Comment on "Microscopic mechanisms of electric-field-induced alignment of block copolymer microdomains"

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Böker *et al.* [1] identified experimentally two distinct microscopic mechanisms of electric-field-induced alignment of diblock copolymer microdomains. Close to order-disorder transition (ODT) the scattering peak from the lamellae parallel to the electrodes quickly disappears and a new peak from the perpendicular lamellae emerges. Further from ODT the peak merely rotates from the initial position towards the final one. Using computer simulation, we are able to reproduce the observed scattering behavior. However, we suggest a microscopic picture different from the one put forward in [1].

The microphase separation in a diblock copolymer is described by the order parameter $\psi(\mathbf{r}, t)$. Using the expression for the chemical potential $\mu = \mu^0 - (\partial\epsilon/\partial\psi)_T E^2/8\pi$[2] and expanding the dielectric constant ϵ and the Maxwell equation div$\mathbf{D} = 0$ in the leading power of ψ, we find for the time evolution

$$\dot{\psi} = M\nabla^2\mu^0 + \alpha\nabla_z^2\psi + \eta,$$

where μ^0 is the chemical potential without electrostatics, which is calculated using self-consistent field theory for ideal Gaussian chains with mean field interactions. The mobility is M, the parameter α is quadratic in the electric field (applied in the z direction), and η is the noise. The starting structure, Fig. 1 (at $t = 5$), can be aligned either by preferentially attracting surfaces [3] or by shearing. Then the electric field is applied.

Böker *et al.* argue that the two mechanisms (grain boundary migration and grain rotation) are distinguished due to kinetic factors (different initial grain size, different mobility, and viscosity). Our simulation shows that the behaviors are discriminated by energetics, namely, by the balance of the ponderomotive force [2] and the surface tension (and higher terms such as bending) of a single lamella, which is related to the block interaction ε_{AB}, the only varied parameter. The initial grain size, Fig. 1 (at $t = 5$) was nearly the same. Close to ODT the surface tension cannot withstand the electric field, and undulations appear in lamellae (Fig. 1) (waves at $t = 5.2$). In addition to existing grains new perpendicular grains form in the body of the parallel lamellae. They appear via a transition to an intermediate micellar and/or bicontinuous phase. As this phase is a structured one (not "selective melting" into disorder) there is no considerable broadening of the scattering peak. The migration of grain boundaries follows the same transition [row of micelles in the square (Fig. 1)]. Farther from ODT the undulation instability is suppressed and the lamellae collectively rotate. The process is assisted by single defect migration. The kinetic factors [1] will modify only the time scale of the processes. As to the initial misalignment (here created on purpose by shearing), it is indeed responsible for the choice of rotation direction [1].

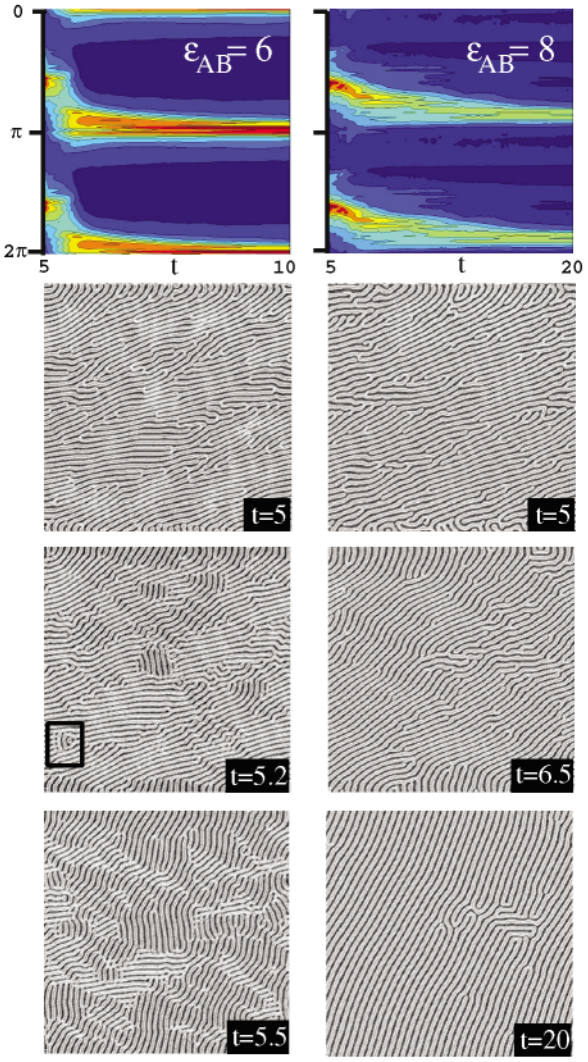

FIG. 1 (color). Top: the scattering intensity as a function of the azimuthal angle and dimensionless time ($t \times 10^3$) for the A_4B_4 melt in 2D. Below: simulation snapshots. Left: closer to ODT. Right: farther from ODT. The z axis is vertical. The electric field strength parameter $\alpha/kTM\nu = 0.2$.

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