Influence of confinement on the orientational phase transitions in the lamellar phase of a block copolymer melt under shear flow

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Abstract

In this work we incorporate some real-system effects into the theory of orientational phase transitions under shear flow (M. E. Cates and S. T. Milner, Phys. Rev. Lett. 62 1856 (1989) and G. H. Fredrickson, J. Rheol. 38, 1045 (1994)). 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. We show 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 shear rate increases. This behaviour might be misinterpreted as an additional perpendicular to parallel transition recently discussed in literature.
I. 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 \cite{1,2}), but also transitions between different orientations of these morphologies with respect to the shear geometry. Experimental literature extensively discusses this effect for lamellar \cite{3,4} and hexagonal phases \cite{5,6}.

The theoretical description of the lamellar reorientation was developed in \cite{7,8}. The same method was applied in \cite{9} to study the hexagonal pattern. In these theories orientational transitions appear as a result of interaction of shear flow with critical fluctuations in melt. There are two distinct regimes: a slow flow only slightly perturbs the fluctuation spectrum while a fast flow 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.1.

However, there is an experimental evidence that this picture is not complete. At very high shear rates the parallel orientation was found to be the only stable one \cite{10,11}. This cannot be explained in the discussed framework of \cite{8}, since it predicts the stability region for the perpendicular phase to increase as $D \to \infty$.

In this work we propose an explanation of the additional transition (C-transition in Fig.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 film 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 $D \to \infty$ 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 \[12,13\]. 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 \[14\] 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 is somewhat 4 orders of magnitude smaller. Under shear Laurer et. al \[15\] observed that independently 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 \[12,13,16–22\]. Some questions about dynamics of such an ordering were addressed in \[23,20\]. However, until now this theory was never applied to non-equilibrium systems.

Our paper is organized as follows. In Section II 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 the first part of Section III we estimate the shear rate of the A-transition while the other two transitions (B and C) are analyzed in the second part. In conclusion we discuss in detail properties of the obtained phase diagram. In Appendix we provide an example clarifying the role of thermal fluctuations.

**II. 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 $\mathbf{v} = Dy\mathbf{e}_x$ (see Fig.2). We ignore
any alteration of this velocity profile and assume that it is kept through the whole system. We choose the local deviation of composition from its average to be an order parameter \( \phi(r) \) and define its Fourier transform as

\[
\phi(k) = \int dr \ e^{-ikr} \phi(r) \quad \text{and} \quad \phi(r) = \int_k e^{ikr} \phi(k)
\]

where

\[
\int_k \equiv \frac{1}{L} \sum_k \int \frac{dk_x dk_z}{(2\pi)^2} \quad \text{and} \quad \int dr \equiv \int_{-\infty}^{\infty} dx \int_{-L/2}^{L/2} dy \int_{-\infty}^{\infty} dz
\]

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

Following \[2,4,7,8\] we assume that the dynamics under shear flow is governed by the Fokker-Planck equation:

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

where \( P[\phi,t] \) is the probability to realize the order parameter profile \( \phi(r) \) at time \( t \), and \( \mu \) is an Onsager coefficient. In Appendix we provide arguments for using the Fokker-Planck equation instead of any other deterministic equation.

In eq.(2.3) the Hamiltonian \( \mathcal{H} \) consist of two contributions: the bulk Hamiltonian derived by Leibler \[2\]

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

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

and the surface energy \[12,13\]

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

where \( N \) is a number of monomers in a molecule, \( H_1 \sim (\chi \mathcal{N})_{cop-surf} \) 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
perature in the vicinity of the surface). Our goal is to construct a real-space version of the
Leibler Hamiltonian $H_L$. In \cite{25,26,12} it was shown how to deal with the second-order vertex
function. Separating small- and large-wave-vector asymptotic behaviour, one can show that
\[
\Gamma_2(q) \approx \frac{A}{q^2} + B q^2 - \bar{\chi}
\]  
where
\[
A = \frac{3}{2 R_G^2 f^2 (1 - f)^2}
\]
\[
B = \frac{R_G^2}{2 f (1 - f)}
\]
\[
\bar{\chi} = 2 \left( \chi - \langle \chi \rangle \right) + \left( \frac{3}{f^2 (1 - f)^3} \right)^{1/2}
\]
with $f = N_A/N$ being the volume fraction of the A-component. In \cite{12} the third- and
fourth-order vertex functions were assumed to be constant. However, as it was noticed in
\cite{8,9,27}, it is crucial to keep the angle-dependence of the fourth-order vertex function in
order to discriminate between the parallel and the perpendicular orientations. There, the
following approximation was made:
\[
\Gamma_3(q_1, q_2, q_3) = \delta(q_1 + q_2 + q_3) \Gamma_3
\]
\[
\Gamma_4(k, \hat{q}, -k, -\hat{q}) = \lambda \left( 1 - \beta (k \cdot \hat{q})^2 \right), \quad \beta \ll 1
\]  
where $\hat{k} = k/k$. In eq.(2.8) all the wave-vectors are assumed to have the same length
$q_0 = \sqrt{A/B}$, which corresponds to the first unstable mode on the spinodal \cite{2}. The assumption
$\beta \ll 1$ was shown to be correct for almost every architecture of AB block-copolymer
molecules \cite{27} (for example, for diblocks $\beta \leq 0.1$). For an arbitrary star of 4 $q$’s one can
write to the lowest order in angles \cite{28,29}
\[
\Gamma_4(q_1, \hat{q}_2, \hat{q}_3, \hat{q}_4) = \delta (\hat{q}_1 + \hat{q}_2 + \hat{q}_3 + \hat{q}_4) \times
\]
\[
\left[ \lambda_0 + \lambda_1 \left( (\hat{q}_1 \cdot \hat{q}_2)(\hat{q}_3 \cdot \hat{q}_4) + (\hat{q}_1 \cdot \hat{q}_3)(\hat{q}_2 \cdot \hat{q}_4) + (\hat{q}_1 \cdot \hat{q}_4)(\hat{q}_2 \cdot \hat{q}_3) \right) \right]
\]  
(2.9)
\[ + \lambda_2 \left( (\mathbf{q}_1 \cdot \mathbf{q}_2)^2 + (\mathbf{q}_1 \cdot \mathbf{q}_3)^2 + (\mathbf{q}_1 \cdot \mathbf{q}_4)^2 + (\mathbf{q}_2 \cdot \mathbf{q}_3)^2 + (\mathbf{q}_2 \cdot \mathbf{q}_4)^2 + (\mathbf{q}_3 \cdot \mathbf{q}_4)^2 \right) \]

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

Comparison with eq.(2.8) gives

\[ \lambda = \lambda_0 + \lambda_1 + 2\lambda_2, \quad \beta = -\frac{2\lambda_1 + 4\lambda_2}{\lambda_0 + \lambda_1 + 2\lambda_2} \] (2.10)

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

\[
N\mathcal{H}[\phi] = \int dr \left[ \frac{B}{2} \left( \nabla \phi(r) \right)^2 - \frac{1}{2} \chi \phi(r)^2 + \frac{A}{2} \int dr' G(r-r') \phi(r) \phi(r') + \frac{\Gamma_3}{3!} \phi(r)^3 + \frac{\lambda_0}{4!} \phi(r)^4 \right.
\]

\[ + \frac{3\lambda_1}{4!} \left( \frac{\nabla \phi(r) \cdot \nabla \phi(r)}{q_0^2} \right)^2 + \frac{6\lambda_2}{4!} \phi(r)^2 \left( \frac{\nabla_a \nabla_{\beta} \phi(r)}{q_0^2} \right)^2 - h(r) \phi(r) \] + \( N\mathcal{H}_s \) (2.11)

where

\[ G(r-r') = \int_q \frac{e^{iq(r-r')}}{q^2} \] (2.12)

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

The Fokker-Planck equation (2.3) together with eqns.(2.11,2.7,2.5) 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 [8] we use the method of Zwanzig [30] to derive a system of coupled equations for the first two cumulants of \( P[\phi, t] \)

\[ c(r) = \langle \phi(r) \rangle \]

\[ S(r_1, r_2) = \langle \phi(r_1) \phi(r_2) \rangle - \langle \phi(r_1) \rangle \langle \phi(r_2) \rangle \] (2.13)

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

\[ G[\xi, t] = \log \int d\phi \exp \left[ \int d\mathbf{r} \phi(\mathbf{r})\xi(\mathbf{r}) \right] P[\phi, t], \] (2.14)
use eq. (2.3) 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:

\[
\frac{1}{\mu} \frac{\partial c(r)}{\partial t} = -\frac{D}{\mu} y \frac{\partial c(r)}{\partial x} + B\Delta c(r) + \tilde{\chi}(r) - A \int dr' \mathcal{G}(r-r')c(r') - \frac{\Gamma_3}{2} [c(r)^2 + S(0)] - \frac{\lambda_0}{3!} [c(r)^2 + 3S(0)] c(r) + \frac{\lambda_1}{2q_0} \left[ \nabla_\alpha \left( \nabla_\alpha c(r) \{ \nabla c(r) \}^2 \right) + \tilde{S}_{\alpha\alpha} \Delta c(r) \right]
\]

\[
-\frac{\lambda_2}{2q_0^4} \left[ c(r) \left( \nabla_\alpha \nabla_\beta c(r) \right)^2 + c(r) \tilde{S} + \nabla_\alpha \nabla_\beta \left( c(r)^2 \nabla_\alpha \nabla_\beta c(r) \right) + S(0) \Delta^2 c(r) \right] (2.15)
\]

\[
\int dr' \mathcal{G}(r-r')S(r' - r_1) - \frac{\Gamma_3}{2} [S(0) + 2c(r)S(r-r_1)] - \frac{\lambda_0}{2} [c(r)^2 + S(0)] S(r-r_1) - \frac{\lambda_1}{q_0^4} \tilde{S}_{\alpha\beta} \nabla_\alpha \nabla_\beta S(r-r_1) + \frac{\lambda_1}{2q_0^4} \nabla_\alpha \left[ 2 \left( \nabla_\alpha c(r) \right) \left( \nabla c(r) \cdot \nabla S(r-r_1) \right) \right] + \left( \nabla_\alpha S(r-r_1) \right) \left( \nabla c(r) \right)^2 + \tilde{S}_{\beta\beta} \nabla_\alpha S(r-r_1) - \frac{\lambda_2}{2q_0^4} \left[ S(r-r_1) \left( \nabla_\alpha \nabla_\beta c(r) \right)^2 \right] + S(r-r_1) \tilde{S} + 2c(r) \left( \nabla_\alpha \nabla_\beta c(r) \right) \left( \nabla_\alpha \nabla_\beta S(r-r_1) \right) + S(0) \Delta^2 S(r-r_1) + 2\nabla_\alpha \nabla_\beta \left( c(r)S(r-r_1) \nabla_\alpha \nabla_\beta c(r) \right) + \nabla_\alpha \nabla_\beta \left( c(r)^2 \nabla_\alpha \nabla_\beta S(r-r_1) \right) - a_1 S(r-r_1) \left[ \delta \left( y + \frac{L}{2} \right) + \delta \left( y - \frac{L}{2} \right) \right] \]  

(2.16)

where

\[
\tilde{S}_{\alpha\beta} = \left. \nabla'_\alpha \nabla'_\beta S(r-r') \right|_{r'=r}, \quad \tilde{S} = \left. \nabla_\alpha \nabla_\beta \nabla'_\alpha \nabla'_\beta S(r-r') \right|_{r'=r} \]  

(2.17)

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, eqns. (2.15, 2.16) are the real-space analog of the eqns. (2.25-26) from \[8\]. Here the terms proportional to \( S(0) \) play the role of the fluctuation integral \( \sigma(\hat{k}) \) from \[8\]:

\[
\sigma(\hat{k}) = \frac{\lambda}{2} \int q S(q) \left[ 1 - \beta (\hat{k} \cdot \hat{q})^2 \right] \]  

(2.18)
To keep our model as simple as possible we leave only the linear term in the surface energy (2.3) and put $a_1 = 0$. Then we set

$$c(r) = 2a \cos(q_0 n \cdot r + \phi)$$

$$h(r) = 2h \cos(q_0 n \cdot r + \phi)$$

where $a$ is yet to be determined amplitude, $n$ is a unit vector perpendicular to the surface of the lamellae and $\phi$ 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 [12] that in equilibrium the presence of the 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 (2.19), we ignore the spatial 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.(2.16) reads

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

where

$$S_0^{-1}(k) = r - \hat{k} \cdot \hat{e} \cdot \hat{k} + B\hat{k}^2 + \frac{A}{\hat{k}^2} - \chi_s$$

$$r - \hat{k} \cdot \hat{e} \cdot \hat{k} = 2\left((\chi N)_s - \chi N\right) + \lambda a^2 \left(1 - \beta (n \cdot \hat{k})^2\right) + \sigma(\hat{k})$$

Here we have introduced the same notation as in [8,9]. In eq.(2.21) $S_0(k)$ 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

$$r - \hat{k} \cdot \hat{e} \cdot \hat{k} \Big|_{a=0} = 0$$

differs from the mean-field value $\left((\chi N)_s - \chi N\right)$ of the mean-field value $\left((\chi N)_s - \chi N\right)$. In the case $\beta = 0$ such a fluctuation correction was discussed in [31]. The presence of shear breaks the rotational symmetry and the spinodal temperature becomes orientation-dependent. This gives rise to the $-\hat{k} \cdot \hat{e} \cdot \hat{k}$ term, with $e_{ij} \sim \beta$ (see eq.(2.8)). Here the role of the angle-dependency in $\Gamma_4$ is especially transparent: if $\beta = 0$, we would not be able to discriminate between different orientations.
The method of characteristics gives a formal solution for the eq. (2.20):

\[ S(k, t) = \mu \int_0^t d\tau \exp \left[ -\mu \int_0^\tau ds S_0^{-1}(k_x, k_y + \frac{1}{2}Dsk_x, k_z) \right] \]  

(2.23)

The steady-state regime is approached as \( t \to \infty \). The integration in (2.23) 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 (2.19) into eq. (2.15) and perform an averaging over the lamellar period

\[ \langle \cdots \rangle = \frac{n_x n_y n_z q_0^3}{(2\pi)^3} \int_0^{2\pi} dx \int_0^{2\pi} dy \int_0^{2\pi} dz \cos (q_0 n \cdot r + \varphi) \cdots \]  

(2.24)

Discarding the transverse orientations with \( n_x \neq 0 \) \([24, 7, 8]\), we obtain

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

(2.25)

where \( \eta = \frac{q_0}{\pi} H_1 \), and \( \delta_{n_y, 1} \) is the Kronecker delta-symbol which is non-zero only for the parallel \((|n_y| = 1)\) orientation. Following \([8]\) we notice that the equation (2.25) has a gradient form (with \( h = 0 \)):

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

(2.26)

Since the potential \( \Phi \) can only decrease with time:

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

(2.27)

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

\[ h = \frac{1}{2} \frac{\partial \Phi}{\partial a} \]  

(2.28)

Using \( h \) from eq. (2.25), we obtain

\[ \Phi = \Phi_0 - 2\eta a \delta_{n_y, 1} \]  

(2.29)

where
\[ \Phi_0 = -\frac{1}{4} \lambda (1 - \beta) a^4 + 2 \int_0^a da' (r - \mathbf{n} \cdot \hat{\mathbf{e}} \cdot \mathbf{n}) a' \]  

(2.30)

In eq.(2.29) 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 dependency of \( r - \mathbf{n} \cdot \hat{\mathbf{e}} \cdot \mathbf{n} \) on \( a \) comes from the term proportional to \( \sigma(\hat{k}) \) in (2.21) and the potential \( \Phi \) appears to be dependent on the fluctuation integral via eq.(2.30). Now we are ready to discuss the stable orientations in different regimes.

**III. PHASE TRANSITIONS**

**Crossover from small- to high-shear rate behaviour**

In this subsection we analyze the transition from the parallel to perpendicular orientation caused by increase of shear rate (the A-transition in Fig.1). We start with noticing that at low shear rates the parallel orientation is the only stable one. Indeed, as it was shown by Fredrickson [8], \( \Phi_0 \) is minimal for \( n_y^2 = 1 \) in the limit \( D \to 0 \). The surface term in eq.(2.29) also favours the parallel orientation. Thus, our theory does not modify Fredrickson’s prediction for small shear rates.

At high shear rates \( D \to \infty \), the integration in eq.(2.23) can be performed [24], yielding

\[ S_\infty(k) = c_0 \left( \frac{\mu q_0^2}{\sqrt{\alpha D |k_x k_y|}} \right)^{2/3} \]

where

\[ c_0 = \frac{\Gamma \left( \frac{1}{3} \right)}{(9\pi)^{1/3}} \quad \text{and} \quad \alpha = \frac{q_0^2 B}{\pi} \]

(3.1)

(3.2)

For the intermediate shear rates \( S(k) \) can be interpolated between \( S_0 \) and \( S_\infty \)[7]

\[ S(k) = \left[ r - \hat{k} \cdot \hat{e} \cdot \hat{k} + B k^2 + \frac{A}{k^2} - \bar{\chi} s + \frac{1}{c_0} \left( \frac{\sqrt{\alpha D |k_x k_y|}}{\mu q_0^2} \right)^{2/3} \right]^{-1} \]

(3.3)

One should realize that the previous equation is an analytic continuation of the \( D \to \infty \) behaviour to \( D < \infty \) values. As a result, a small-\( D \) behaviour of eq.(3.3) does not correspond
to the $D \to 0$ behaviour of eq. (2.23). On contrary, it describes the $D \sim O(1)$ region. Since we expect the A-transition to lay in-between the $D \sim O(1)$ and $D \to \infty$ regions, we need to calculate the fluctuation integral $\sigma(\hat{k})$ in-between these regions. This can be done in several steps. First, we use $S(\hat{k})$ from eq. (3.3) to perform the radial part of the integral in eq. (2.18). This gives

$$\sigma(\hat{k}) \approx \frac{\lambda q_0^2 \sqrt{c_0}}{16 \pi^3} \left( \frac{\mu}{D \sqrt{\alpha}} \right)^{1/3} \int d\Omega \frac{1 - \beta (\hat{k} \cdot \hat{q})^2}{|\hat{k}_x \hat{k}_y|^{1/3}} \left[ \frac{\pi}{2} + \arctan \left( \frac{q_0 \sqrt{c_0}}{|\hat{k}_x \hat{k}_y|^{1/3}} \left( \frac{\mu}{D \sqrt{\alpha}} \right)^{1/3} \right) \right].$$

(3.4)

As a next step we expand the integrand for $D \ll 1$ and $D \gg 1$ and sum these expressions keeping only the few first terms. Integration over the orientation $s$ of the unit vector $\hat{q}$ ($\int d\Omega = \int_0^{\pi} d\theta \sin \theta \int_0^{2\pi} d\phi$) then gives

$$\sigma(\hat{k}) = \frac{\lambda}{64 \pi^{5/2}} \sqrt{\frac{\alpha}{3}} \left\{ -4\pi \left( 1 - \frac{\beta}{3} \right) + \frac{1}{3} Z^3 \left[ I_1 - \beta \left( I_2 (k_x^2 + k_y^2) + I_3 k_z^2 \right) \right] \right. + \left. 4\pi^2 (1 - \beta) \left[ I_4 \right] + Z^2 \left[ I_5 - \beta \left( I_6 (k_x^2 + k_y^2) + I_7 k_z^2 \right) \right] \right\}$$

(3.5)

where

$$Z = \sqrt{4\pi c_0} \left[ \sqrt{\frac{\alpha D_*}{\lambda D}} \right]^{1/3}, \quad D_* = \lambda \mu \sqrt{\alpha}$$

$$I_1 = 2 \sqrt{\frac{\pi}{6}} \left( \frac{2}{3} \right)^2 \frac{\Gamma \left( \frac{5}{6} \right) \Gamma \left( \frac{11}{6} \right)}{\Gamma \left( \frac{19}{6} \right)} \quad I_2 = 2 \sqrt{\frac{\pi}{6}} \left( \frac{2}{3} \right)^2 \frac{\Gamma \left( \frac{7}{6} \right) \Gamma \left( \frac{11}{6} \right)}{\Gamma \left( \frac{19}{6} \right)} \quad I_3 = 2 \left( \frac{2}{3} \right)^2 \frac{\Gamma \left( \frac{7}{6} \right) \Gamma \left( \frac{17}{6} \right)}{\Gamma \left( \frac{25}{6} \right)} \quad I_4 = 2 \frac{\Gamma \left( \frac{5}{6} \right) \Gamma \left( \frac{11}{6} \right)}{\sqrt{\pi}} \quad I_5 = 2 \sqrt{\frac{\pi}{6}} \left( \frac{2}{3} \right)^2 \frac{\Gamma \left( \frac{7}{6} \right) \Gamma \left( \frac{11}{6} \right)}{\Gamma \left( \frac{19}{6} \right)} \quad I_6 = 2 \left( \frac{2}{3} \right)^2 \frac{\Gamma \left( \frac{7}{6} \right) \Gamma \left( \frac{17}{6} \right)}{\Gamma \left( \frac{25}{6} \right)}$$

This procedure is ill-defined from mathematical point of view. However, any direct analysis of eq. (2.23) is impossible and we use eq. (3.5) for moderate shear rates.

Since eq. (3.5) does not depend on the renormalized temperature, the integration in eq. (2.30) is trivial and gives

$$\Phi = [\tau + \sigma(n)] a^2 + \frac{1}{4} \lambda a^4 (1 - \beta) - 2\eta a \delta_{n^2,1}$$

(3.6)

where

$$\tau = 2 (\chi N)_a - \chi N$$
Minimization with respect to $a$ gives to the first order in $\eta$

$$\Phi = -\frac{[\tau + \sigma(n)]^2}{\lambda(1-\beta)} - 2\eta \sqrt{-2\frac{\tau + \sigma(n)}{\lambda(1-\beta)} \delta_{n^2,1}}$$  \hspace{1cm} (3.7)$$

The order-disorder transition (ODT) occurs when $\Phi$ becomes negative. The corresponding transition temperature is

$$\tau_s(n) = -\sigma(n)$$ \hspace{1cm} (3.8)$$

which coincides with eq. (2.22). The orientation with the lowest $\sigma$ will appear immediately below the ODT temperature. The crossover (the A-transition) is then located at such a value of $D$ that $\sigma_\parallel - \sigma_\perp$ changes its sign. From eq. (3.5) this point is given by

$$\sigma_\parallel - \sigma_\perp \sim \frac{1}{3Z^2}(I_3 - I_2) + \frac{4\pi^2}{7} 2^{1/3} \sqrt{3Z + Z^2}(I_6 - I_5) = 0$$ \hspace{1cm} (3.9)$$

and is found to be

$$D_{cr} \approx 2.64 \mu \alpha$$ \hspace{1cm} (3.10)$$

From eq. (3.3) it also follows that $\tau_s^\parallel > \tau_s^\perp$ for $D < D_{cr}$, which fits the small-shear behaviour discussed in the beginning of this subsection. When $D > D_{cr}$, the perpendicular orientation first appear below the spinodal. This crossover is depicted in Fig. 3.

As it was noticed before [7,8], the mean-field behaviour is restored in the limit $D \to \infty$. On the other hand, the small-$D$ region is dominated by fluctuations. Thus, $D_{cr}$ can be interpreted as a position of a crossover from the fluctuation to mean-field behaviour. The scaling properties of $D_{cr}$ follow from eq. (3.10) and are determined by the Onsager coefficient $\mu$. Using the results of [33–36] ($\mu \equiv q_0^2 \lambda(q_0)/N$ with $\lambda$ from [34,35]) we obtain

$$D_{cr} \sim N^{-3}$$ \hspace{1cm} (3.11)$$

which shows that the fluctuation region disappears in the limit $N \to \infty$. In equilibrium the same conclusion was drawn in [33].

Finally, we emphasize that the results of this subsection are independent of the surface interaction. The same results can be obtained within the Fredrickson theory [8] ($\eta = 0$).
**B- and C-transitions**

In the previous subsection we have discussed the order-disorder transitions. Now we consider lower temperatures and look for transitions between different orientations in the high-shear limit. The corresponding free energies are given by eq. (3.7)

\[
\Phi_\parallel = -\frac{(\tau + \sigma_\parallel)^2}{\lambda(1 - \beta)} - 2\eta\sqrt{-2\frac{\tau + \sigma_\parallel}{\lambda(1 - \beta)}}
\]

\[
\Phi_\perp = -\frac{(\tau + \sigma_\perp)^2}{\lambda(1 - \beta)}
\]

where \(\sigma(n)\) is given by its high-shear limit of eq. (3.5)

\[
\sigma(n) = \left(\frac{\alpha\lambda}{B^{3/2}}\right)^{2/3} \left(\frac{D_*/D}{8}\right)^{1/3} \sqrt{\frac{3}{8}} c_0 \left[1 - \frac{\beta}{7}(2n_y^2 + 3n_z^2)\right]
\]

To the leading order in \(D_*/D\), the transition from the perpendicular to parallel orientation occurs at temperatures which are the roots of the equation \(\Phi_\parallel = \Phi_\perp\)

\[
\tau_1 = -\sigma_\parallel - \frac{(\sigma_\parallel - \sigma_\perp)^4}{8\eta^2\lambda(1 - \beta)} \quad \tau_2 = -\frac{2\eta^2\lambda(1 - \beta)}{(\sigma_\parallel - \sigma_\perp)^2} \quad \text{if} \quad \eta^2\lambda(1 - \beta) > (\sigma_\parallel - \sigma_\perp)^3
\]

where

\[
\sigma_\parallel - \sigma_\perp = \beta \frac{2^{1/3} \sqrt{3c_0} (\alpha\lambda)^{2/3}}{56} \left(\frac{D_*}{D}\right)^{1/3}
\]

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.

**IV. DISCUSSION OF THE PHASE DIAGRAM AND CONCLUSION**

In this work we incorporated some real-system properties into the previously developed theory of the orientational phase transitions under shear flow \[7,9\]. 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 \[12,13\]. 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 \[7,8\]. The interplay between
these two factors produces the non-trivial phase diagram shown in Fig.4.

At low shear rates the parallel orientation is preferred by both the shear and surface
terms in eq.\(2.29\). 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.\(3.10\), 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.\(3.14\)

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

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 loses its stability again at \(\tau = \tau_2\) given
by eq.\(3.14\). 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 \[12,13\]. We therefore argue that there
is no sharp C-transition as shown in Fig.4. Since the region between the spinodal and the
parallel phase shrinks with an increase of the shear rate, there 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 \cite{8}, 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 high-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 depicting 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 $\parallel \rightarrow \perp$ transition at very low temperatures in high-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 \cite{14,13}. This statement can be checked experimentally. We have shown that the positions of the transition lines in the high-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 dependency will provide arguments for or against our theory.

In this work we have considered the influence of the walls in the gradient direction. We also want to comment on the role of the 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 the developed theory. 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 dependency in the amplitude $a$ and deriving the corresponding amplitude equation from eq.(2.15). In the absence of shear this problem was solved in [12]. 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 [37,38]. With some modifications eq.(2.13,2.16) can be a starting point for the corresponding theory. Importance of such a theory for a system in electric field and simultaneously under shear was outlined in [38].

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APPENDIX: INFLUENCE OF THERMAL FLUCTUATIONS

Here we want to emphasize the role of fluctuations in our theory. We are going to show that if the Fokker-Planck equation (2.3) is replaced by a deterministic one, the theory will not be able to discriminate between different orientations. What follows should not be considered as a proof but, more likely, as an illustration that has general features.

Let us consider a Langevin equation equivalent to the Fokker-Planck equation (2.3). If we now remove the noise term, it reads

$$\frac{\partial \phi}{\partial t} + \mathbf{v} \cdot \nabla \phi = \tilde{\mu} \nabla^2 \frac{\delta \mathcal{H}_L}{\delta \phi}$$  (A.1)

where an Onsager mobility $\tilde{\mu}$ differs from $\mu$ in eq.(2.3) and $\mathcal{H}_L$ is the Leibler Hamiltonian (eq.(2.11)) without $\mathcal{H}_s$ and $h = 0$. A similar equation was considered in [39]. There the
authors used a Hamiltonian with $\lambda_1 = \lambda_2 = 0$ and showed that in steady-state the theory predicts both orientations to be equally stable at all shear rates. This is not surprising since their theory does not contain fluctuations and the angular dependence of the fourth-order vertex function $\Gamma_4$ – the two ingredients that were argued to be crucial in explaining the reorientation phenomena \[8,9,27\].

In order to separate these two effects we keep the angular dependence in $\Gamma_4 (\lambda_1, \lambda_2 \neq 0)$, but use the deterministic equation (A.1). We follow the approach of \[39\] and derive an amplitude equation from eq.(A.1) assuming a single plane-wave density profile. The solution of this equation is

$$A(t) = \left[ \frac{P(t)}{A(0)^2} + 3P(t) \int_0^t d\tau f(\tau) P^{-1}(\tau) \right]^{-1/2}$$  \hspace{1cm} (A.2)

and

$$f(t) = 1 + 4Q^4 \left( \frac{\lambda_1 + 2\lambda_2}{\lambda_0} \right) , \quad P(t) = \exp \left[ -2 \int_0^t d\tau \sigma(\tau) \right]$$

$$\sigma(t) = (1 + \epsilon) Q^2 - Q^4 - \frac{1}{4} , \quad Q^2 = q_z^2 + (q_y - Dtq_x)^2 + q_z^2$$

where $A$ is the amplitude, $\epsilon = (\bar{\chi} - \bar{\chi}_s)/\bar{\chi}_s$, and the amplitude and the units of length and time are scaled with $\sqrt{\bar{\chi}_s/\lambda_0}$, $\sqrt{B/\bar{\chi}_s}$ and $B/(\bar{\mu}\bar{\chi}_s^2)$, respectively. We see that the equation becomes symmetric with respect to the interchange $q_y \leftrightarrow q_z$. Thus, even in the presence of the angular dependence in $\Gamma_4$ it is impossible to distinguish between the parallel and perpendicular orientations starting from eq.(A.1).

We believe that a theory without fluctuations of the order parameter is not capable of describing the reorientational transitions. There are phenomena where fluctuations only modify a deterministic behaviour \[40–42\]. However, the orientational behaviour under shear flow does not belong to this class of phenomena. It can only occur in the presence of thermal fluctuations.
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APPENDIX: FIGURE CAPTIONS

Fig.1. Schematic phase diagram “temperature vs. shear rate” as a compilation of the theoretical predictions by Fredrickson and the experimentally observed C-transition. The order-disorder transition line behaves as $\tau \sim D^2$ for small shear rates $D$ and $\tau \sim D^{-1/3}$ for $D \to \infty$. The B-transition line levels off in Fredrickson’s theory.

Fig.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 ($v$), $y$ is the gradient direction ($\nabla v_x$) and $z$ is the vorticity direction ($\nabla \times v$). In the parallel orientation the normal to the lamellar layers is oriented parallel to the gradient direction, in the perpendicular - to the vorticity direction. The walls in $y$ direction interact with the melt and prefer one of the components.

Fig.3. Schematic behaviour of the spinodal temperatures for the parallel and perpendicular orientations in the vicinity of the crossover point.

Fig.4. Phase diagram for the lamellar phase under steady simple shear flow as predicted in this work.
\[ \tau_{MF} = 0 \]

\[ D/D^* \]

FIG. 1.
FIG. 3.
\[ D_{A} = 0, \quad D_{B} \]

**FIG. 4.**

fluctuations mean-field

\[ \tau_{MF} = 0 \]

\[ \tau_{f} \]

\[ -\tau \]