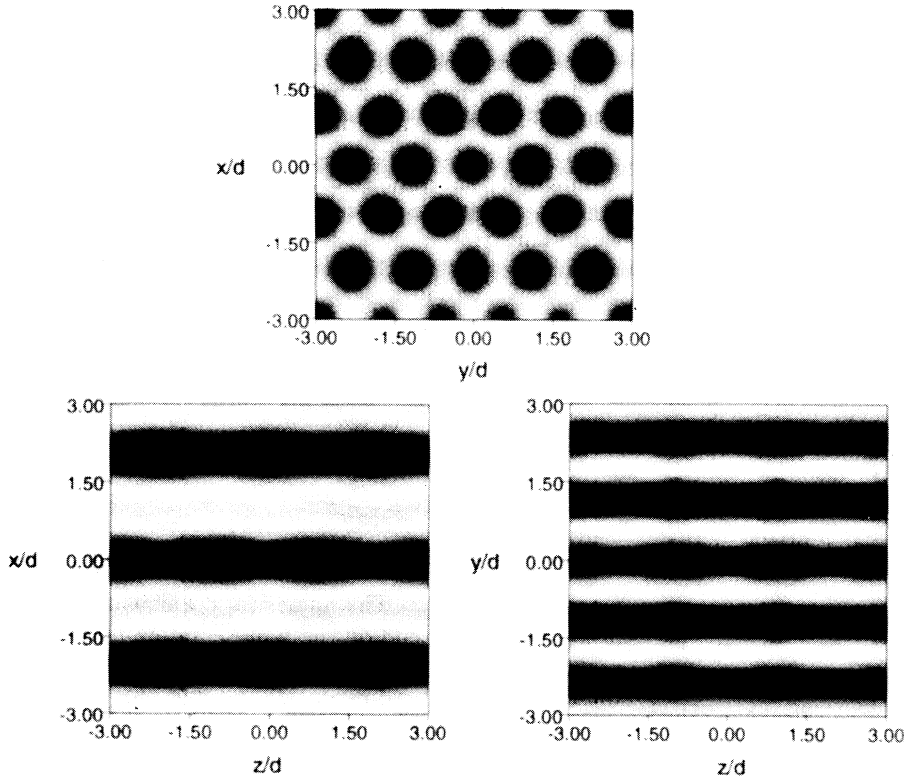


FIG. 3. Representative contour plots of the density in three orthogonal planes in the square modulated hexagonal-packed cylinder phase. The density parametrization is described in the text.

2. Case (ii)

This corresponds to a saddle-splay deformation, specified by the vector field $\mathbf{v}(\mathbf{r}) = (v_x, v_y)$. The term saddle splay may be used because the cross term in the free

energy, Eq. (3), $\partial_x v_x \partial_y v_y < 0$, i.e., displacements in two orthogonal directions are of opposite sign. The free energy density for a strain in the (xy) plane: $\boldsymbol{\varepsilon} = \varepsilon_x \mathbf{i} + \varepsilon_y \mathbf{j}$, specified by $v_x = \varepsilon_x x + u_x(\mathbf{r})$, $v_y = \varepsilon_y y + u_y(\mathbf{r})$, can be obtained by integrating Eq. (4):

$$f = (1/V) \int d\mathbf{r} \left\{ \frac{\bar{B}}{2} [\varepsilon_x + \partial_x u_x + \varepsilon_y + \partial_y u_y - \frac{1}{2}(\partial_1 u_x)^2 - \frac{1}{2}(\partial_1 u_y)^2] \right. \\ \left. + \frac{C}{2} [\varepsilon_x + \partial_x u_x - \varepsilon_y - \partial_y u_y + \frac{1}{2}(\partial_1 u_x)^2 + \frac{1}{2}(\partial_1 u_y)^2]^2 + \frac{C}{2} [\partial_y u_x + \partial_x u_y]^2 + \frac{K_3}{2} [(\partial_2^2 u_x)^2 + (\partial_2^2 u_y)^2] \right\}. \quad (10)$$

Vector field deformations were not considered further, because it turns out that this is not the structural instability predicted for diblock copolymers. Preliminary work indicates that a variety of helicoidal-type structures are possible but further details will be the subject of future work.

B. Brazovskii fluctuation theory

A free energy functional for a weak first-order phase transition allowing for compositional fluctuations was derived by Brazovskii within the Hartree approximation. This theory was applied to weakly segregated block copolymers by Fredrickson and Helfand [13], and it was

shown that the phase diagram becomes dependent on the degree of polymerization, N , in addition to the mean field variables f and χN . Also the phase transition for symmetric diblocks, which in mean field theory is second order, becomes first order when compositional fluctuations are considered. The fluctuation-induced first-order phase transition differs from the mean field first-order phase transition because it is not the consequence of a cubic term in a Landau free energy. For a symmetric diblock copolymer, where the cubic term in the Landau free energy is zero, a fluctuation-induced first-order phase transition results from the sign change of the quartic term in the potential (so that it must be expanded to sixth order to ensure stability). For an asymmetric diblock copoly-

mer, the effective Hamiltonian can be written as an expansion in the average compositional order parameter ψ :

$$\beta H[\psi(\mathbf{r})] = \int d\mathbf{r} \left\{ \frac{1}{2} \tau \psi^2 + \frac{1}{2} e [q_0^4 \psi^2 + 2q_0^2 (\nabla \psi)^2 + (\nabla^2 \psi)^2] + \frac{t}{3!} \psi^3 + \frac{u}{4!} \psi^4 + \frac{v}{5!} \psi^5 + \frac{w}{6!} \psi^6 \right\}. \quad (11)$$

Here $\beta = 1/k_B T$ is the Boltzmann factor, $\psi = c\bar{N}^{-1/4} \phi$ is the scaled order parameter with $\phi(r)$ the compositional order parameter, and q_0 is the scaled wave number at the structure factor peak. $\bar{N} = Na^6/v^2$, with a and v denoting segmental length and volume, respectively, is a Ginzburg parameter [15]. The coefficient c is defined in Ref. [13], and in dimensionless units $e = (1/24x^*)$, with $x^* = q_0^2 R_g^2$, R_g being the copolymer radius of gyration. $\tau = 2[(\chi N)_s - \chi N]/c^2$ with $(\chi N)_s$ the value of χN at the spinodal,

$$t = N\Gamma_3/(\bar{N}^{-1/2} c^3) = \mu \bar{N}^{-1/2},$$

$$u = N\Gamma_4/(\bar{N}^{-1/2} c^4) = \lambda \bar{N}^{-1/2},$$

etc., where the Γ_n are vertex functions calculated within the random phase approximation [4]. For consistency with previous work, the term u is used in this paper both for a fourth-order coefficient in a Landau expansion and for the displacement field $u(\mathbf{r})$, although its meaning should be clear from the context.

The Hartree potential for the hexagonal rod phase can then be written, extending the analysis for the lamellar phase given in Ref. [15], as

$$\beta \Gamma_H[\phi(\mathbf{r})] = \int d\mathbf{r} \left\{ \frac{1}{2} \tau_R \bar{\psi}^2 + \frac{1}{2} e [q_0^4 \bar{\psi}^2 + 2q_0^2 (\nabla \bar{\psi})^2 + (\nabla^2 \bar{\psi})^2] + \frac{t_R}{3!} \bar{\psi}^3 + \frac{u_R}{4!} \bar{\psi}^4 + \frac{v_R}{5!} \bar{\psi}^5 + \frac{w_R}{6!} \bar{\psi}^6 \right\}. \quad (12)$$

The order parameter $\bar{\psi} = \langle \psi(\mathbf{r}) \rangle$, and the coefficient τ_R is the renormalized inverse susceptibility, while t_R through w_R are coefficients that are multiples of higher order ver-

tex functions. The procedure for calculating these coefficients is given in Ref. [15], which also contains explicit expressions for τ_R , u_R , and w_R for a symmetric diblock copolymer (for which $t_R, v_R = 0$). The approach described in the Appendix of Ref. [15] was extended to calculate the renormalized coefficients for a hexagonal cylinder phase. Within the Hartree approximation and performing a self-consistent one-loop calculation [22,15], we obtain

$$\tau_R = \tau + d u \tau_R^{-1/2}, \quad (13)$$

$$t_R = 6t, \quad (14)$$

$$u_R = 3u \left[5 - \frac{3du \tau_R^{-1/2}}{5(1 + \frac{1}{2} du \tau_R^{-1/2})} \right], \quad (15)$$

$$v_R = 15v, \quad (16)$$

$$w_R = \frac{891 d u^3}{496 \tau_R^{-5/2} (1 + \frac{1}{2} du \tau_R^{-3/2})^3}, \quad (17)$$

where $d = 3x^*/2\pi$. The numerical coefficients $\frac{3}{5}$ and $\frac{891}{496}$ in u_R and w_R depend on the representation for the order parameter [and are here consistent with Eq. (18)] due to the isotropic approximation [22] adopted for the fourth- and sixth-order vertex functions.

For a hexagonal-packed cylinder phase with anisotropic fluctuations parametrized as $\mathbf{u}(\mathbf{r}) = (u_x(\mathbf{r}), u_y(\mathbf{r}))$ as in the preceding section, the compositional order parameter can be written as

$$\bar{\psi}(\mathbf{r}) = 2A \cos[2q_x(x + u_x)] + 2A \cos[q_x(x + u_x) + q_y(y + u_y)] + 2A \cos[-q_x(x + u_x) + q_y(y + u_y)], \quad (18)$$

where q_x and q_y are defined after Eq. (9). This expression is then substituted into Eq. (12) to give a free energy density. In the phase approximation [12], the phase shift is assumed to be a slowly varying function (over several structural periods). Then averages of the type

$$\langle \cos^2[a(x + ux) + b(y + uy)] \rangle = \frac{1}{2},$$

where a, b are multiples of q_x and q_y , respectively, and $\langle \rangle$ denotes an average over one period. Within this approximation, and using the order parameter representation (18), we obtain a free energy density,

$$f = f_0(A) + (1/V) A^2 e \int d\mathbf{r} \{ 6q_0^4 - 24q_0^2 q_x^2 [1 + \partial_x u_x + \partial_y u_x + \partial_z u_x]^2 - 8q_0^2 q_y^2 [1 + \partial_x u_y + \partial_y u_y + \partial_z u_y]^2 + 36q_x^4 [(1 + \partial_x u_x)^2 + (\partial_y u_x)^2 + (\partial_z u_x)^2]^2 + 4q_y^4 [(\partial_x u_y)^2 + (1 + \partial_y u_y)^2 + (\partial_z u_y)^2]^2 + 8q_x^2 q_y^2 \{ (1 + \partial_x u_x)^2 + (\partial_y u_x)^2 + (\partial_z u_x)^2 \} \{ (\partial_x u_y)^2 + (1 + \partial_y u_y)^2 + (\partial_z u_y)^2 \} + 2(1 + \partial_x u_x)(\partial_x u_y) [(1 + \partial_x u_x)(\partial_x u_y) + 2(\partial_y u_x)(1 + \partial_y u_y) + 2(\partial_z u_x)(\partial_z u_y)] + 2(\partial_y u_x)(1 + \partial_y u_y) [(\partial_y u_x)(1 + \partial_y u_y) + 2(\partial_z u_x)(\partial_z u_y)] + 2(\partial_z u_x)^2 (\partial_z u_y)^2 + 129x^2 (\partial_z^2 u_x)^2 + 49y^2 (\partial_z^2 u_y)^2 \}. \quad (19)$$

Here,

$$f_0(A) = 3[\tau_R + e(q^2 - q_0^2)^2]A^2 + 2t_R A^3 + \frac{15}{4}u_R A^4 + 3v_R A^5 + \frac{169}{60}w_R A^6 \quad (20)$$

is the local part of the free energy density, where the numerical coefficients are $m/n!$, where m is the number of closed wave vector circuits of order n . The number of layers is fixed during the quasistatic deformation considered here. The deformation is along a general direction in the (x, y) plane: $\epsilon = \epsilon_x \mathbf{i} + \epsilon_y \mathbf{j}$. In the sample of equilibrium dimensions $L_{0,x}, L_{0,y}$, the x and y periodicities are $D_{0,x} = 2\pi/q_{0,x}$ and $D_{0,y} = 2\pi/q_{0,y}$. In the stretched sample of dimensions L_x, L_y , we have $D_x = 2\pi/q_x$, $D_y = 2\pi/q_y$, so that

$$L_x/D_x = (1 + \epsilon_x) = q_{0,x}/q_x$$

and

$$L_y/D_y = (1 + \epsilon_y) = q_{0,y}/q_y .$$

Then for small ϵ ,

$$q_x^2 = (\frac{1}{2}q_0)^2(1 - 2\epsilon_x) , \quad q_y^2 = \left[\frac{\sqrt{3}}{2}q_0 \right]^2 (1 - 2\epsilon_y) .$$

Substituting these expressions for q_x^2 and q_y^2 into Eq. (19), we obtain a free energy density,

$$\begin{aligned} f = f_0(A) + (1/V)A^2 e \int d\mathbf{r} \{ & 6q_0^4 [\epsilon_x + \partial_x u_x + \epsilon_y + \partial_y u_y - \frac{1}{2}(\partial_z u_x)^2 - \frac{1}{2}(\partial_z u_y)^2]^2 \\ & + 3q_0^4 [\epsilon_x + \partial_x u_x - \epsilon_y - \partial_y u_y + \frac{1}{2}(\partial_z u_x)^2 + \frac{1}{2}(\partial_z u_y)^2]^2 + 3q_0^4 [\partial_x u_y + \partial_y u_x]^2 \\ & + 3q_0^2 [(\partial_z^2 u_x)^2 + (\partial_z^2 u_y)^2] \} , \end{aligned} \quad (21)$$

where u_x has been changed to $-u_x$ and u_y to $-u_y$. The strain dependent part of this equation has the same form as the de Gennes-Prost expression (4) so that the elastic constants for the hexagonal-packed cylinder phase of block copolymers can be identified as

$$\bar{B} = 12eq_0^4 A^2 , \quad (22)$$

$$C = 6eq_0^4 A^2 , \quad (23)$$

$$K_3 = 6eq_0^2 A^2 . \quad (24)$$

These can be converted to dimensional units by multiplication by $k_B T / (N^{3/2} a^3)$ for \bar{B} and C , or $a^2 k_B T / (N^{3/2} a^3)$ for K_3 [10]. According to the inequalities derived in the preceding section, since $\bar{B} = 2C$, block copolymers in the hexagonal-packed cylinder phase subject to small uniaxial tension should undergo a transition to a modulated structure above the critical strain given by Eq. (8). Furthermore, as this deformation is specified by the scalar field $u(\mathbf{r})$, it has the same symmetry as that occurring in a lamellar phase under tension, i.e., a square modulated structure. We also note that this result is independent of the direction of the strain in the (x, y) plane.

C. Calculation of the elastic constants for a block copolymer

The three elastic constants can be expressed in scaled dimensionless units as functions of eA^2 . In principle, the amplitude A can be determined from the minimum of the free energy density in the absence of distortion, Eq. (20) [11]. However, an analysis analogous to that for a lamellar phase [15] would involve calculation of the fifth-order

vertex functions in the random phase approximation, since the fifth-order term for the hexagonal rod phase is nonzero, and these have not been computed to date. In addition, the roots of the cubic equation resulting from the minimization of Eq. (20) with respect to A would need to be solved numerically. An alternative, and simpler, procedure for the hexagonal rod phase is to return to the Brazovskii representation for the thermodynamic potential. Although this obscures the origin of the fluctuation-induced phase transition, the amplitude A can be calculated in a straightforward manner following the procedure described in [13].

Here we determine the minimum of the thermodynamic potentials for the lamellar and hexagonal phases [14,13]:

$$\Phi_l(A_l) = \frac{1}{2\lambda}(r_l^2 - r_0^2) + \frac{d}{\bar{N}^{1/2}}(r_l^{1/2} - r_0^{1/2}) - \frac{\lambda}{4}A_l^4 , \quad (25)$$

$$\begin{aligned} \Phi_h(A_h) = & \frac{1}{2\lambda}(r_h^2 - r_0^2) + \frac{d}{\bar{N}^{1/2}}(r_h^{1/2} - r_0^{1/2}) \\ & + 2\mu A_h^3 - \frac{3\lambda}{4}A_h^4 , \end{aligned} \quad (26)$$

where the renormalized inverse susceptibilities are given by

$$r_0 = \tau + \frac{d\lambda}{r_0 \bar{N}^{1/2}} , \quad (27)$$

$$r_l = \tau + \frac{d\lambda}{r_l \bar{N}^{1/2}} + \lambda A_l^2 , \quad (28)$$

$$r_h = \tau + \frac{d\lambda}{r_h \bar{N}^{1/2}} + 3\lambda A_h^2 . \quad (29)$$

At the minimum of the potential, the Brazovskii equations of state are [14]

$$h_l = r_l A_l - \frac{\lambda}{2} A_l^3 = 0, \quad (30)$$

$$h_h = r_h A_h + \mu A_h^2 - \frac{\lambda}{2} A_h^3 = 0. \quad (31)$$

These equations, together with (27), (28), and (29), can be solved simultaneously for the amplitudes and inverse susceptibilities in the lamellar and hexagonal phases. The transition between these phases occurs when the potentials are equal, and the order-disorder transition is located at $\Phi=0$. The quantities x^* , μ , and λ were extracted from the Table in [13]. Substitution of the amplitudes into Eqs. (22)–(24) then enables the scaled elastic constants to be calculated. Figure 4 shows representative calculations as a function of

$$\tau' = \tau_R - d\lambda \tau_R^{-1/2} \bar{N}^{-1/2},$$

where u has been expressed in dimensionless units [15]. Two values of f and \bar{N} have been chosen such that the hexagonal rod phase is the high τ (temperature) ordered phase (phase diagrams for these values of \bar{N} are given in [13]). As noted by Fredrickson and Helfand, these values of \bar{N} correspond to Ginzburg parameters lower than those for which the Hartree approximation is rigorously valid. However, quantitative comparison between the predictions of fluctuation theory for the structure factor in the disordered phase and small angle neutron scatter-

ing experiments has been obtained for degrees of polymerization $\bar{N} \sim 10^4$ [23]. The essential features of these calculations are that (i) the elastic moduli decrease monotonically with increasing τ (because the order parameter amplitude does); (ii) they are of the same order of magnitude as those for lamellae, but smaller when comparisons are made for a given τ for a particular system; and (iii) as for lamellae [11], the ordered phase can persist as a metastable state above the order-disorder transition.

III. DISCUSSION AND SUMMARY

Instabilities in hexagonal columnar phases formed by liquid crystals and block copolymers have been studied theoretically in this paper. Detailed calculations were presented for the mechanical properties of the hexagonal-packed rod phase in diblock copolymers subject to a uniaxial tensile strain. In contrast to the case of thermotropic liquid crystals, the elastic constants of block copolymers are simple to compute using the random phase approximation, where details of chemical structure are not required.

We have shown that because the saddle-splay elastic constant C satisfies $C \geq \frac{1}{2}\bar{B}$ (as an equality), where \bar{B} is the compressional modulus, diblock copolymers subject to a uniaxial tensile strain should undergo a Helfrich-Hurault transition to a square modulated structure. The critical strain for this transition is

$$\varepsilon_c = 2\kappa[K_3/(\bar{B} + C)]^{1/2},$$

where $\kappa = \pi/L$ is the wave vector orthogonal to the planes of rods and K_3 is the column bending modulus. This transition should be independent of the orientation of the strain in the plane orthogonal to the rod axis.

This work complements previous studies on the lamellar phase of diblock copolymers subject to uniaxial tensile strains [11,12] or tensile and compressive stresses [10]. Small compressive strains change the layer period but do not lead to a structural instability for the lamellar phase, and the same should hold for the hexagonal columnar phase when strains are applied orthogonal to the column axis. Qualitatively, it has been shown that under a compressive strain the lamellar phase will undergo a quasithermodynamic melting to the isotropic phase prior to the spinodal if the nucleation barrier is not too high [10]. If the barrier is high or the strain is increased at a rate where the formation of the isotropic phase is preempted, then the strain can be increased beyond the quasithermodynamic melting point to the spinodal, where melting to the isotropic state will occur directly. For an applied stress, however, a mechanical instability sets in before the spinodal, which cannot be accessed in this case. Similar effects are anticipated for the hexagonal columnar phase, which behaves as a layered phase when deformations are applied orthogonal to the columns. The theoretical analysis will not be as tractable as that for lamellae [10] because the free energy density will contain third- and fifth-order terms. For a columnar phase subject to compression along the column axis, a buckling instability results if the stress frequency is high enough such that flow does not occur along the fluid

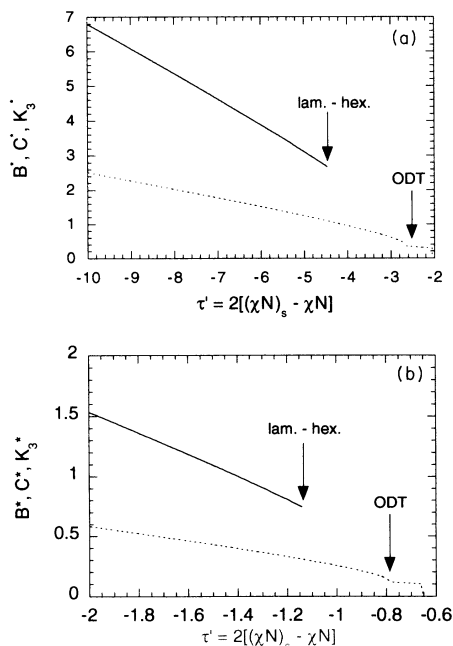


FIG. 4. Scaled dimensionless elastic constants as a function of $\tau' = 2[(\chi N)_s - \chi N]$, which is an increasing function of temperature. Solid line, lamellar phase; dashed line, hexagonal-packed cylinder phase. Here, $B^* = R_g^4 \bar{B} / c^2$, $C^* = B^* / 2$, and $K_3^* = 2K_3 R_g^4 q_0^2 / c^2$. The diblock compositions and scaled degrees of polymerization are (a) $f=0.40$, $\bar{N}=10^4$ and (b) $f=0.45$, $\bar{N}=10^6$.

direction and providing molecular permeation between columns can be neglected [7]. This deformation has already been analyzed in detail by a number of authors [7,19,20].

Inclusion of higher-order terms in the Fourier series representation of the displacement field for the Helfrich-Hurault instability in a lamellar phase has recently been considered [24]. It was shown that a chevron-type structure, where the undulating layers develop sharp changes in orientation, should result when boundary conditions are absent, even for small strains. However, at the instability threshold a single mode analysis is valid [24]. A chevron structure is inconsistent near boundaries because undulations must vanish continuously as the boundaries are approached. As the strain increases above the critical value, the elastic free energy density employed here becomes a poorer approximation, and higher order terms would need to be included. The possible subsequent development of defect structures, such as the arrays of focal conics observed for lamellar phases, is beyond the scope of the quasistatic theory.

As discussed in the Introduction, this paper is concerned with quasistatic deformations, i.e., the effects of polymer flow have been neglected. This should not be a significant drawback in practice when the polymers are below or at their entanglement molecular weights and yet are still microphase separated [10]. A recent calculation for the diffusion of a strongly segregated diblock chain across an interface in the lamellar phase supports our assumption that structural rearrangements can be slow on molecular time scales because this diffusion is found to be a very slow process [25].

Another refinement to the present work would be to allow for block copolymer "conformational asymmetry," i.e., different segment lengths $b = R_g \sqrt{N}/6$ within the blocks. The phase diagram for diblock copolymers has

been shown theoretically [26,27] and experimentally [6,28] to depend on $\epsilon = (\rho_B b_B^2)/(\rho_A b_A^2)$, where ρ_A and ρ_B denote pure component densities, as well as f , χN , and N . In particular, regions of complex phases recently observed near $f = 0.65$ are distinct from those near $f = 0.35$, and this difference has been ascribed to conformational asymmetry. Particularly interesting in the context of the present work and previous studies of mechanical instabilities in the lamellar phase is that modulated lamellar and deformed hexagonal-packed cylinder phases have been observed in the region of the phase diagram near $f_A = 0.65$ (where f_A is the volume fraction of the block with the larger segment length) for diblocks aligned using reciprocating shear [5,6]. It may be that the hexagonal modulated lamellar and modulated cylinder structures observed are metastable structures induced by mechanical deformation, or they may be in thermodynamic equilibrium. This has not yet been resolved because the structures have been determined using aligned samples. We have seen that the continuum elastic theory for lamellar and hexagonal columnar phases allows for in-plane deformations when small strains or stresses are applied. The Curie principle states that the microstructure should retain those symmetry elements which are common with those of the deformation field [29], i.e., two-dimensional deformations such as shear lead to structures other than the square one expected for a tensile deformation. Whether such structures are in thermodynamic equilibrium or not, mechanical deformations will influence their stability. A complete analysis for more general elastic distortions and, additionally, considering dynamic mechanical deformations should yield insight into complex phase behavior, and contribute toward the development of new applications based on unusual polymeric mechanical properties.

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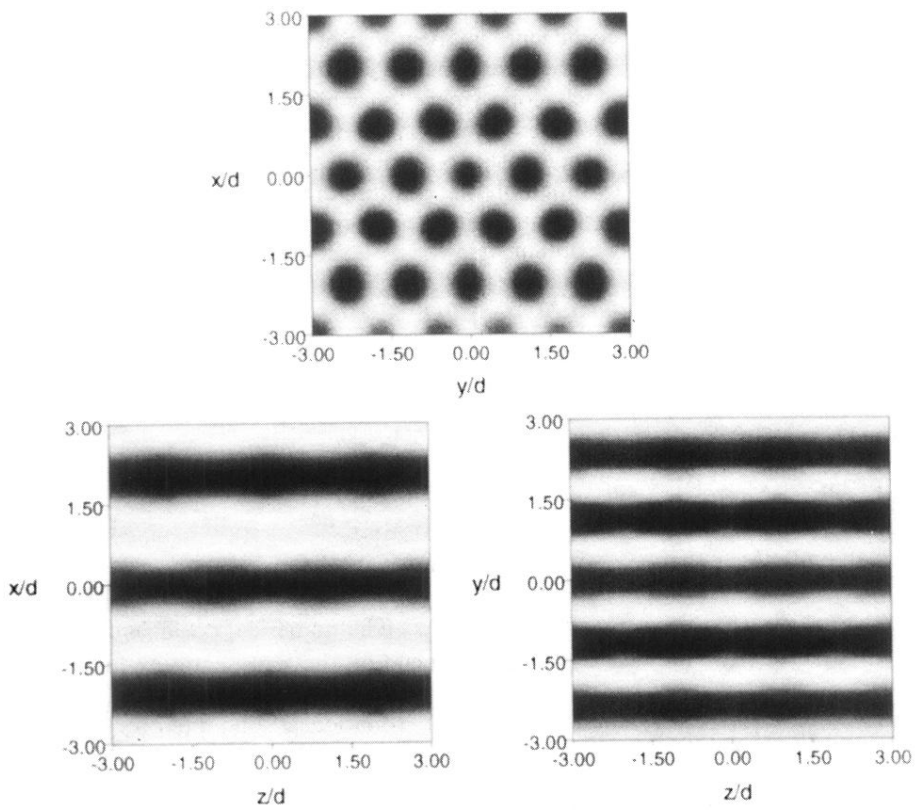


FIG. 3. Representative contour plots of the density in three orthogonal planes in the square modulated hexagonal-packed cylinder phase. The density parametrization is described in the text.