

Analysis of the stability of the nematic phase consisting of semiflexible surfaces^{a)}

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The stability of the nematic phase composed of structureless semiflexible surfaces interacting via their mutual excluded volume is analyzed. A highly oriented state would be unfeasible in the second virial approximation. It is argued that higher-order virial terms could stabilize the nematic state.

I. INTRODUCTION

A considerable amount of experimental research has been devoted to elucidating the smectic–nematic transition for concentrated solutions of bidimensional micelles (see, e.g., Refs. 1–14). A consensus is emerging of the structural changes occurring near the transition^{9–14}: The disks in the nematic phase have a comparatively small diameter (≈ 10 nm); in order to form the smectic phase they align into layers maintaining their integrity more or less; at the continuous transition these layers coexist with inhomogeneous lamellae containing isolated disks and others defects; the defects in the smectic phase persist well beyond the transition. This picture is particularly clear judging from the freeze-fracture micrographs of saline decylammonium chloride solutions.¹³ Thus, there is no evidence so far for the existence of a nematic phase of rippled or semiflexible sheet-like micelles (i.e., a phase without positional order). This has prompted us to investigate the stability of such a state. We shall view the micelles as surfaces without any structure so that our analysis may pertain to other systems as well.

The nematic phase of long worm-like micelles is stable as has been shown recently.¹⁵ This work is based on the theory of confined persistent chains as developed by polymer theorists.^{16–23} It has been pointed out²³ that these ideas are very similar in concept to those introduced for confined surfaces.^{24–30} In spite of this similarity one anticipates that certain phenomena may vary qualitatively as a function of the dimension of the fluctuating surface. For instance, the excluded volume between thin disks or platelets is proportional to their diameter cubed but this is no longer true for slender rods. As will be pointed out in the last section this is ultimately the reason for the difference in stability mechanisms for the respective (semiflexible) particles.

The outline of the paper is as follows. The orientational entropy or free energy ΔF_{or} is calculated as a function of the variational parameter α occurring in a Gaussian trial function. In Sec. III a deflection length λ is introduced by a scaling argument. The orientational free energy derived via λ agrees with ΔF_{or} with regard to its functional dependence on α and allows us to specify a previously unknown constant. The excluded-volume effect is given as a virial expansion, each of the terms except the third depending on the effective platelet size proportional to λ . The total free energy is mini-

mized in Sec. V and a discussion of the limitations of this work is given in Sec. VI.

II. ORIENTATIONAL ENTROPY OF A NEMATIC OF SEMIFLEXIBLE SURFACES

First, we briefly review the statistical properties of an unconfined elastic surface. Let the configuration of minimum elastic free energy be the flat interface in which we define the coordinate system (x, y) and let every point of this plane be specified by the vector $\mathbf{r} = (x, y)$. Thermal motion induced by the system temperature T will cause a displacement $\zeta(\mathbf{r})$ of the surface from this reference configuration. To a first approximation the free energy of the surface described by the configuration $\zeta(\mathbf{r})$ is³¹

$$\Delta F_b = \frac{1}{2} K' \int d\mathbf{r} (\Delta_r \zeta)^2, \quad (1)$$

where K' denotes the elastic modulus of curvature and the integration is implied on the area A of the reference surface. We delete higher-order terms and contributions arising from compression and extension of the surface^{24,26–31}. The disregard of the surface tension is discussed in Sec. VI.

In order to infer various averages from Eq. (1) we follow the analysis of Ref. 25 switching to Fourier transforms like

$$\zeta(\mathbf{r}) = \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \zeta_{\mathbf{q}}. \quad (2)$$

Equation (1) is rewritten as

$$\Delta F_b = \sum_{\mathbf{q}} \Delta F_{\mathbf{q}} \quad (3)$$

with

$$\Delta F_{\mathbf{q}} = \frac{1}{2} K' A q^4 |\zeta_{\mathbf{q}}|^2. \quad (4)$$

On canonical averaging, every mode contributes $\frac{1}{2} k_B T$ in view of the equipartition theorem. Hence, we have

$$\langle |\zeta_{\mathbf{q}}|^2 \rangle = (K A q^4)^{-1}, \quad (5)$$

where the dimensionless modulus K is K' scaled by $k_B T$. We are interested especially in the orientational surface fluctuations described by $\boldsymbol{\theta}(\mathbf{r}) = [\theta_x(\mathbf{r}), \theta_y(\mathbf{r})]$, i.e., the angle between the normal to the rippling surface and the normal to the reference plane. If the deviations are small ($\theta_x, \theta_y \ll 1$) we have $\theta_x \approx -\partial\zeta/\partial x$ and $\theta_y \approx -\partial\zeta/\partial y$ so that the Fourier component of the orientation is simply

^{a)} Work carried out in part while the author was at the Department of Physical Chemistry, University of Leiden.

$$\langle |\theta_{\mathbf{q}}|^2 \rangle_{\text{iso}} = (KAq^2)^{-1}. \quad (6)$$

As shown in Ref. 25, Eq. (6) eventually yields the following expression for the orientational correlation function for two points \mathbf{s} and \mathbf{t} on the surface:

$$\begin{aligned} \langle \theta^2(\mathbf{s} - \mathbf{t}) \rangle_{\text{iso}} &= \langle |\theta(\mathbf{s}) - \theta(\mathbf{t})|^2 \rangle_{\text{iso}} \\ &\simeq (\pi K)^{-1} \ln \frac{|\mathbf{s} - \mathbf{t}|}{a}. \end{aligned} \quad (7)$$

A short distance cutoff a of about the size of a molecule must be introduced in order to avoid a divergence. Equation (7) leads to a persistence length

$$P \simeq a \exp 2\pi K. \quad (8)$$

Note that $|\mathbf{s} - \mathbf{t}| \gg a$ since the surface is regarded as a continuum.

Let us now consider a suspension of surfaces packed sufficiently to cause a presumably stable nematic phase. Provided the surfaces are large enough, the orientational order can be specified by a distribution function $f(\psi)$ where ψ is now defined as the angle between the normal to the surface and the director. For large surfaces the director is simply the normal to the reference plane so that ψ^2 is identical with $\theta^2(\mathbf{r})$ for all \mathbf{r} . The function f pertains to all surface elements of the micelles except those very close to the rims. Assuming the degree of ordering is not too low, we approximate f by a Gaussian²³ depending on a variational parameter α :

$$f(\psi) \simeq \frac{1}{2} \alpha \exp -\frac{1}{2} \alpha \psi^2 \quad (0 \leq \psi < \frac{1}{2} \pi), \quad (\alpha \gg 1), \quad (9)$$

$$f(\psi) = f(\pi - \psi), \quad \int_0^\pi f \sin \psi \, d\psi = 1 + O(\alpha^{-1}).$$

This is generally the leading order solution to integral equations arising from the minimization of the total free energy.^{23,33} It is useful to view Eq. (9) as a constraint. But for a calculation to leading order of the orientational entropy it suffices to use a weaker restriction or second moment condition:

$$\langle \psi^2 \rangle_{\text{nem}} = \frac{2}{\alpha}. \quad (10)$$

This constraint alludes to Helfrich's ruse of calculating the change in the confinement free energy.²⁴ Every mode (\mathbf{q}) of a rippling surface experiences a constant torque τ because the same f applies to all possible sections. Therefore, we can write

$$\begin{aligned} \langle |\theta_{\mathbf{q}}|^2 \rangle_{\text{nem}}^{-1} &= \langle |\theta_{\mathbf{q}}|^2 \rangle_{\text{iso}}^{-1} + \tau \\ &= KAq^2 + \tau. \end{aligned} \quad (11)$$

Fortunately, we can eliminate τ since the following relation applies:

$$\begin{aligned} \langle \psi^2 \rangle_{\text{nem}} &= A^{-1} \int d\mathbf{s} \langle |\theta(\mathbf{s})|^2 \rangle_{\text{nem}} \\ &= \sum_{\mathbf{q}} \langle |\theta_{\mathbf{q}}|^2 \rangle_{\text{nem}} \\ &= (4\pi K)^{-1} \ln \left(\frac{AK}{a^2 \tau} + 1 \right). \end{aligned} \quad (12)$$

Thus, on using the constraint [Eq. (10)] we get

$$\tau = \frac{AK}{a^2} (e^\gamma - 1)^{-1}, \quad (13)$$

where the dimensionless parameter γ has been introduced for convenience:

$$\gamma \equiv 8\pi K \alpha^{-1}. \quad (14)$$

Lastly, we derive the orientational free energy of N semi-flexible surfaces in the nematic state by employing Helfrich's expression for the free energy per mode²⁴:

$$\begin{aligned} \Delta F_{\text{or}} &= \frac{1}{2} N k_B T \sum_{\mathbf{q}} \ln \left(\frac{\langle |\theta_{\mathbf{q}}|^2 \rangle_{\text{iso}}}{\langle |\theta_{\mathbf{q}}|^2 \rangle_{\text{nem}}} \right) \\ &\simeq \frac{NAk_B T g(\gamma)}{8\pi a^2} \end{aligned} \quad (15)$$

with

$$g(\gamma) \equiv \gamma(1 - e^{-\gamma})^{-1} - \ln(e^\gamma - 1), \quad (16)$$

$$g = -\ln \gamma + 1 + O(\gamma^2), \quad \gamma \rightarrow 0,$$

$$g = (\gamma + 1)e^{-\gamma} + O(\gamma e^{-2\gamma}), \quad \gamma \gg 1.$$

Note that Eq. (15) can be understood heuristically as follows. One can associate a two-dimensional harmonic oscillator with a force constant $k_{\mathbf{q}}$ proportional to $\langle |\theta_{\mathbf{q}}|^2 \rangle^{-1}$ with every mode \mathbf{q} . The entropy of such an oscillator in a canonical ensemble is easily shown to be $-\ln k_{\mathbf{q}} + \text{a constant}$. Thus, if the system is viewed as a sum of independent oscillators we attain Eq. (15).

III. DEFLECTION LENGTH

It is possible to understand the qualitative form of the orientational free energy [Eq. (15)] by appealing to a scaling argument. We first formulate a deflection length λ : This is analogous to the λ of Ref. 19 for a worm-like chain within a cylindrical tube, to the length scale ξ_u of Ref. 25 for a fluctuating surface in a lamellar phase and to the roughness length $A_l^{1/2}$ of Ref. 27 for wandering walls (note that the logarithmic terms in the expression for the free energy¹⁹ should be deleted²³).

Let us focus on two points \mathbf{s} and \mathbf{t} on a test surface. When the distance $|\mathbf{s} - \mathbf{t}|$ is comparatively small the surrounding layers exert very little influence on the correlation between the normals to the surface at \mathbf{s} and \mathbf{t} . Therefore, to a first approximation we have $\langle \theta^2(|\mathbf{s} - \mathbf{t}|) \rangle_{\text{nem}} \simeq \langle \theta^2(|\mathbf{s} - \mathbf{t}|) \rangle_{\text{iso}}$ but only as long as $|\mathbf{s} - \mathbf{t}|$ is so small that $\langle \theta^2(|\mathbf{s} - \mathbf{t}|) \rangle_{\text{iso}} \ll \langle \psi^2 \rangle_{\text{nem}}$. Thus, a section of the surface with area of order $|\mathbf{s} - \mathbf{t}|^2$ has its normal pointing towards the director on the average and deviations of the section as a whole are described by Eq. (9). But the internal orientational fluctuations given by $\langle \theta^2(|\mathbf{s} - \mathbf{t}|) \rangle_{\text{nem}}$ are much smaller so to a first approximation the section behaves effectively like a rigid platelet.

Evidently the relation $\langle \theta^2(|\mathbf{s} - \mathbf{t}|) \rangle_{\text{nem}} \simeq \langle \theta^2(|\mathbf{s} - \mathbf{t}|) \rangle_{\text{iso}}$ cannot hold for all $|\mathbf{s} - \mathbf{t}|$ since the isotropic correlation function increases monotonically with $|\mathbf{s} - \mathbf{t}|$ whereas Eqs. (9) and (10) imply that $\langle \theta^2(|\mathbf{s} - \mathbf{t}|) \rangle_{\text{nem}}$ must be severely restricted because of the prevailing nematic order. In effect, we can write

$$\begin{aligned} \langle \theta^2(|\mathbf{s} - \mathbf{t}|) \rangle_{\text{nem}} &\simeq \langle \theta^2(\mathbf{s}) \rangle_{\text{nem}} + \langle \theta^2(\mathbf{t}) \rangle_{\text{nem}} \\ &= 2 \langle \psi^2 \rangle_{\text{nem}} \end{aligned} \quad (17)$$

for $|\mathbf{s} - \mathbf{t}| \gg \lambda$ where λ is an intensive length scale independent of the surface area A . Hence, for very large surfaces the expression

$$\lim_{A \rightarrow \infty} A^{-2} \int \int ds dt \langle \theta^2(|\mathbf{s} - \mathbf{t}|) \rangle_{\text{nem}} = 2 \langle \psi^2 \rangle_{\text{nem}} \quad (18)$$

exhibits the boundedness of the nematic correlation function.

The crossover length λ is explicitly derived by using the following scaling postulate:

$$\langle \theta^2(\lambda) \rangle_{\text{iso}} \simeq \langle \psi^2 \rangle_{\text{nem}}. \quad (19)$$

On the one hand, the relation $\langle \theta^2(|\mathbf{s} - \mathbf{t}|) \rangle_{\text{nem}} \langle \theta^2(|\mathbf{s} - \mathbf{t}|) \rangle_{\text{iso}}$ is pushed to its outer limit of validity, i.e., as $|\mathbf{s} - \mathbf{t}|$ increases towards λ . On the other, the bound on $\langle \theta^2(|\mathbf{s} - \mathbf{t}|) \rangle_{\text{nem}}$ implied by Eq. (18) is assumed to be a reasonable estimate as we decrease $|\mathbf{s} - \mathbf{t}|$ down to λ . This type of reasoning—connecting different physical regimes—is often used in qualitative analysis.

Equations (7), (10), and (19) lead to

$$\lambda = ae^{\eta\nu}, \quad (20)$$

where we have had to introduce an as yet unknown numerical coefficient η because Eq. (19) is not an exact equality. The scale λ is rightly called a *deflection length*. Locally a probe surface behaves ideally according to Eq. (7) ($|\mathbf{s} - \mathbf{t}| \lesssim \lambda$). Globally, i.e., when $|\mathbf{s} - \mathbf{t}| \gg \lambda$ the orientational correlation function is markedly restrained by the nematic field [see Eq. (17)]. Geometrically there is only one way we can visualize the fluctuating surface; it must be rippled, the characteristic length scale of the ripples being λ . In other words, the nematic field exerted by the surrounding surfaces continually deflects the probe surface to and fro so that every normal to it points toward the director on average and their orientational distribution conforms to Eq. (9). Surfaces of area A much larger than λ^2 must be viewed as semiflexible.³⁴

Because we have postulated that $\alpha \gg 1$, the deflection length λ is much smaller than the persistence length P [Eq. (8)] pertaining to the isotropic state. Thus, we reach the *apparent paradox* that a sheet of area A such that $\lambda^2 \ll A \ll P^2$ behaves like a rigid surface in dilute solution although its rippling would be crucial in the nematic state.

We conclude that there are effectively $NA\lambda^{-2}$ units or platelets each contributing about $k_B T$ to the orientational free energy:

$$\Delta F_{\text{or}} \simeq NA\lambda^{-2} k_B T \quad (A \gg \lambda^2). \quad (21)$$

It is remarked that the free energy per semiflexible sheet must be extensive, i.e., proportional to A when $A \gg \lambda^2$. If we disregard terms of logarithmic order as is consistent with the analysis of the previous section, we discern that Eqs. (20) and (21) agree with Eq. (15) provided $\eta = \frac{1}{2}$. Since we now have a precise expression for the deflection length, we next formulate the excluded-volume interactions.

IV. EXCLUDED-VOLUME EFFECT

We have argued that our system in volume V consists of $NA\lambda^{-2}$ effective platelets of area λ^2 . We now postulate that

the interactions can be represented by a virial expansion of the form

$$F_{\text{ex}} = k_B T NA\lambda^{-2} \sum_{n=2}^{\infty} (n-1)^{-1} B_n \left(\frac{NA}{\lambda^2 V} \right)^{n-1} \quad (22)$$

with

$$B_n = \lambda^{3(n-1)} h_n(\alpha), \quad (23)$$

where B_n are the virial coefficients and $NA\lambda^{-2} V^{-1}$ is the platelet density. Very little is known about the functions $h_n(\alpha)$ for $n \geq 3$. For unconnected thin disks we do know that the second virial term can dominate the others when the solution is highly ordered.³³ In that case a Gaussian ansatz like Eq. (9) works remarkably well.

The function $h_2(\alpha)$ is simply proportional to $\langle \sin \gamma \rangle_{\text{nem}}$ where γ denotes the angle between the normals of two platelets. Hence we have

$$h_2(\alpha) = b_2 \alpha^{-1/2}, \quad (24)$$

where the constant b_2 is of order unity. The ternary terms must be calculated by adding a third platelet to another already touching pair so that

$$h_3(\alpha) = b_3 \alpha^{-1/2-p}. \quad (25)$$

The constant p is positive for the additional factor should decrease with increasing order. Note that $p \approx 1/4$ for slender rods.²³ The other functions have the property

$$\frac{d|h_n(\alpha)|}{d\alpha} < 0. \quad (26)$$

Note that $h_n(\alpha)$ need not be positive for all n .³³

If we introduce the volume fraction $\varphi = AaN V^{-1}$ we can rewrite Eq. (22):

$$F_{\text{ex}} = k_B T NAa^{-2} [b_2 \varphi \alpha^{-1/2} e^{-1/2\nu} + \frac{1}{2} b_3 \varphi^2 \alpha^{-p-1/2} + \Sigma_4] \quad (27)$$

with

$$\Sigma_4 \equiv \sum_{n=4}^{\infty} (n-1)^{-1} \varphi^{n-1} h_n(\alpha) e^{(1/2)(n-3)\nu}. \quad (28)$$

Here we have extracted the second and third virial terms from the series.

V. MINIMIZATION OF THE FREE ENERGY

We assume the surface area A of every sheet is an invariant quantity. Accordingly, we need to minimize the total Helmholtz free energy $\Delta F_{\text{tot}} = \Delta F_1 + \Delta F_{\text{or}} + \Delta F_{\text{ex}}$, where ΔF_1 is a term independent of α . If the number of molecules in a surface were to vary (as for a micelle for instance), we would have to focus on the chemical potential μ of a molecule instead. This is given by $\mu = a^2 A^{-1} \partial \Delta F_{\text{tot}} / \partial N$ and ΔF_1 would still be independent of α provided $A \gg \lambda^2$. We emphasize that growth and order cannot couple for large systems.¹⁵ It turns out that our conclusions are independent of whether the surface is kept fixed or not, so here we analyze ΔF_{tot} only. When it is minimized with respect to α , we get [see Eqs. (14), (15), (20), and (27)]

$$y^2(1 - e^{-y})^2 = 4\pi b_2 \alpha^{-(1/2)} \varphi e^{(1/2)y} (1 - y) + 4\pi(p + \frac{1}{2}) b_3 \alpha^{-p-1/2} \varphi^2 e^y - 8\pi \alpha \Sigma_4^1 \quad (29)$$

with

$$\Sigma_4^1 = \sum_{n=4}^{\infty} (n-1)^{-1} h_n^1(\alpha) (\varphi e^{(1/2)y})^{n-1} - \frac{1}{2} y \alpha^{-1} \left[\sum_{n=4}^{\infty} h_n(\alpha) (\varphi e^{(1/2)y})^{n-1} - 2e^y \Sigma_4 \right]. \quad (30)$$

In discussing the solution to Eq. (20) we proceed by stages:

(i) First, we assume the second virial approximation is adequate, setting b_3 and h_n ($n \geq 4$) equal to zero. Then, Eq. (29) possesses a solution only if y is smaller than unity. Since our surfaces are viewed as continuous we must demand $\lambda \gg a$ or $y > 1$. Hence, the second virial approximation denies the existence of a highly ordered nematic.

(ii) Next, we take the third virial coefficient into account. In that case, Eq. (29) is best attacked numerically. In the concentration range $0.001 \lesssim \varphi \ll 1$ we find that $\alpha = \omega K$ where ω is a factor varying from about unity to 4 and only slightly dependent on the constants p_1 , b_2 , and b_3 (b_2 and b_3 are of order unity; $0 < p \lesssim 2$). The term on the left-hand side of Eq. (29), which arises from the orientational free energy, does not play a role in determining this solution. Thus, the third virial term stabilizes the second. The dominating influence of the factors $e^{1/2y}$ and e^y in Eq. (29) explains the insensitivity of the end result to the precise values of b_2 , b_3 , and p and to the orientational confinement term.

(iii) It is impossible to make headway with regard to the higher-order terms unless further suppositions are made. Let us hypothesize that the virial coefficients [Eq. (23)] are close to those pertaining to the hard disk gas. Then, Σ_4^1 would be negative except perhaps under exceptional circumstances. Furthermore, it is reasonable to suppose that the n th term of one of the series is of the same order of magnitude as the sum of the remaining terms beyond n , provided the orientational ordering is high enough. This is true for the Monte Carlo simulations of disks.³³ Hence, if $\varphi e^{(1/2)y}$ is not too large and α is not too small we reach a plausible upper bound on $|\Sigma_4^1|$:

$$|\Sigma_4^1| \lesssim y \alpha^{-1} h_3 \varphi^2 e^{-y}. \quad (31)$$

Equations (29) and (31) lead to virtually the same conclusions as those of the previous paragraph. Again, the exponential terms dominate the solution so the precise magnitude of the various constants is almost irrelevant. The fact that the inclusion of the estimate equation (31) makes little difference with regard to the end result is consistent with our assumptions concerning the virial series.

VI. CONCLUDING REMARKS

The instability of the nematic phase in the second virial approximation stems from the peculiar dependence of the excluded-volume effect on the deflection length λ . This scale representing an effective platelet size is a rapidly decreasing

function of α , a parameter related to the degree of orientational order. In effect, the excluded volume between platelets scales as λ^3 , whereas the number of binary collisions between platelets is proportional to λ^{-4} since the number of platelets scales as λ^{-2} . Thus, the free energy of interaction is proportional to λ^{-1} . Although there is an orientational factor $h_2(\alpha)$ in the excluded volume which diminishes as the particles align, this reduction is not enough by far to compensate for the decrease in the deflection length. By contrast, in solutions of worm-like micelles the excluded-volume effect is proportional to λ^2 which is exactly compensated by the number of collisions between deflection segments ($\sim \lambda^{-2}$) so that the theory is markedly different.¹⁵

We have reasoned that the instability due to binary collisions between platelets might be overcome by higher-order interactions. When a plausible though far from rigorous form for the third virial coefficient B_3 is postulated, the nematic state is stabilized under certain conditions. The additional free energy taken into consideration is in fact, independent of λ because B_3 is proportional to λ^6 , whereas the number of ternary collisions scales as λ^{-6} . Our analysis of terms higher than the third is even more speculative. It is conceivable, though highly unlikely, that they could destabilize the nematic phase. However, if the suspension is viewed as a solution of effective platelets of size λ , the higher-order terms would stabilize the nematic a bit more. Another effect that could influence the stability is the interfacial tension σ . It can be disregarded when $\sigma \lambda^2 \ll k_B T$. This condition is justified by noting that the calculation in Secs. II and III allows the platelet area to be stretched between λ^2 and $\lambda^2(1 + \alpha^{-1})$ because each platelet is displaced by $\lambda \alpha^{-1/2}$ along the director, on average.

In addition, our analysis has several other limitations. The parameter α must be large enough ($\alpha > 10$, 5 say). Hence, the conclusions regarding stability imply rather high values for K ; the theory could be of use in describing membranes, micelles, and other stiff surfaces, but would probably not be helpful in assessing the feasibility of nematic states for bicontinuous microemulsions. An investigation of slightly ordered states would be interesting. However, a bifurcation analysis does not appear trivial because we would have to know the functional dependence of the total free energy on the distribution function.³⁴ The incorporation of forces other than purely repulsive is also of interest since they might restrain the rapid decrease of the deflection length λ with decreasing order. Furthermore, it is well to stress that we are modeling real systems by continuous surfaces. It is conceivable, though barely so, that highly wrinkled nematic surfaces might exist whose order is induced on a molecular scale.

Finally, it is pertinent to point out that the existence of smectic order is governed by rules of a different nature. Positional ordering of micellar or other layers imposes a characteristic thickness d between them. In view of the fact that $\langle \zeta^2(\mathbf{r}) \rangle \simeq r^2 \langle \theta^2(\mathbf{r}) \rangle$, the deflection length is approximately given by $\lambda_s \simeq dK^{1/2}$. Since d can vary within narrow bounds only, the same applies to λ_s , in contrast to the behavior of λ in the nematic. Likewise, the excluded-volume manifests itself differently in the smectic. Every platelet in the nematic is

subject to the prevailing orientational order but it can still sample the whole volume of the system. This sampling is no longer possible in the smectic phase. Unfortunately, we are not able to answer the problem posed in the Introduction, namely the relative stability of the smectic for micellar surfaces. At present there are simply too many uncertainties in the magnitude of the interactions involved.

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³³For surfaces, the trial function [Eq. (9)] has to be viewed as a postulate since the equation determining f is unknown as yet.
³⁴The last few paragraphs have been somewhat verbose for the benefit of those who have difficulty in visualizing mathematical equations.