EPJ manuscript No.
(will be inserted by the editor)

Vertical Melting of a Stack of Membranes

M.E.S. Borelli [a], H. Kleinert [b], and Adriaan M.J. Schakel[c]

Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

July 24, 2000

Abstract. A stack of tensionless membranes with nonlinear curvature energy and vertical harmonic interaction is studied. At low temperatures, the system forms a lamellar phase. At a critical temperature, the stack disorders vertically in a melting-like transition.

PACS. 82.65.Dp Thermodynamics of surfaces and interfaces – 68.35.Rh Phase transitions and critical phenomena

1 Introduction

Under suitable conditions, lipid membranes in aqueous solution are known to form lamellar structures, characterized by a parallel arrangement of the membranes alternating with thin layers of water [1]. The existence of such structures is in contrast to the behavior of a single tensionless membrane subject to thermal fluctuations, which is always in a disordered, crumpled phase, filling the embedding space completely [2]. In a stack, this phase is suppressed by the steric repulsion between the membranes which prevents them from passing through each other [1], thus constraining the amplitude of the height fluctuations of each membrane to be less than the distance to its nearest neighbors.

In this note, we investigate the question whether the lamellar structure exists at all temperatures, or whether thermal fluctuations can destroy the vertical order at some critical temperature.

Such a transition does not take place in the simplest model of a stack proposed by Helfrich [1], where the membranes possess only a linearized curvature energy and a harmonic repulsive term accounts for the vertical forces in the stack, approximating in a rough way the steric repulsion. In this purely Gaussian approximation, the theory is equivalent to de Gennes' theory of smectic-A liquid crystals, having only an ordered phase [3].

---

[a] e-mail: `borelli@physik.fu-berlin.de`

[b] e-mail: `kleinert@physik.fu-berlin.de`

[c] e-mail: `schakel@physik.fu-berlin.de`

In this paper we extend the simplest model by taking into account higher-order terms of the curvature energy, and show that thermal fluctuations cause a finite stack of membranes to disorder vertically, a process which we may call vertical melting. A similar phase was previously described in a different context by Huse and Leibler [4], and by Kleinert [5], who related the molten phase to the directionally ordered phase of a nematic liquid crystal. We shall find that thermal fluctuations renormalize both the coefficient of the curvature term and the vertical compressibility of the stack. Analyzing the renormalization group equations, we find, besides the Gaussian fixed point governing the low-temperature phase, a nontrivial fixed point determining the critical exponents of the vertical melting transition.

2 The Model

We consider a generalization of the Helfrich model due to Janke and Kleinert [7], in which a multilayer system is made up of $(N+1)$ fluid membranes, parallel to the xy plane of a Cartesian coordinate system, separated a distance l. If the vertical displacement of the mth membrane with respect to this reference plane is described by a function $u_m(\mathbf{x}) \equiv u(\mathbf{x}_\perp, ml)$, where $\mathbf{x}_\perp = (x, y)$, the energy of the stack reads:

$$E = \sum_m \int \mathrm{d}^2 x_\perp \sqrt{g_m} \left[r_0 + \tfrac{1}{2}\kappa_0 H_m^2 + \frac{B_0}{2l}(u_m - u_{m-1})^2 \right]. \tag{1}$$

Here, $H_m = \partial_i N_{m,i}$ is the mean curvature, where $\mathbf{N}_m \propto (-\partial_1 u_m, -\partial_2 u_m, 1)$ is the unit normal to the mth membrane, and $g_{m,ij} = \delta_{ij} + \partial_i u_m \partial_j u_m$ the induced metric, with $i, j = 1, 2$, $\partial_1 = \partial/\partial x$, $\partial_2 = \partial/\partial y$ and $g_m = \det[g_{m,ij}]$. The parameter r_0 is the surface tension of a single membrane, κ_0 its bending rigidity, and B_0 the compressibility of the stack. In Eq. (1), as in the following, the subscript 0 denotes bare quantities, whereas renormalized parameters will carry no subscript.

In the original Helfrich model, the surface tension r_0 was not included because the membranes in the stack are tensionless. We have included r_0 in the energy (1) as an infrared regulator which also serves to absorb ultraviolet infinities. After carrying out the various integrals, the renormalized physical tension will be set equal to zero.

For slow spatial variations, the discrete variable ml may be replaced with a continuous one, and $u(\mathbf{x}_\perp, ml) \to u(\mathbf{x})$, where $\mathbf{x} = (\mathbf{x}_\perp, z)$. In this limit, the energy (1) reduces to

$$E = \int_0^{L_\parallel} \mathrm{d}z \int \mathrm{d}^2 x_\perp \sqrt{g} \left[\sigma_0 + \tfrac{1}{2} K_0 H^2 + \tfrac{1}{2} B_0 (\partial_z u)^2 \right]. \tag{2}$$

Here we have introduced bulk versions of the surface tension $\sigma_0 \equiv r_0/l$ and bending rigidity $K_0 \equiv \kappa_0/l$, and defined $L_\parallel \equiv Nl$. In Ref. [5] the vertical gradient energy $(\partial_z u)^2$ was replaced by the normal gradient energy $(\mathbf{N} \cdot \nabla u)^2$, which is physically more correct and has the advantage of being reparametrization invariant (see also Ref. [6]). In the following, we shall derive all results for both terms and analyze the difference between the two.

We study the stack perturbatively, starting with the lamellar configuration, and expand the theory in the inverse parameter $\alpha_0 = 1/K_0$, which is assumed to be small.

To keep our notation in conformity with the literature, we use K_0 throughout the text and resort to its inverse only when necessary.

3 Renormalization

The phase transition to be described in this note is caused by a competition between the softening of the bending rigidity due to thermal fluctuations and the stack-preserving vertical elastic forces. To understand this competition we study how thermal fluctuations renormalize the parameters of the theory. For this we expand the energy (2) up to fourth order in the displacement field $u(\mathbf{x})$, where it reads

$$
\begin{aligned}
E = \int_0^{L_\parallel} \mathrm{d}z \int \mathrm{d}^2 x_\perp \Big[& \tfrac{1}{2}\,\sigma_0(\partial_i u)^2 + \tfrac{1}{2}K_0(\partial_i^2 u)^2 + \tfrac{1}{2}B_0(\partial_z u)^2 \\
& - \tfrac{1}{8}\sigma_0(\partial_i u)^2(\partial_j u)^2 - \tfrac{1}{4}K_0(\partial_i^2 u)^2(\partial_j u)^2 \\
& - K_0(\partial_i u)(\partial_j u)(\partial_i \partial_j u)(\partial_k^2 u) \\
& \pm \tfrac{1}{4}B_0(\partial_z u)^2(\partial_i u)^2 \Big], \qquad (3)
\end{aligned}
$$

where the lower sign in the last term refers to the more physical normal gradient energy $(\mathbf{N}\cdot\nabla u)^2$. For zero surface tension, the lowest-order contribution to the energy due to longitudinal displacements is of the usual elastic form $\frac{1}{2}B_0(\partial_z u)^2$, while that due to transverse displacements is of higher order, viz. $\frac{1}{2}K_0(\partial_i^2 u)^2$.

The one-loop contributions can be calculated either by using Feynman diagrams, or by a derivative expansion, as in Ref. [8]. Following standard procedure, we integrate out fluctuations with transverse wavevectors in a momentum shell. Since the stack is periodic and of finite extent in the z-direction, the Fourier transform includes a sum $(1/L_\parallel)\sum_{n=-N/2}^{N/2}$ over the discrete wavevector components

$$
\omega_n = \frac{2\pi}{L_\parallel} n. \qquad (4)
$$

We take into account the interlayer spacing l in a rough way by restricting the values of the discrete variables to $|\omega_n| < \pi/l$, so that the summation index n lies in the interval $-\frac{1}{2}N < n < \frac{1}{2}N$. To one-loop order, the bare parameters are renormalized to

$$
\sigma_0 \to \sigma_0(1+I_1), \quad K_0 \to K_0(1-\tfrac{3}{2}I_2), \quad B_0 \to B_0(1\pm\tfrac{1}{2}I_2), \qquad (5)
$$

where

$$
I_1 = \frac{k_\mathrm{B}T}{L_\parallel}\sum_{n=-N/2}^{N/2}\int \frac{\mathrm{d}^2 q_\perp}{(2\pi)^2}\, \frac{\frac{1}{2}\frac{B_0}{\sigma_0}\omega_n^2 - q_\perp^2 - \frac{3}{2}\frac{K_0}{\sigma_0}q_\perp^4}{B_0\omega_n^2 + \sigma_0 q_\perp^2 + K_0 q_\perp^4} \qquad (6)
$$

$$
I_2 = \frac{k_\mathrm{B}T}{L_\parallel}\sum_{n=-N/2}^{N/2}\int \frac{\mathrm{d}^2 q_\perp}{(2\pi)^2}\, \frac{q_\perp^2}{B_0\omega_n^2 + \sigma_0 q_\perp^2 + K_0 q_\perp^4}. \qquad (7)
$$

We regularize the integrals in the ultraviolet by introducing a sharp transverse wavevector cutoff Λ inversely proportional to the lateral size a of a lipid molecule. Actually, the divergent contributions to the above integrals are independent of B_0. This is due to the discrete nature of the stack. By restricting the values of the discrete wavevectors ω_n to account for the interlayer spacing, as explained above, all divergences proportional to B_0 are suppressed.

The renormalization flow is obtained by integrating out transverse wavevectors in a momentum shell $\Lambda/s < q_\perp < \Lambda$, and subsequently rescaling the coordinates. We thus obtain,

$$
I_1 = \tfrac{1}{2}I_2 = \frac{1}{4\pi}\frac{k_\mathrm{B}T}{L_\parallel}\frac{1}{K_0}(N+1)\ln s. \qquad (8)
$$

Since these results are independent of σ_0, we can safely set the surface tension to zero, thus describing a stack of tensionless membranes, characterized by the two remaining parameters, B and K. Under a rescaling $\mathbf{x}_\perp \to \mathbf{x}_\perp/s$ of the coordinates in the plane and $z \to z/s^{z_\mathrm{c}}$ along the stack axis, the expansion parameter of perturbation theory $\alpha \equiv 1/K$ scales like $\alpha \to s^{-z_\mathrm{c}}\alpha$, and the compressibility scales like $B \to s^{4-z_\mathrm{c}}B$. Here, z_c allows for the possibility of anisotropic scaling. From Eq. (3) with $\sigma = 0$, it follows that $z_\mathrm{c} = 2$ in the Helfrich model. Using the above results, one readily generates differential recursion relations to lowest nontrivial order

$$\frac{\mathrm{d}\alpha}{\mathrm{d}\ln s} = -z_\mathrm{c}\alpha + \frac{3}{4\pi}\frac{k_\mathrm{B}T}{L_\parallel}\alpha^2(N+1) \tag{9}$$

$$\frac{\mathrm{d}B}{\mathrm{d}\ln s} = (4-z_\mathrm{c})B \pm \frac{1}{4\pi}\frac{k_\mathrm{B}T}{L_\parallel}B\alpha(N+1). \tag{10}$$

Besides the Gaussian fixed point ($\alpha = 0, B = 0$) which is stable in the infrared, the flow equations also admit a nontrivial, unstable fixed point at

$$\alpha^* = \frac{4\pi}{3}\frac{L_\parallel}{k_\mathrm{B}T}\frac{z_\mathrm{c}}{N+1}, \quad B = 0. \tag{11}$$

The latter implies the presence of a phase transition at a critical temperature

$$k_\mathrm{B}T_\mathrm{c} = \frac{4\pi}{3}\frac{N}{N+1}\frac{l z_\mathrm{c}}{\alpha^*}. \tag{12}$$

The flow diagram corresponding to the above system of differential equations is shown in Fig. 1. For $T < T_\mathrm{c}$, the inverse bending rigidity α flows to the Gaussian fixed point at the origin. In this low-temperature phase, the bending rigidity of the membranes increases with their lateral size, and thermal fluctuations are suppressed. This weak-coupling phase is the lamellar phase, where the rotational symmetry is spontaneously broken. For $T > T_\mathrm{c}$, on the other hand, α flows with increasing length scales away from the nontrivial fixed point at α^* in the opposite direction. As α increases, the bending rigidity decreases and the membrane fluctuations become stronger. At the critical point α^*, the stack disorders vertically and the system enters a strong-coupling disordered phase. Note that the critical temperature (12) depends only weakly on the number $(N+1)$ of membranes.

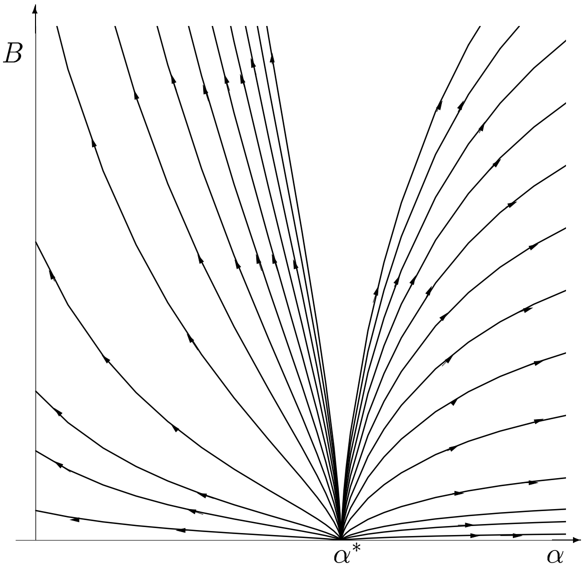

Fig. 1. Flow diagram in the (α, B)-plane. The diagram is plotted using the lower sign in the last term in Eq. (10).

The flow equations (9) and (10) can be integrated exactly, yielding:

$$B = c\,\alpha^{\pm 1/3}\left|\frac{\alpha-\alpha^*}{\alpha}\right|^{4/z_\mathrm{c}-1\pm 1/3}, \tag{13}$$

where c is an integration constant. For $z_\mathrm{c} = 2$, the exponent is equal to $1\pm 1/3$. Explicitly, as we approach T_c from below, B goes to zero as

$$B \sim |T-T_\mathrm{c}|^{1\pm 1/3}. \tag{14}$$

The free energy density of the model in the lamellar phase can be calculated in the harmonic approximation, as in Ref. [1]. For a finite stack, it reads

$$f = \frac{1}{16\pi} \frac{k_{\mathrm{B}}T}{L_{\parallel}^2} \left(\frac{B}{K} \right)^{1/2} N(N+2) \tag{15}$$

Thus, as T approaches T_{c} from below, the free energy density behaves for $z_{\mathrm{c}} = 2$ like

$$f \sim |T - T_{\mathrm{c}}|^{1/2 \pm 1/6}, \tag{16}$$

and the specific heat of the stack diverges as

$$C \sim |T - T_{\mathrm{c}}|^{-3/2 \pm 1/6}. \tag{17}$$

Figure 2 shows a plot of the free energy density and specific heat of the stack for the lower sign in Eqs. (16) and (17).

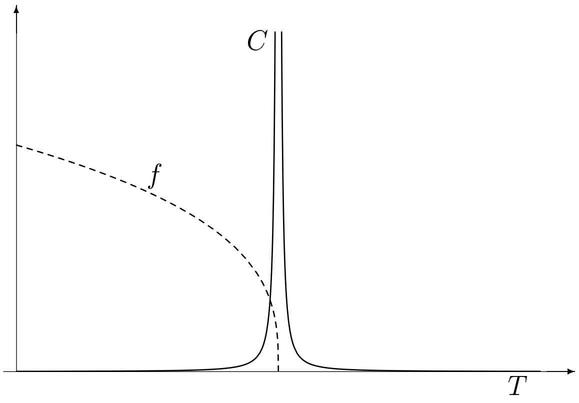

Fig. 2. Free energy density and specific heat of a stack of membranes, with the lower sign in Eqs. (16) and (17).

We thus see that by using either the vertical gradient energy $(\partial_z u)^2$ or the more physical normal gradient energy $(\mathbf{N} \cdot \nabla u)^2$, the qualitative behavior of the stack of membranes is not altered, but the critical exponents of the melting transition differ from each other. This is due to the fact that the normal gradient energy is zero for the in-plane flow of molecules inside the membranes. The vertical gradient energy $(\partial_z u)^2$, on the other hand, includes the energies of the tangential flow. Tangential elasticity has been shown to be irrelevant for the renormalization of a single membrane [9,10]. Our result implies that this is not the case for a stack of membranes.

The properties of a single membrane are obtained by letting $N \to 0$ and $z_{\mathrm{c}} \to 0$. In particular, the flow equation (9) of the bending rigidity reduces in this limit to the known result [11]. It has no fixed point other than the trivial one, which is unstable now, implying that a single membrane is always in the crumpled strong-coupling phase.

4 Weak-coupling ordered phase

We next wish to study the low-temperature phase of the stack in more detail, where the coupling constant α is weak. As in smectic-A liquid crystals, the theory (3) can here safely be approximated by taking into account only the quadratic terms. An important characteristic is the vertical fluctuation width or roughness ℓ of a membrane in the stack defined by the mean square *height* fluctuation as $\ell^2 = \langle u^2 \rangle$ [12]. In the harmonic approximation, it is given by the one-loop integral

$$\ell^2 = \langle u^2 \rangle = \frac{k_{\mathrm{B}}T}{L_{\parallel}} \sum_{n=-N/2}^{N/2} \int_{1/L_{\perp}}^{\Lambda} \frac{\mathrm{d}^2 q_{\perp}}{(2\pi)^2} \frac{1}{B\omega_n^2 + K q_{\perp}^4}, \tag{18}$$

where, in the absence of a surface tension, the largest wavelength is equal to the inverse lateral size $1/L_{\perp}$ of the membranes. As first observed by Peierls and Landau, the mean square fluctuations diverge in the infrared. They thus destroy the long-range *positional* order in the layered system at any finite temperature. More specifically, one finds [12,13]

$$\ell^2 \sim \frac{k_{\rm B}T}{2\pi}\left[\frac{L_\perp^2}{KL_\parallel} + \frac{1}{\sqrt{BK}}\ln(L_\perp/a)\right]. \tag{19}$$

The first contribution, only present in a finite stack, stems from the $n = 0$ term in the sum in Eq. (18). It corresponds to a super soft mode, where the membranes undulate coherently with constant interlayer distance. The second contribution, on the other hand, is also present when the stack is infinite. This contribution increases slowly with the lateral size.

Before proceeding, let us pause for a moment and consider the roughness of the two limiting cases of our theory: a single, tensionless membrane and an infinite, continuum stack of such membranes. In this way, we find

$$\ell^2 = \begin{cases} \displaystyle\int \frac{{\rm d}^D q_\perp}{(2\pi)^D}\frac{k_{\rm B}T}{\kappa q_\perp^4}, & \text{(single membrane)} \\ \displaystyle\int \frac{{\rm d}q_z{\rm d}^D q_\perp}{(2\pi)^{D+1}}\frac{k_{\rm B}T}{Bq_z^2 + Kq_\perp^4}, & \text{(infinite stack),} \end{cases} \tag{20}$$

where instead of a 2-dimensional membrane we consider a D-dimensional object. It follows that for $D > D_{\rm u} = 4 - z_{\rm c}$, the roughness is finite in the infrared, indicating that $D_{\rm u} = 4 - z_{\rm c}$ is the upper critical dimension. Recall that for a single membrane $z_{\rm c} = 0$, while for an infinite stack $z_{\rm c} = 2$. To determine the lower critical dimension, we consider the mean square normal, or *orientational* fluctuations $\langle(\partial_\perp u)^2\rangle$. This results in an additional factor of $q_\perp^2$ in the numerator of the integrands in (20). The resulting expressions are finite in the infrared for $D > D_{\rm l} = 2 - z_{\rm c}$, identifying $D_{\rm l}$ as the lower critical dimension. Hence, in going from the limit of a single, tensionless 2-dimensional ($D = 2$) membrane to the opposite limit of an infinite stack, we go from the lower critical dimension of the former to the upper critical dimension of the latter.

Another characteristic of the weak-coupling phase of low-temperature is the behavior of the structure factor

$$S_n(\mathbf{x}) = \langle\exp\{inq_0[u(\mathbf{x}) - u(0)]\}\rangle, \tag{21}$$

where q_0 is parallel to the $z-$axis, with $|q_0| = 2\pi/l$. This correlation function can be directly observed in X-ray scattering experiments, where the fluctuation spectrum is expressed as half-widths at half-maximum of the anomalous Bragg peaks. As in smectic-A liquid crystals [14,15], the Fourier transform of the structure factor has algebraic singularities at $q_z = nq_0$:

$$S_n(0,q_z) \sim (q_z - nq_0)^{-2+n^2\eta}, \quad S(q_\perp,0) \sim q_\perp^{-4+2n^2\eta}, \tag{22}$$

with exponent η. In the harmonic approximation, η can be calculated from Eq. (21) and turns out to be the same as for an infinite stack [14]

$$\eta = \frac{k_{\rm B}T}{8\pi}\frac{q_0^2}{\sqrt{BK}}. \tag{23}$$

The algebraic singularities in (22) reflect the quasi-long-range periodic order along the stack axis. As for smectic-A liquid crystals, the exponent η is temperature independent. This can be seen by remembering that by simple scaling arguments [1]

$$B \sim \frac{(k_{\rm B}T)^2}{\kappa}\frac{l}{(l-w)^4}, \tag{24}$$

for a stack of membranes of rigidity κ and thickness w. Specifically,

$$\eta \sim \left(1 - \frac{w}{l}\right)^2. \tag{25}$$

For smectic-A liquid crystals, this expression was confirmed experimentally [16].

As the temperature increases, thermal fluctuations become stronger, and eventually overcome the vertical forces of the B-term leading to a vertical disordering of the stack. In the strong-coupling disordered phase, the Gaussian approximation used in this section to investigate the weak-coupling ordered phase breaks down. To study this phase, a nonperturbative method is required.

5 Conclusions

We have shown that a stack of membranes with nonlinear curvature energy melts at some critical temperature T_c. In the weak-coupling low-temperature phase the system forms a periodic array of well-defined surfaces. There is long-range orientational order in the planes, and quasi-long-range positional order along the stack axis. This phase can be accurately described by the harmonic approximation of the Helfrich model, which coincides with the de Gennes' theory of smectic-A liquid crystals.

Upon approaching T_c, the stack melts and the lamellar phase goes over into a strong-coupling disordered phase. This phase cannot be described by the harmonic approximation. Its properties will be investigated separately in a nonperturbative framework, in the limit of infinite embedding space dimension.

References

1. W. Helfrich, Z. Naturforsch. **33a**, 305 (1978).
2. *Statistical Mechanics of Membranes and Surfaces*, Proceedings of the Fifth Jerusalem Winter School for Theoretical Physics, 1987/1988, edited by D. Nelson, T. Piran, and S. Weinberg (World Scientific, Singapore, 1989).
3. P. G. de Gennes, J. Phys. (Paris), Colloque **4**, 65 (1969).
4. D. A. Huse and S. Leibler, J. Phys. (Paris) **49**, 605 (1988).
5. H. Kleinert, *Smectic-Nematic Phase Transition as Wrinkling Transition in a Stack of Membranes*, Berlin preprint (1989), http://www.physik.fu-berlin.de/~kleinert/173.
6. G. Foltin, Phys. Rev. E **49**, 5243 (1994).
7. W. Janke and H. Kleinert, Phys. Rev. Lett. **58**, 145 (1987).
8. M. E. S. Borelli, H. Kleinert, and A. M. J. Schakel, Phys. Lett. A **253**, 239 (1999); Phys. Lett. A **267**, 201 (2000).
9. H. Kleinert, Phys. Lett. A **53**, 130 (1988); S. Ami and H. Kleinert, Phys. Lett. A **120**, 207 (1987), http://www.physik.fu-berlin.de/~kleinert/157.
10. F. David, Europhys. Lett. **6**, 603 (1988).
11. L. Peliti and S. Leibler, Phys. Rev. Lett. **54**, 1690 (1985), H. Kleinert, Phys. Lett. A **114**, 263 (1986), D. Förster, Phys. Lett. A **114**, 115 (1986).
12. R. Lipowsky, in *Structure and Dynamics of Membranes*, Vol. 1B of *Handbook of Biological Physics*, ed. by R. Lipowsky and E. Sackmann (North-Holland, Amsterdam, 1995).
13. P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford University Press, London, 1974).
14. A. Caillé, C. R. Acad. Sci. Ser. B **274**, 981 (1972).
15. P. M. Chaikan and T. C. Lubensky, *Principles of Condensed Matter Physics.* (Cambridge Press, New York, 1995).

16. C. R. Safinya, D. Roux, G. S. Smith, S. K. Sinha, P. Dimon, N. A, Clark, and A. M. Bellocq, Phys. Rev. Lett. **57**, 2718 (1986).