Fluctuation Effects in the Ordering of Thin Diblock Copolymer Films

In a recent Letter Menelle *et al.* studied the ordering transition of symmetric *A-B* diblock copolymers in thin films [1]. Because of the differential interaction of each of the blocks with the solid-polymer and polymer-air interfaces, some smectic ordering is seen to grow from the interface, above the temperature T_{ODT} where the isotropic-smectic transition normally occurs for bulk specimens. This incipient ordering, which induces local deviations from the average monomer contents, is well described for each of the interfaces by a single sinusoidal wave of amplitude $\exp(-z/\xi)$. The decay length ξ increases as the temperature is lowered and becomes of the order of the sample thickness at some temperature $T_{\infty,t}$. In order to explain these observations the authors refer to a *mean-field* theory developed by Fredrikson [2] which predicts the following: a concentration profile of the form used by the authors; an inverse square-root dependence for the decay length ξ with the temperature difference $T - T_{ODT}$; and an order transition temperature for the sample which coincides with the bulk ordering transition. This last prediction is in contradiction with the experimental results, the temperature at which the film order clearly depends on its own thickness.

It is now well established that fluctuations play an important role in the ordering transition of bulk diblock copolymer blends [3,4], where the mean-field treatment is unsatisfactory. The role of the fluctuations in the ordering of thin films needs to be clarified. As a first step —formally identical to Fredrikson's calculation [2]—one can deduce the effect of the fluctuations by studying the effect of a surface field on the bulk correlation function. In the bulk, when fluctuations are taken into account, the transition can be shown to be first order and the temperature transition to be lower than the mean-field prediction [5]. At the level of a self-consistent Hartree approxima-

FIG. 1. Behavior of the decay length ξ as a function of the reduced temperature τ. Here ξ is given in units of $N^{2/3}/(d\lambda)^{1/3}$ and τ in units of $(d\lambda N^{-1/2})^{2/3}$—see Ref. [5] for notation. The bulk transition temperature would occur for $\tau = -2.03$. The full line (for $\tau > -2.03$) is the solution of the cubic equation $\xi^{-3} - \tau\xi^{-1} = 1$.

tion the renormalized susceptibility r is calculated from

$$r = \tau + \frac{k_0^2}{4\pi} \frac{\lambda}{r^{1/2}} ,\tag{1}$$

where τ is the usual reduced temperature parameter (see Ref. [5] for details). The decay length for the profile does not diverge at the transition temperature but should instead be calculated from $\xi = r^{-1/2}$, with r given by Eq. (1). This leads to a slow variation of ξ for temperatures above the (thickness dependent) transition temperature and to a sudden jump at $T_{\infty,t}$. This behavior, which I believe is patent on Fig. 2 of Ref. [1], is sketched in Fig. 1.

The confinement changes, however, the correlation function itself, and it can be shown, by applying the standard RPA method to chains confined in between two neutral surfaces, that the scattering function $S(k_z,\tau)$ for diblock copolymers, first calculated by Leibler [6], should be replaced by

$$S(k_z,\tau,D) = \left\{\tau - 58.63\frac{R_G}{D} + 1.21N\left[1 - 0.36\frac{R_G}{D}\right]\left[k_z - \left[1 + 0.011\frac{R_G}{D}\right]k_0\right]^2\right\}^{-1}\tag{2}$$

in the limit where the film thickness D is much larger than R_G, the radius of gyration of the polymers. In terms of the Flory interaction parameter χ and of the polymerization index N the correction to the transition temperature reads

$$(\chi N)_t = 10.50 - 58.63\frac{R_G}{D} + 41.022\frac{1}{N^{1/3}}\left[1 - 0.343\frac{R_G}{D}\right].\tag{3}$$

The confinement has two effects. The strongest is to increase the temperature transition at the mean-field level but it also reduces the effect of fluctuations on the phase transition.
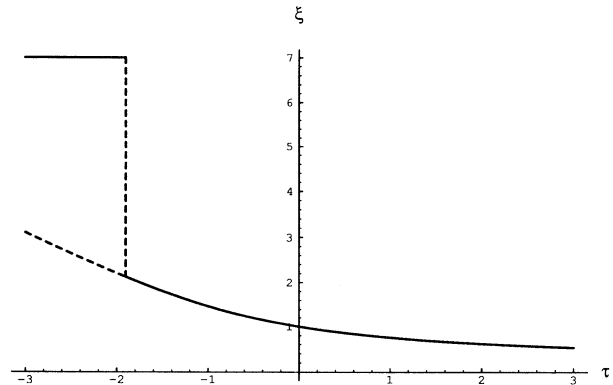
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[1] A. Menelle, T. P. Russel, S. H. Anastasiadis, S. K. Satija, and C. F. Majkrzak, Phys. Rev. Lett. **68**, 67 (1992).
[2] G. H. Fredrickson, Macromolecules **20**, 2535 (1987).
[3] F. S. Bates, J. H. Rosedale, and G. H. Fredrikson, J. Chem. Phys. **92**, 6255 (1990).
[4] K. Almdal, J. H. Rosedale, F. S. Bates, G. D. Wignall, and G. H. Fredrikson, Phys. Rev. Lett. **65**, 1112 (1990).
[5] G. H. Fredrickson and E. Helfand, J. Chem. Phys. **87**, 697 (1987).
[6] L. Leibler, Macromolecules **13**, 1602 (1980).