Extreme Swelling of Lamellar Phases

In a recent Letter,[1] Larche *et al.* reported an unusual observation of extremely dilute lamellar phases of lyotropic liquid crystals. They evoke the steric repulsion between fluctuating lamellae[2] as a possible origin of stabilization of such phases. Recently we have studied[3] an analogous problem of the interaction between membranes, and have predicted the existence of *critical* unbinding transitions, driven by *fluctuations*, between a state in which the membranes are bound and the state in which they are separated. It is argued in this Comment that the process of swelling of a stack of lamellae can be viewed as a new kind of unbinding transition, named here *complete unbinding.* This unifying theoretical picture clarifies the notion and the use of the *steric repulsive potential,*[2] and shows that the detailed study of the swollen phases can bring new insight into the nature of molecular interactions in lyotropic liquid crystals.

Our theory is based on a simple effective Hamiltonian for a pair of lamellae,[3]

$$\mathcal{H}\{l(\mathbf{x})\} = \int d^{d-1}x\left[\tfrac{1}{2}\kappa_0(\nabla^2 l)^2 + V(l(\mathbf{x}))\right]/k_BT, \qquad (1)$$

where $l(\mathbf{x})$ is the separation between the lamellae and κ_0 is the rigidity constant. To describe the swelling process one should consider *constrained systems,* since the mean separation $\bar{l}$ between the lamellae is determined by the global composition of the mixture, or by the osmotic pressure inside the lamellar phase. We therefore add to the microscopic interaction $V_0(l)$, an extra pressurelike term, Pl. The swelling process can then be viewed as relaxing the constraint, i.e., as taking the limit $P\to 0$ (see Fig. 1). If the molecular potential, $V_0(l)$, has a sufficiently small minimum, then the lamellae will separate completely in this limit. This happens, for example, when the Hamaker constant W, which governs the attractive part $V_A(l)$, is smaller than some critical value W_c. This new transition is characterized by $\bar{l}\sim P^{-\psi}$ $(P\to 0)$. A self-consistent perturbation treatment of the model (1) which we have performed[4] yields the following results: (i) For sufficiently short-ranged molecular potentials $V_0(l)$ [or more precisely for the potentials such that for large l, $V(l)l^{2(d-1)/(5-d)}\to 0$] the critical exponent ψ is given by $\psi=(5-d)/(3+d)$, which implies $\psi=\frac{1}{3}$ in three dimensions; and (ii) if one includes in the potential $V_0(l)$ an unscreened electrostatic repulsive interaction, then $\psi=\frac{1}{2}$ $(d=3)$.

The result (i) can also be obtained in $d=3$ by our simply adding the effective steric repulsion term,[2] $V_{st}\sim(k_BT)^2/\kappa l^2$, to the potential $V(l)$ and then using a simple minimization procedure. This approach is *not always correct*, however, as shown for the case of critical unbinding transitions (see Ref. 3), and one should in general perform a complete statistical (e.g., renormalization group) treatment of the model (1). On the other hand, our theory[4] shows that for *complete* unbinding the fluctuations are weak enough that their effect can be taken into account by this simple approach.

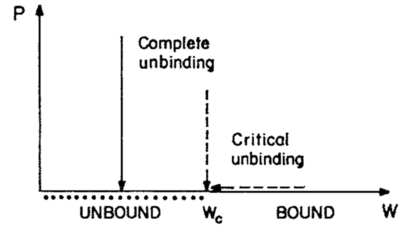

FIG. 1. Complete unbinding occurs for $W<W_c$ as $P\to 0$; the critical unbinding transition occurs at the point $(W,P)=(W_c,0)$. Instead of the Hamaker constant W, one could vary the rigidity or the inverse temperature.

The model (1) can be generalized to the case of *a stack of lamellae*, and an effective Gaussian Hamiltonian can be derived.[4] This Hamiltonian leads to the prediction of *quasi long-range order* with characteristic exponent X_m. Asymptotically, for separations $\bar{l}$ large compared to the thickness of the lamellae δ, we predict that $X_m\sim m^2$ is a pure number for case (i), and $X_m\sim\bar{l}^{-1/2}$ for case (ii). Thus it should be possible to distinguish experimentally the situation where the "hyper-swollen" phases are stabilized by fluctuations of lamellae, or by unscreened electrostatic forces.[5]

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