Chapter 5

Influence of confinement on the orientational phase transitions in the lamellar phase

In this chapter we incorporate some real-system effects into the theory of orientational phase transitions under shear flow. In particular, we study the influence of the shear-cell boundaries on the orientation of the lamellar phase. We predict that at low shear rates, the parallel orientation appears to be stable. Before we have shown that there is a critical value of the shear rate at which the parallel orientation loses its stability and the perpendicular one appears immediately below the spinodal. We associate this transition with a crossover from the fluctuation to the mean-field behaviour. At lower temperatures, the stability of the parallel orientation is restored. We find that the region of stability of the perpendicular orientation rapidly decreases as the shear rate increases. This behaviour might be misinterpreted as an additional perpendicular to parallel transition recently discussed in the literature.

5.1 Introduction

When subjected to a shear flow, AB block copolymer melts exhibit an orientational phase behaviour which is absent in equilibrium. A system under shear shows not only transitions between different morphologies (typically lamellar, hexagonal, cubic, and gyroid [1, 67]), but also transitions between different orientations of these morphologies with respect to the shear geometry. This effect is extensively discussed in the experimental literature for the lamellar [5, 15] and hexagonal phases [41, 42].

The theoretical description of the lamellar reorientation was developed in [53, 56] (see Chapter 2). The same method was applied in Chapter 3 to study the hexagonal pattern. In these theories, the orientational transitions appear as
a result of the interaction of shear flow with the critical fluctuations in the melt. There are two distinct regimes: weak shear only slightly perturbs the fluctuation spectrum while strong shear significantly dumps fluctuations, restoring the mean-field behaviour in the limit of infinite shear rate $D \to \infty$. Correspondingly, the parallel lamellae (their normal is parallel to the shear gradient direction) are found to be stable in the small shear rate regime, while the perpendicular lamellae (their normal is perpendicular to both the gradient and flow directions) are stable at high shear rates. Fredrickson has shown that if one takes into account the difference in viscosities of the pure melt components, the perpendicular phase loses its stability at low enough temperatures and the parallel orientation is restored. Schematically this behaviour is summarized in Fig. 5.1.

However, there is experimental evidence that this picture is not complete. At very high shear rates, the parallel orientation was found to be the only stable one [18, 27]. This cannot be explained in the discussed framework of [56], since it predicts the stability region for the perpendicular phase to increase as $D \to \infty$.

Here we propose an explanation of the additional transition (the C-transition
in Fig.5.1. We argue that the missing element of the theory is the interaction of the block copolymer melt with the walls of the shear cell. We consider a block copolymer confined in-between two walls in the gradient direction and subjected to a steady shear flow. Usually the distance between the interfaces in the other two directions is much larger and we ignore their influence. This model will predict the parallel orientation to be stable in the \( D \rightarrow \infty \) limit since the influence of shear and fluctuations vanishes in this limit. The only symmetry-breaking factor is then the wall-copolymer interaction which stabilizes the parallel orientation [118, 136]. The complex behaviour at lower shear rates will arise from the interplay of three factors: shear flow, fluctuations, and wall-melt interactions.

We admit that the influence of the surface interactions is possibly small. However, Balsara et. al. reported [137] that in the absence of shear the walls of their shear cell induced the parallel alignment through the whole 0.5-mm-sample, although the lamellar spacing was somewhat four orders of magnitude smaller. Under shear, Laurer et. al. [138] observed that independent of the bulk orientation, there is always a near-surface layer of the parallel lamellae which penetrates up to 2 \( \mu \)m into the bulk. Thus, even a weak symmetry-breaking field can be crucial in the absence of other factors.

We also want to mention that the equilibrium theory of block-copolymer melt ordering near surfaces is well developed [118, 136, 139, 140, 141, 142, 143, 144, 145, 146] (see Appendixes A and B). Some questions concerning the dynamics of such an ordering were addressed in [147, 143]. However, until now, this theory has not been applied to non-equilibrium systems.

This chapter is organized as follows. In Section 5.2 we derive the equations governing the dynamics of the melt and construct a non-equilibrium potential whose minimal value will determine the stable orientation. In Section 5.3 we analyze the B- and C-transitions (the shear rate of the A-transition has already been estimated in Section 2.4). In conclusion we discuss in detail the properties of the phase diagram obtained.

### 5.2 Dynamic equations

Let us consider a block copolymer melt confined in-between two surfaces in the \( y \)-direction. It is also subjected to a steady shear flow \( v = D_y e_x \) (see Fig.5.2). We ignore any alteration of this velocity profile and assume that it is kept throughout the whole system. We choose the local deviation of the composition from its average to be an order parameter \( \phi(\mathbf{r}) \) and define its Fourier transform as

\[
\phi(\mathbf{k}) = \int d\mathbf{r} \, e^{-i\mathbf{k}\mathbf{r}} \phi(\mathbf{r}) \quad \text{and} \quad \phi(\mathbf{r}) = \int_k e^{i\mathbf{k}\mathbf{r}} \phi(\mathbf{k})
\]
Figure 5.2: Orientations of the lamellar phase in a simple shear flow. The axes of the coordinate system correspond to the shear geometry: $x$ is the flow direction ($\mathbf{v}$), $y$ is the gradient direction ($\nabla v_x$) and $z$ is the vorticity direction ($\nabla \times \mathbf{v}$). In the parallel orientation the normal to the lamellar layers is oriented parallel to the gradient direction, in the perpendicular one – to the vorticity direction. The walls in $y$ direction interact with the melt and prefer one of the components.

where

$$
\int_k \equiv \frac{1}{L} \sum_{k_y} \int \frac{dk_x dk_z}{(2\pi)^2} \quad \text{and} \quad \int d\mathbf{r} \equiv \int_{-\infty}^{\infty} dx \int_{-L/2}^{L/2} dy \int_{-\infty}^{\infty} dz
$$

(5.2)

It is convenient to work in dimensionless units and we rescale lengths and wavevectors: $\mathbf{r} \rightarrow b^{-1} \mathbf{r}$ and $\mathbf{k} \rightarrow b \mathbf{k}$, $b$ being the size of a monomer.

Following [51, 53, 56] we assume that the dynamics under shear flow is governed by the Fokker-Planck equation:

$$
\frac{\partial P[\phi, t]}{\partial t} = \int d\mathbf{r} \frac{\delta}{\delta \phi(\mathbf{r})} \left[ \mu \left( \frac{\delta}{\delta \phi(\mathbf{r})} + \frac{\delta \mathcal{H}}{\delta \phi(\mathbf{r})} \right) + D_y \frac{\partial \phi}{\partial x} \right] P[\mathbf{r}, t]
$$

(5.3)

where $P[\phi, t]$ is the probability to realize the order parameter profile $\phi(\mathbf{r})$ at time $t$, and $\mu$ is an Onsager coefficient.

In eq.(5.3) the Hamiltonian $\mathcal{H}$ consist of two contributions: the bulk Hamil-
tonian derived by Leibler [67]

\[ N\mathcal{H}_L[\phi] = \frac{1}{2} \int_{q} \Gamma_2(q)\phi(q)\phi(-q) + \frac{1}{3!} \int_{q_1} \int_{q_2} \int_{q_3} \Gamma_3(q_1, q_2, q_3)\phi(q_1)\phi(q_2)\phi(q_3) \]

\[ + \frac{1}{4!} \int_{q_1} \int_{q_2} \int_{q_3} \int_{q_4} \Gamma_4(q_1, q_2, q_3, q_4)\phi(q_1)\phi(q_2)\phi(q_3)\phi(q_4) \]

(5.4)

and the surface energy [118, 136]

\[ N\mathcal{H}_s = \int d\mathbf{r} \left[ -H_1(\mathbf{r}) + \frac{a_1}{2} \phi(\mathbf{r})^2 \right] \left[ \delta \left( y + \frac{L}{2} \right) + \delta \left( y - \frac{L}{2} \right) \right] \]

(5.5)

where \( N \) is a number of monomers in a molecule, \( H_1 \sim (\chi N)_{cop-surf} \) is the strength of the interaction between the surface and the copolymer melt, and \( a_1 \) describes the additional interaction in the melt induced by the presence of the surface (it changes the local temperature in the vicinity of the surface). Our goal is to construct a real-space version of the Leibler Hamiltonian \( \mathcal{H}_L \). In [87, 77, 118] it was shown how to deal with the second-order vertex function. Separating small- and large-wave-vector asymptotic behaviour, one can show that

\[ \Gamma_2(q) \approx \frac{A}{q^2} + Bq^2 - \bar{\chi} \]

(5.6)

where

\[ A = \frac{3}{2R_G^2 f^2 (1 - f)^2} \]

\[ B = \frac{R_G^2}{2f(1 - f)} \]

\[ \bar{\chi} = 2 \left( \chi N - (\chi N)_s \right) + \left( \frac{3}{f^3 (1 - f)^3} \right)^{1/2} \]

(5.7)

with \( f = N_A/N \) being the volume fraction of the A-component. In [118] the third- and fourth-order vertex functions were assumed to be constant. However, as it was noted in [56] and in Chapters 2.3 and 4, it is crucial to keep the angular dependence of the fourth-order vertex function in order to discriminate between the parallel and the perpendicular orientations. There, the following approximation was made:

\[ \Gamma_3(q_1, q_2, q_3) = \delta(q_1 + q_2 + q_3)\Gamma_3 \]

\[ \Gamma_4(\mathbf{k}, q_1, -\mathbf{k}, -q_1) = \lambda \left( 1 - \beta (\mathbf{k} \cdot \mathbf{q})^2 \right) \]

(5.8)

where \( \mathbf{k} = k/k \). In eq.(5.8) all the wave-vectors are assumed to have the same length \( k_0 = (A/B)^{1/4} \), which corresponds to the first unstable mode on the spinodal [67]. The assumption \( \beta \ll 1 \) was shown to be correct for almost any architecture of AB block-copolymer molecules (for example, for diblocks \( \beta \leq 0.1 \), see
Chapter 4). For an arbitrary star of 4 \( q \)'s one can write to the lowest order in angles [130, 131]

\[
\Gamma_4(q_1, q_2, q_3, q_4) = \delta (q_1 + q_2 + q_3 + q_4) \times \\
\left[ \lambda_0 + \frac{\lambda_1}{\lambda_0} \left( (q_1 \cdot q_2)(q_3 \cdot q_4) + (q_1 \cdot q_4)(q_2 \cdot q_3) + (q_1 \cdot q_3)(q_2 \cdot q_4) \right) \right] \\
+ \frac{\lambda_2}{\lambda_0} \left( (q_1 \cdot q_2)^2 + (q_1 \cdot q_3)^2 + (q_1 \cdot q_4)^2 + (q_2 \cdot q_3)^2 + (q_2 \cdot q_4)^2 + (q_3 \cdot q_4)^2 \right)
\]

(5.9)

\[
\frac{\lambda_1}{\lambda_0}, \frac{\lambda_2}{\lambda_0} \ll 1
\]

Comparison with eq.(5.8) gives

\[
\lambda = \lambda_0 + \lambda_1 + 2\lambda_2 \quad , \quad \beta = -\frac{2\lambda_1 + 4\lambda_2}{\lambda_0 + \lambda_1 + 2\lambda_2}
\]

(5.10)

Thus, the required real-space representation of the Hamiltonian \( \mathcal{H} \) can be written as

\[
\mathcal{N}\mathcal{H}[\phi] = \int d\mathbf{r} \left[ \frac{B}{2} \left( \nabla \phi (\mathbf{r}) \right)^2 - \frac{1}{2} \chi \phi (\mathbf{r})^2 + \frac{A}{2} \int d\mathbf{r}' \mathcal{G}(\mathbf{r} - \mathbf{r'}) \phi (\mathbf{r}) \phi (\mathbf{r}') \\
+ \frac{\Gamma_4}{3!} \phi (\mathbf{r})^3 + \frac{\lambda_0}{4!} \phi (\mathbf{r})^4 + \frac{3\lambda_1}{4!} \frac{\left( \nabla \phi (\mathbf{r}) \cdot \nabla \phi (\mathbf{r}) \right)^2}{k_0^4} \\
+ \frac{6\lambda_2}{4!} \phi (\mathbf{r})^2 \frac{\left( \nabla_\alpha \nabla_\beta \phi (\mathbf{r}) \right)^2}{k_0^4} - \chi (\mathbf{r}) \phi (\mathbf{r}) \right] + \mathcal{N}\mathcal{H}_s
\]

(5.11)

where

\[
\mathcal{G}(\mathbf{r} - \mathbf{r'}) = \int_q \frac{e^{i\mathbf{q}(\mathbf{r} - \mathbf{r'})}}{q^2}
\]

(5.12)

Here we have added an auxiliary field \( \chi \) which will help us to construct a thermodynamic potential governing the dynamics under shear. Afterwards it will be set to zero.

The Fokker-Planck equation (5.3) together with eqs.(5.11,5.7,5.5) form a phenomenological set of equations describing the dynamics of block-copolymer melt under shear flow in the presence of surfaces. We do not solve these equations directly, but following [56] we use the method of Zwanzig [129] to derive a system of coupled equations for the first two cumulants of \( P[\phi, t] \) (see Appendix 2.B)

\[
c(\mathbf{r}) = \langle \phi (\mathbf{r}) \rangle \\
S(\mathbf{r}_1, \mathbf{r}_2) = \langle \phi (\mathbf{r}_1) \phi (\mathbf{r}_2) \rangle - \langle \phi (\mathbf{r}_1) \rangle \langle \phi (\mathbf{r}_2) \rangle
\]

(5.13)
where $c$ is the average order-parameter profile, and the structure factor $S$ is a measure of the fluctuations’ strength. We introduce a generating functional

$$G[\xi, t] = \log \int \mathcal{D}[\phi] \exp \left[ \int dr \, \phi(r) \xi(r) \right] P[\phi, t], \quad (5.14)$$

use eq.(5.3) to derive an equation of motion for $G[\xi, t]$, and then expand this equation in terms of $\xi$. The two lowest-order equations read

$$\frac{1}{\mu} \frac{\partial c(r)}{\partial t} = -\frac{D}{\mu} \frac{\partial c(r)}{\partial x} + B \Delta c(r) + \bar{\chi} c(r) - A \int dr' \, G(r - r') c(r')$$

$$+ \frac{\Gamma_3}{2} \left[ c(r)^2 + S(0) \right] - \frac{\lambda_0}{3!} \left[ c(r)^2 + 3S(0) \right] c(r) - \frac{2\lambda_1 + 4\lambda_2}{k_0^4} \left( \nabla_\alpha \nabla_\beta c(r) \right) \tilde{S}_{\alpha\beta}$$

$$+ \frac{\lambda_1}{2k_0^4} \nabla_\alpha \left( \nabla_\alpha c(r) \{\nabla c(r)\}^2 \right) + \tilde{S}_{\alpha\alpha} \Delta c(r)$$

$$- \frac{\lambda_2}{2k_0^4} \left[ c(r) \left( \nabla_\alpha \nabla_\beta c(r) \right) \right] + c(r) \tilde{S} + \nabla_\alpha \nabla_\beta \left( c(r)^2 \nabla_\alpha \nabla_\beta c(r) \right) + S(0) \Delta^2 c(r)$$

$$+ h(r) + \left( H_1 - a_1 c(r) \right) \left[ \delta \left( y + \frac{L}{2} \right) + \delta \left( y - \frac{L}{2} \right) \right]$$

and

$$\frac{1}{2\mu} \frac{\partial S(r - r_1)}{\partial t} = \delta(r - r_1) - \frac{D}{\mu} \frac{S(r - r_1)}{\partial x} + B \Delta S(r - r_1) + \bar{\chi} S(r - r_1)$$

$$- A \int dr' \, G(r - r') S(r' - r_1) - \frac{\Gamma_3}{2} \left[ S(0) + 2c(r) S(r - r_1) \right]$$

$$- \frac{\lambda_0}{2} \left[ c(r)^2 + S(0) \right] S(r - r_1) - \frac{\lambda_1 + 2\lambda_2}{k_0^4} \tilde{S}_{\alpha\beta} \nabla_\alpha \nabla_\beta S(r - r_1)$$

$$+ \left( \nabla_\alpha S(r - r_1) \right) \left( \nabla c(r) \right)^2 + \tilde{S}_{\beta\gamma} \nabla_\alpha S(r - r_1)$$

$$- \frac{\lambda_2}{2k_0^4} \left[ S(r - r_1) \left( \nabla_\alpha \nabla_\beta c(r) \right)^2 \right] + S(r - r_1) \tilde{S} + 2c(r) \left( \nabla_\alpha \nabla_\beta c(r) \right) \left( \nabla_\alpha \nabla_\beta S(r - r_1) \right) + S(0) \Delta^2 S(r - r_1)$$

$$+ 2\nabla_\alpha \nabla_\beta \left( c(r) S(r - r_1) \nabla_\alpha \nabla_\beta c(r) \right) + \nabla_\alpha \nabla_\beta \left( c(r)^2 \nabla_\alpha \nabla_\beta S(r - r_1) \right)$$

$$- a_1 S(r - r_1) \left[ \delta \left( y + \frac{L}{2} \right) + \delta \left( y - \frac{L}{2} \right) \right]$$

where

$$\tilde{S}_{\alpha\beta} = \nabla_\alpha \nabla_\beta S(r - r') \bigg|_{r' = r}, \quad \tilde{S} = \nabla_\alpha \nabla_\beta \nabla_\alpha \nabla_\beta S(r - r') \bigg|_{r' = r} \quad (5.17)$$
Here we have neglected all higher cumulants and made use of a natural assumption \( S(r_1, r_2) = S(r_1 - r_2) \).

Apart from the surface terms, eqs.(5.15,5.16) are the real-space analog of eqs.(2.B.6,2.B.7). Here the terms proportional to \( S(0) \) play the role of the fluctuation integral \( \sigma(k) \) from [56]:

\[
s(k) = \frac{\lambda}{2} \int_q S(q) \left[ 1 - \beta (\hat{k} \cdot \hat{q})^2 \right] \quad (5.18)
\]

To keep our model as simple as possible, we leave only the linear term in the surface energy (5.5) and put \( a_1 = 0 \). Then we set

\[
c(r) = 2a \cos(k_0 n \cdot r + \varphi) \quad (5.19)
\]

\[
h(r) = 2h \cos(k_0 n \cdot r + \varphi)
\]

where \( a \) is the yet to be determined amplitude, \( n \) is a unit vector perpendicular to the surface of the lamellae, and \( \varphi \) is a phase shift which will be chosen to minimize the surface energy. The auxiliary field \( h \) simply follows the behaviour of \( c \). Fredrickson has shown [118] that in equilibrium, the presence of surfaces causes spatial variations of the amplitude \( a \) which decay exponentially away from the surface. Since we are only interested in the orientation of the lamellar profile (5.19), we ignore the spacial dependence of \( a \) and set it constant. With these simplifications the equation for the Fourier transform \( S(k) \) of \( S(r_1 - r_2) \) from eq.(5.16) reads

\[
\frac{1}{2\mu} \frac{\partial S(k)}{\partial t} = 1 + \frac{D}{2\mu} k_x \frac{\partial S(k)}{\partial k_y} - S_0^{-1}(k) S(k) \quad (5.20)
\]

where

\[
S_0^{-1}(k) = r - \hat{k} \cdot \hat{e} \cdot \hat{k} + B k^2 + \frac{A}{k^2} - \bar{\chi}_s
\]

\[
r - \hat{k} \cdot \hat{e} \cdot \hat{k} = 2 \left( \chi_N^r - \chi_N \right) + \lambda a^2 \left( 1 - \beta (n \cdot \hat{k})^2 \right) + \sigma(k) \quad (5.21)
\]

Here we have introduced the same notation as before. In eq.(5.21) \( S_0(k) \) is the equilibrium structure factor and \( r - \hat{k} \cdot \hat{e} \cdot \hat{k} \) denotes the renormalized temperature. Within the fluctuation theory the spinodal temperature determined from the condition

\[
r - \hat{k} \cdot \hat{e} \cdot \hat{k} \bigg|_{a=0} = 0 \quad (5.22)
\]

differs from the mean-field value \( (\chi N)_s \). In the case \( \beta = 0 \) such a fluctuation correction was discussed in [68]. The presence of shear breaks the rotational
symmetry and the spinodal temperature becomes orientation-dependent. This gives rise to the \( \mathbf{k} \cdot \mathbf{e} \cdot \mathbf{k} \) term, with \( e_{ij} \sim \beta \) (see eq.(5.8)). Here the role of the angular dependence in \( \Gamma_i \) is especially transparent: if \( \beta = 0 \), we would not be able to discriminate between different orientations.

The method of characteristics (Appendix 2.C) gives a formal solution for eq.(5.20):

\[
S(\mathbf{k}, t) = 2\mu \int_0^t d\tau \exp \left[ -2\mu \int_0^\tau dS_0^{-1}(k_x, k_y + Dsk_x, k_z) \right]
\]

The steady-state regime is approached as \( t \to \infty \). The integration in (5.23) can be performed in the limiting cases \( D \to 0 \) and \( D \to \infty \) and will be discussed in the next section.

Now we derive an equation for the amplitude \( a \). We substitute the lamellar profile (5.19) into eq.(5.15) and perform an averaging over the lamellar period

\[
\langle \cdots \rangle = \frac{n_x n_y n_z k_0^3}{(2\pi)^3} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} d\varphi \, dy \, dz \cos (k_0 \mathbf{n} \cdot \mathbf{r} + \varphi) \cdots
\]

Discarding the transverse orientations with \( n_x \neq 0 \) [51, 53, 56], we obtain

\[
\frac{1}{\mu} \frac{\partial a}{\partial t} = h - (r - \mathbf{n} \cdot \mathbf{e} \cdot \mathbf{n})a + \frac{1}{2} \lambda (1 - \beta) a^3 + \eta \cos(\varphi) \delta_{n_z,1}
\]

where \( \eta = \frac{k_0}{\pi} H_1 \), and \( \delta_{n_z,1} \) is the Kronecker delta-symbol which is non-zero only for the parallel \( (|n_y| = 1) \) orientation. Following [56] we notice that equation (5.25) has a gradient form (with \( h = 0 \))

\[
\frac{1}{\mu} \frac{\partial a}{\partial t} = -\frac{1}{2} \frac{\partial \mathcal{F}}{\partial a}
\]

Since the potential \( \mathcal{F} \) can only decrease with time

\[
\frac{\partial \mathcal{F}}{\partial t} = \frac{\partial \mathcal{F}}{\partial a} \frac{\partial a}{\partial t} = -\frac{\mu}{2} \left( \frac{\partial \mathcal{F}}{\partial a} \right)^2 < 0
\]

the steady state of the system will be determined by the minimum of \( \mathcal{F} \). Now we use the auxiliary field \( h \) to construct \( \mathcal{F} \). In the steady state \( \partial a/\partial t = 0 \), and \( \mathcal{F} \) is obtained by integrating

\[
\frac{1}{\mu} \frac{\partial a}{\partial t} = \frac{1}{2} \frac{\partial \mathcal{F}}{\partial a}
\]

Using \( h \) from eq.(5.25), we obtain

\[
\mathcal{F} = \mathcal{F}_0 - 2\eta a \delta_{n_z,1}
\]
where
\[ \mathcal{F}_0 = -\frac{1}{4}\lambda(1 - \beta)a^4 + 2 \int_0^a da' (r - n \cdot \hat{e} \cdot n)a' \]  
(5.30)

In eq.(5.29) we have already minimized with respect to the phase shift \( \varphi \), assuming that \( a > 0 \) (the other terms depend only on even powers of \( a \) and are not influenced by this choice).

The non-trivial dependence of \( r - n \cdot \hat{e} \cdot n \) on \( a \) comes from the term proportional to \( \sigma(k) \) in (5.21) and the potential \( \mathcal{F} \) appears to be dependent on the fluctuation integral via eq.(5.30). Now we are ready to discuss the stable orientations in different regimes.

### 5.3 B- and C-transitions

We start with noticing that at low shear rates the parallel orientation is the only stable one. Indeed, as it was shown in Section 2.5, \( \mathcal{F}_0 \) is minimal for \( n_y^2 = 1 \) in the limit \( D \to 0 \). The surface term in eq.(5.29) also favours the parallel orientation. Thus, our theory does not modify Fredrickson’s prediction for small shear rates.

As we discussed before, at intermediate shear rates there is a cross-over from weak to strong shear. Its position is estimated by eq.(2.56)
\[ D_{cr} \approx 4 \cdot 10^3 \mu \alpha \]  
(5.31)

For \( D > D_{cr} \) the fluctuation integral is given by
\[ \sigma(n) = \frac{(\alpha \lambda)^{2/3}}{B^{3/2}} \left( \frac{D_s}{D} \right)^{1/3} \left( \frac{2^{1/3}}{8} \sqrt{3} \right) c_1 \left[ 1 - \frac{\beta}{7}(2n_y^2 + 3n_z^2) \right] \]  
(5.32)

If one puts \( 4B \equiv 1 \), the previous equation coincides with eq.(2.23). Since eq.(5.32) does not depend on the renormalized temperature, the integration in eq.(5.30) is trivial and gives
\[ \mathcal{F} = [\tau + \sigma(n)] a^2 + \frac{1}{4}\lambda a^4(1 - \beta) - 2\eta a\delta n_{y,1}^2 \]  
(5.33)

where
\[ \tau = 2 \left( \chi N_s - \chi N \right) \]

Minimization with respect to \( a \) gives to the first order in \( \eta \)
\[ \mathcal{F} = -\frac{[\tau + \sigma(n)]^2}{\lambda(1 - \beta)} - 2\eta \sqrt{-2\frac{\tau + \sigma(n)}{\lambda(1 - \beta)} \delta n_{y,1}^2} \]  
(5.34)
The order-disorder transition (ODT) occurs when $\mathcal{F}$ becomes negative. The corresponding transition temperature is

$$
\tau_s(n) = -\sigma(n)
$$

which coincides with eq.(5.22). The perpendicular orientation has the lowest $\sigma$, and thus appears immediately below the ODT.

Now we consider lower temperatures and look for transitions between different orientations in the strong-shear limit. The corresponding free energies are given by eq.(5.34)

$$
\mathcal{F}_\parallel = -\left(\frac{\tau + \sigma_\parallel}{\lambda(1 - \beta)}\right)^2 - 2\eta\sqrt{-\frac{2\tau + \sigma_\parallel}{\lambda(1 - \beta)}}
$$

$$
\mathcal{F}_\perp = -\frac{(\tau + \sigma_\perp)^2}{\lambda(1 - \beta)}
$$

To the leading order in $D_s/D$, the transition from the perpendicular to parallel orientation occurs at temperatures which are the roots of the equation $\mathcal{F}_\parallel = \mathcal{F}_\perp$

$$
\tau_1 = -\sigma_\parallel - \frac{(\sigma_\parallel - \sigma_\perp)^4}{8\eta^2\lambda(1 - \beta)}
$$

$$
\tau_2 = -\frac{2\eta^2\lambda(1 - \beta)}{(\sigma_\parallel - \sigma_\perp)^2} \quad \text{if} \quad \eta^2\lambda(1 - \beta) > (\sigma_\parallel - \sigma_\perp)^3
$$

where

$$
\sigma_\parallel - \sigma_\perp = \beta \frac{2^{1/3}\sqrt{3c_1}(\alpha\lambda)^{2/3}}{56} \left(\frac{D_s}{D}\right)^{1/3}
$$

There $\tau_1$ corresponds to the $\perp \rightarrow \parallel$ transition, while $\tau_2$ - to the reverse one. Now we summarize our results in a phase diagram.

### 5.4 Discussion of the phase diagram and Conclusion

In this chapter we incorporated some real-system properties into the previously developed theory of the orientational phase transitions under shear flow. In particular, we considered the influence of the shear-cell boundaries in the gradient direction on the orientation of the lamellar phase. In equilibrium, the lamellae are known to orient parallel with respect to the boundaries [118, 136]. Under shear, the tendency to orient parallel to the surfaces competes with the orientation favoured by the flow which appears as a result of the coupling between the flow velocity field and the order-parameter fluctuations [53, 56]. The interplay between these two factors produces the non-trivial phase diagram shown in Fig.5.3.
Figure 5.3: Phase diagram for the lamellar phase under steady simple shear flow.

At low shear rates the parallel orientation is preferred by both the shear and surface terms in eq.(5.29). Therefore, it is the only stable orientation in that part of the phase diagram. When shear rate reaches the value $D_{cr}$ given by eq.(2.56), the perpendicular orientation becomes stable immediately below the ODT temperature. We associate this change in orientation with the crossover from the fluctuation-dominated behaviour to the mean-field one. Indeed, at very small shear rates the equilibrium fluctuation spectrum is only slightly modified by the flow, while at high shear rates the flow strongly suppresses fluctuations and restores the mean-field behaviour. Therefore, there is a crossover point and the corresponding change of orientation.

At high shear rates and away from the spinodal, the surface influence starts to play an important role. In the narrow region between $D_{cr}$ and $D_1$, estimated from the condition in eq.(5.37)

$$D_1 = 2 \frac{(3c_0)^{3/2}}{56^3} \frac{\beta}{1 - \beta} D_s \frac{\lambda \alpha^2}{\eta^2 B^{9/2}}$$

the influence of shear is still very strong and is capable of stabilizing the perpendicular orientation at all temperatures. The size of this region is very small due to the scaling $D_1 \sim N^{-13/2}$. When $D > D_1$, there appears a region where the parallel orientation is stable. It takes over the perpendicular one at $\tau = \tau_1$ and looses its stability again at $\tau = \tau_2$ given by eq.(5.37). This region grows as the
shear rate increases, and in the limit $D = \infty$ the parallel orientation occupies the whole range of temperatures $(0, -\infty)$. This coincides with the predictions of the equilibrium mean-field theory [118, 136]. We therefore argue that there is no sharp C-transition as shown in Fig.5.1. Since the region between the spinodal and the parallel phase shrinks with an increase of the shear rate, there will always be some value $D_2$ such that for $D > D_2$ the size of this region will be smaller than the resolution of the experimental device. This value $D_2$ can be misinterpreted as a position of an additional transition.

An important feature of our theory is that it is able to reproduce the B-transition without additional assumptions. In the previous theory [56], Fredrickson had to take into account the difference in viscosities of the pure components in order to reproduce the B-transition. Namely, he put $\eta[\phi] = \eta_0 + \eta_1 \phi$ which can be considered as a Taylor expansion of the viscosity $\eta[\phi]$. As a result, in strong-shear limit the size of the stability region for the perpendicular phase is of order of $(\eta_0/\eta_1)^2$ and grows as $D \to \infty$. While capturing the main physics, this approach has internal problems since the derivative $\eta_1$ is not a well-defined object and therefore the whole theory depends on a phenomenological parameter which is difficult to estimate. Moreover, Fredrickson’s theory does not predict the C-transition. Our theory is free from these problems. It, however, predicts the $\parallel \to \perp$ transition at very low temperatures in the strong-shear limit which was not observed. There could be several explanations of this prediction. First, this transition occurs at very low temperatures ($\tau_2$) where the weak-segregation theory does not work. Second, this transition might be an artifact of the $O(\eta)$ expansion. Finally, this transition can be removed if we use Fredrickson’s argument about the viscosity dependence on the order parameter. It stabilizes the parallel orientation at low temperatures.

It is possible that the absolute value of the surface interaction is small. However, since it acts as a symmetry-breaking factor, its influence is very important [137, 138] (see Fig.5.4 for an encouraging example). This statement can be verified experimentally. We have shown that the positions of the transition lines in the strong-shear limit are dependent on the strength of the surface-copolymer interaction $\eta \sim (\chi N)_{\text{cop-surf}}$. Therefore, the phase diagram of a particular copolymer system depends on the material of the shear-cell walls. A systematic study of this dependence will provide arguments for or against our theory.

In this chapter we have considered the influence of walls in the gradient direction. We also want to comment on the role of boundaries in the other shear directions (flow and vorticity). Formally, these walls will also induce alignment parallel to themselves. However, the flow profile near those walls is no longer a simple triangular one and we expect this disordered flow to destroy their orientational tendency. Moreover, the distance between those surfaces is normally much larger than between the walls in the gradient direction and their influence is thus weaker. Therefore we neglected them in our work.

Finally, we want to discuss briefly possible modifications and extensions of
Figure 5.4: Reproduced with permission from Laurer et. al [138], *Macromolecules* **1999**, 32, 4999-5003. Copyright 1999 American Chemical Society. Transmission electron micrographs of the blend of poly(styrene-$b$-isoprene) with homopolystyrene. Comparable results were found in the neat diblock copolymer. In all micrographs presented the horizontal axis corresponds to the gradient direction, while the vertical axis corresponds to the free (vorticity) direction of the flow. a) Isotropic blend in the bulk without shear. Numerous lamellar grains, 100–600 nm across, exist in different orientations. b) The same near the surface of the specimen. A well-defined parallel orientation is found to extend ca. 2 $\mu$m away from the surface. The surface is observed on the right side of the micrograph. c) The perpendicular orientation of the blend under shear obtained near the surface. Lamellae are aligned parallel to the surface but become perpendicular away from the surface (i.e., in the bulk).
the theory developed. A very interesting problem is to calculate the alterations of the density profile in a confined system under shear. This can be achieved by restoring the position dependence in the amplitude $a$ and deriving the corresponding amplitude equation from eq.(5.15). In the absence of shear this problem was solved in [118] (see Appendix 5.A and Appendix 5.B). Another possibility is to use our formalism for other external fields rather than interactions with surfaces. A good example is an electric field which is coupled to the square of the order parameter [4, 148]. With some modifications eq.(5.15,5.16) can be a starting point for the corresponding theory. The importance of such a theory for a system in electric field and simultaneously under shear was pointed out in [148].
Appendix 5.A  Equilibrium mean-field theory of surface-induced phase separation

In order to demonstrate here the influence of boundaries on equilibrium phase separation, we present the main results of Fredrickson [118].

Let us consider a disordered phase of a diblock copolymer melt near a surface. If the surface prefers one component of the melt, then the low-energy state corresponds to the surface covered with this component. Since $A$ and $B$ blocks are chemically connected, the surface layer rich in one component will be followed by a layer rich in the other one. This alteration will penetrate into the bulk up to some typical distance. Thus we see that even if the temperature is higher than the bulk ODT temperature, the presence of an interacting wall results in a surface-induced phase transition from the disordered to lamellar phase.

In order to study this phenomenon we consider the Hamiltonian (5.11) with $\lambda_1 = \lambda_2 = 0$. Since we are interested in 1D problem only, it is convenient to introduce a new order parameter $\psi(x)$ which is an average value of $\phi(r)$ over the other directions. Here the $x$-axis is directed perpendicular to the surface and $x$ measures the distance to the surface. For a single wall located at $x = 0$ the new Hamiltonian reads

$$H[\psi] = \int_0^\infty dx \left[ \frac{1}{2} B \left( \frac{d\psi}{dx} \right)^2 - \frac{1}{2} \bar{\chi} \psi^2 + \frac{\Gamma_3}{3!} \psi^3 + \frac{\lambda}{4!} \psi^4 + \frac{A}{2} \int_0^\infty dx' G(x - x') \psi(x') \psi(x) \right] + \frac{1}{2} a_1 \psi^2(0) - H_1 \psi(0)$$

(A.1)

where $S$ is an area of the surface. The order parameter profile that optimizes this Hamiltonian is found by variation of $H$

$$\frac{\delta H[\psi]}{\delta \psi(x)} = 0 \Rightarrow -B \psi'' - \bar{\chi} \psi + \frac{\Gamma_3}{2!} \psi^2 + \frac{\lambda}{3!} \psi^3 + A \int_0^\infty dx' G(x - x') \psi(x') = 0$$

(A.2)

subjected to the boundary condition

$$a_1 \psi - B \psi' = H_1 , \quad x = 0$$

(A.3)

Above the spinodal

If $\bar{\chi} < \bar{\chi}_s$, the order parameter is small and we can linearize eq.(A.2)

$$B \psi'' + \bar{\chi} \psi + A \psi = 0$$

(A.4)
Figure 5.5: Order-parameter profile in a semi-infinite space

where we took the second derivative and used $\Delta x G(x - x') = -\delta(x - x')$. The
boundary conditions are given by eq.(A.3) together with

$$\psi(x) \to 0 \quad \psi'(x) \to 0 \quad x \to \infty$$  \hspace{1cm} (A.5)

$$\int_{0}^{\infty} dx \psi(x) = 0$$  \hspace{1cm} (A.6)

The last equation assures the conservation of the order parameter.

The solution of eqs.(A.4,A.5,A.6) is easily found

$$\psi(x) = \psi_{s} e^{-\xi x} \left(\cos \Omega x - \frac{\xi}{\Omega} \sin \Omega x\right)$$  \hspace{1cm} (A.7)

$$\xi = \sqrt{1 - \frac{\bar{\chi}}{\bar{\chi}_s}} \ , \ \Omega = \sqrt{1 + \frac{\bar{\chi}}{\bar{\chi}_s}} \ , \ \bar{X} = \frac{xk_{0}}{\sqrt{2}}$$  \hspace{1cm} (A.8)

Its behaviour is plotted in Fig.5.5 for various values of $\tau = \bar{\chi} / \bar{\chi}_s$. As this parameter approaches unity, the density profile becomes more and more developed.

**Below the spinodal**

In this case we are facing a problem of solving the full equation (A.2). This is a
very complicated task even in 1D and instead one tries to simplify the problem
somewhat. This can be done by using the methods developed in the pattern formation field [149].

Below the spinodal the lamellar phase with a typical period \( k_0^{-1} \) appears from a symmetric melt. The idea is that a slow variation superimposed onto the bulk lamellar profile is introduced due to the presence of the surface. In other words, the order parameter can be parameterized as

\[
\psi(x) = Q(x)e^{i(k_0 x + \varphi)} + Q^*(x)e^{-i(k_0 x + \varphi)}
\]

(A.9)

where \( Q(x) \) is a slowly varying amplitude, and \( \varphi \) is an arbitrary phase. The words “slowly varying” mean that it is almost constant on the scale \( k_0^{-1} \) and changes on the scale of \( \xi^{-1} = \sqrt{4B/(\tilde{\chi} - \tilde{\chi}_s)} \). Introducing the relative distance from the spinodal \( \epsilon = (\tilde{\chi} - \tilde{\chi}_s)/\tilde{\chi} \), and separating the slowly varying degree of freedom [150], we obtain the following amplitude equation

\[
Q''(z) + Q(z) \left[ 1 - Q^2(z) \right] = 0 , \quad z = x \xi
\]

(A.10)

with corresponding boundary conditions derived from eq.(A.3). Then the lamellar profile is given by

\[
\psi(z) = \sqrt{\frac{8 \tilde{\chi}_s \epsilon - 1 - \mu \exp \left\{ -\frac{\sqrt{2}z}{\lambda} \right\}}{1 + \mu \exp \left\{ -\frac{\sqrt{2}z}{\lambda} \right\} \cos(k_0 x + \varphi)}
\]

(A.11)

where \( \mu = \frac{1 - Q_s}{1 + Q_s} \). \( Q_s \) is a surface value of the amplitude. The unknown parameters in eq.(A.11) are uniquely found from the boundary conditions.

**Appendix 5.B Various geometries**

Here, as a matter of exercise, we give solutions to eq.(A.4) in various geometries. In all equations we use \( \xi \) and \( \Omega \) from eq.(A.8); \( I_n \) and \( K_n \) are the modified Bessel functions of the first and second kind, respectively.

- Slit of size \( L \). See Fig.5.6.

\[
\begin{align*}
\text{B.C.:} \quad & B \frac{d^2 \psi(x)}{dx^2} + a_1 \psi = H_1 , \quad x = \frac{L}{2} \\
\psi(x) &= \frac{2 \psi_s}{\Omega \sinh \xi l - \xi \sin \Omega l} \left[ \frac{C \Omega l}{2} \sinh \frac{\xi l}{2} f(\Omega, \xi) + \sin \frac{\Omega l}{2} \cosh \frac{\xi l}{2} f(-\xi, \Omega) \right] \\
\psi_s &= \frac{H_1}{a_1 + \sqrt{2} B k_0 \xi \Omega C} , \quad C = \frac{\cos \Omega l - \cosh \xi l}{\xi \sin \Omega l - \Omega \sinh \xi l} \\
y &= \frac{k_0 x}{\sqrt{2}} , \quad l = \frac{k_0 L}{\sqrt{2}}
\end{align*}
\]
Figure 5.6: Order-parameter profile in a slit. $l = 20$

- Cylindrical pore of radius $R$. See Fig. 5.7.

$$B \frac{d \psi(r)}{dr} + a_1 \psi = H_1, \quad r = R$$

$$\psi(r) = \psi_s \frac{k I_0(rk) I_1(Rk) - k^* I_0(rk^*) I_1(Rk)}{k I_0(Rk) I_1(Rk^*) - k^* I_0(Rk^*) I_1(Rk)}$$

$$\psi_s = \frac{H_1}{a_1 + 4B^2 \xi \Omega C}, \quad C = \frac{I_1(Rk^*) I_1(Rk)}{ik^* I_0(Rk^*) I_1(Rk) - ik I_0(Rk) I_1(Rk)}$$

$$k = \frac{k_0}{\sqrt{2}} (\xi + i\Omega)$$

- Outer region of a cylinder of radius $R$.

$$B \frac{d \psi(r)}{dr} + a_1 \psi = H_1, \quad r = R$$

$$\psi(r) = \psi_s \frac{k K_0(rk) K_1(Rk) - k^* K_0(rk^*) K_1(Rk)}{k K_0(Rk) K_1(Rk^*) - k^* K_0(Rk^*) K_1(Rk)}$$

$$\psi_s = \frac{H_1}{a_1 + 4iB\xi\Omega C}, \quad C = \frac{K_1(Rk^*) K_1(Rk)}{k K_0(Rk) K_1(Rk^*) - k^* K_0(Rk^*) K_1(Rk)}$$

$$k = \frac{k_0}{\sqrt{2}} (\xi + i\Omega)$$
Figure 5.7: Order-parameter profile for a cylindrical cavity. $R = 10$

Figure 5.8: A sphere: outer region. $R_1 = 20$
• Outer region of a sphere of radius $R$. See Fig. 5.8

\[
\text{B.C.:} \quad -B \frac{d\psi(r)}{dr} + a_1 \psi = H_1, \quad r = R
\]

\[
\psi(y) = \psi_s \frac{R_1}{y} e^{-\xi(y-R_1)} \left[ \cos \Omega(y - R_1) - \frac{R_1 \xi - r}{\Omega(R_1 + \xi)} \sin \Omega(y - R_1) \right]
\]

\[
\psi_s = \frac{H_1}{a_1 + \frac{Bk_0}{\sqrt{2}} \left( \frac{1}{R_1} + \xi + \frac{R_1 \xi - r}{R_1 \xi + \xi} \right)} \quad R_1 = \frac{Rk_0}{\sqrt{2}} \quad y = \frac{rk_0}{\sqrt{2}}
\]