

# Concerning the free energy of a solid film

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It is shown that, at temperatures higher than that of the roughening phase transition, the free energy of a solid film contains an increment that oscillates with the atomic period and has an amplitude that decreases with thickness in accordance with a power law having an exponent that depends on temperature. As a result, the heat capacity of the film is a decreasing oscillating function of its thickness. The spectrum of the crystallization waves was investigated for a solid  $^4\text{He}$  film in contact with a superfluid liquid. It has been shown, in particular, that the dispersion law for small  $k$  takes the form  $\omega \propto k^{1/2}$ , and the temperature dependence of the surface temperature at low temperature has been obtained.

Multilayer films adsorbed on attracting substrates exhibit a number of remarkable properties. A large number of these properties are connected with the joint influence of surface and bulk properties of the coexisting phases. Among the most interesting sets of phenomena of this class are layering phase transitions (see Ref. 1 and the citations therein). They constitute a discrete filling of atomic layers of the film, which takes place at sufficiently low temperature, as the external pressure is continuously varied. With rise of temperature, the first-order transition lines terminate at critical points of the layering transitions, and at higher temperature the film thickness has a continuous dependence on the pressure.

It was shown in Ref. 1 that the layering-transition critical points condense towards the roughening-transition temperature  $T_R$  like  $T_R - T_{c,n} \propto 1/\ln^2 n$  if the number of layers  $n$  is large. Here  $T_{c,n}$  is the critical point of the layering transition from an  $(n - 1)$ -layer film to an  $n$ -layer film. It might seem that at  $T \gg T_R$  the film thickness depends monotonically on the external pressure. It will be shown below that at  $T \gg T_R$  the free energy of a solid film contains an increment that oscillates with a period of atomic order and its amplitude has a power-law decrease with thickness, and the exponent depends on temperature. As a result, a number of temperature-dependent film properties, such as the heat capacity, become slowly decreasing oscillating functions of the film thickness, i.e., even in the high-temperature region the film “gives preference” to integer (in units of the lattice period) values of its thickness. The physical reason for this behavior is that the roughening transition takes place on a surface that separates bulk phases. The film, on the other hand, by virtue of its finite thickness, is always smooth, so that its surface “feels” the crystalline relief at temperatures above the roughening-transition temperature between the bulk phases. The oscillatory dependence of the film properties on its thickness becomes, of course, weaker with increase of film thickness, and vanishes in the case of a surface that separates bulk phases. The character of the weakening of the dependence on the thickness is determined by the interaction forces between the film and the substrate (in this case—Van der Waals forces). Since Van der Waals forces are long range, only a power-law weakening of the parameters with thickness is possible.

All these premises are confirmed below by a rigorous calculation. In addition, we obtained the dependence of the effective rigidity of the film on thickness and temperature. The most probable object for which our predictions can be verified is a solid  $^4\text{He}$  film in contact with a superfluid liquid. We shall show below how the spectrum of the melting-crystallization waves<sup>2</sup> varies with the surface that separates the bulk phases, and obtain the temperature dependence of the surface tension of a solid helium film. In contrast to the bulk case, the surface tension is proportional to  $(\text{const} \cdot T^5)$  if the corresponding  $T_R$  is low enough.

1. As in Ref. 1, we begin with the effective Hamiltonian

$$H = \int d^2x \left[ \frac{J}{2} (\nabla f)^2 + c f^{-\alpha} + p f - y \cos 2\pi f \right]. \quad (1)$$

Here  $J$  is the effective rigidity of the film;  $f$  is the position of the film surface as measured from the substrate; the second term describes the long-range interaction between the film surface and the substrate (Van der Waals attraction corresponds to  $\alpha = 2$ );  $p$  is the excess free energy per unit film volume compared with the third phase (liquid or gas); the last term takes into account the crystallinity and leads to a transport of the roughness between the bulk phases ( $c$  characterizes the Van der Waals forces,  $y$  is the amplitude of the crystal potential). The non-gradient terms of the Hamiltonian (1) constitute the free energy of the film per unit area, obtained by integration over all the degrees of freedom, except the shifts of the surface position. The renormalization-group equations for the Hamiltonian (1) are given in Ref. 1 and have the form

$$\dot{g} = 2g, \quad (2a)$$

$$\dot{y} = (2 - \pi T/J) y, \quad (2b)$$

$$\dot{J} = 4\pi^4 y^2 / J k_0^4. \quad (2c)$$

Here  $k_0$  is a quantity of the order of the reciprocal of the atomic distance in the film plane, and  $g$  is the curvature of the smooth part of the potential in (1) and is calculated at the point of its minimum  $f = (\alpha c/p)^{1/(\alpha+1)}$ . For large  $f$  (i.e., as  $p \rightarrow 0$ ), we have  $g = g_0 \propto 1/f^{2+\alpha}$ .

Equations (2b) and (2c) are the known Kosterlitz equations. The properties of Eqs. (2) for  $T < T_R$  were con-

sidered in Ref. 1. We, on the other hand, shall investigate the region  $T \gg T_R$ . In this temperature region the system has a single independent length scale, viz., the film thickness; this scale, in turn, makes finite the correlation length of the fluctuations of the film-surface position in its plane. Thermal fluctuations, which cause surface roughness, are significant only over scales within the correlation length. At larger scales the film surface becomes smooth. This means that Eqs. (2b) and (2c) must be integrated up to a large finite scale determined by the film thickness. The dependence of the scale on the length is formally determined in the following manner: for  $T \gg T_R$  the function  $y(l)$  decreases as  $l(f) \rightarrow \infty$ , while  $g(l)$  increases like  $g = g_0 \exp 2l$  [see Eq. (2)] (here  $l$ , the usual renormalization parameter, is the logarithm of the ratio of the running length scale to the initial one). For sufficiently thick films the curvature of the renormalized potential is therefore determined by its smooth part.

Thermal fluctuations are insignificant starting with a scale  $\exp l^*$  at which the curvature of the renormalized potential acquires a value of order  $J$  and increases monotonically at large  $l$ . Hence

$$g_0 \exp 2l^* \approx J, \quad \exp l^* \approx f^{1+\alpha/2}. \quad (3)$$

Since  $J(l)$  has a finite limit as  $l \rightarrow \infty$  (see below), we are justified in changing from the first to the second relations of (3). Arguments similar to those set forth above are used also in Ref. 3 for the problem of wetting transitions.

Since renormalization of the long-range interaction reduces only to a scale transformation (the condition (3) does not contain the temperature), the equation given above can be obtained from elementary considerations. Indeed, in the mean-field approximation, the correlation length  $\xi$  is given by

$$\xi^{-2} = g_0/J. \quad (4)$$

Using the fact that  $\xi \propto \exp l^*$ , we arrive at Eq. (3). It is clear now that the problem reduces to integration of the Kosterlitz equations from zero to  $l^*$ , given by Eq. (3).

A similar situation was encountered in Ref. 4, where the influence of the crystalline relief on the properties of a two-dimensional incommensurate phase was investigated. We shall therefore follow the procedure of Ref. 4 from now on. Our results are reminiscent to some degree of the conclusions drawn in that reference; the main difference is that the measured value of the coefficient  $y$  differs from zero in our case. Expanding (2b) and (2c) near the point  $y = 0$  and  $J = \pi T/2$ , and using the variables

$$K = 2 - \pi T/J, \quad \tilde{y} = 2^{1/2} \pi y / T k_0^2, \quad (5)$$

we obtain

$$\dot{\tilde{y}} = K\tilde{y}, \quad \dot{K} = -\tilde{y}^2. \quad (6)$$

It is convenient to demonstrate the further evolution of the solution using the known Kosterlitz diagram, which shows the phase trajectories of the system (6) (Fig. 1). The solution of the system (6) comprises the hyperbolas  $\tilde{y}^2 - K^2 = \text{const}$ . At  $T \gg T_R$  they cross the abscissa axis  $y = 0$  at the renormalized value of the parameter  $K$  (Fig. 1) (which is connected via the first equation of (5) with the macroscopic rigidity  $J_\infty$  of the surface separating the bulk phases). We

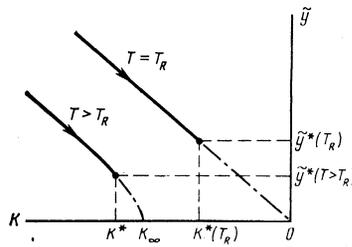


FIG. 1. Phase trajectories of the system (6). The points on the lines at  $T \gg T_R$  mark the stopping places given by the condition (3).

shall be interested in values of  $K^*$  close to  $K_\infty$ , and in values of  $y^*$  close to zero, when the hyperbola  $\tilde{y}^2 - K^2 = \text{const}$  almost reaches the abscissa axis. For  $T > T_R$  the equation for the trajectory is

$$\tilde{y}^2 - K^2 = -K_\infty^2. \quad (7)$$

Substituting it in the first equation of (6) and recalling that we are interested in the asymptotic vanishing of  $y$ , we have

$$\dot{\tilde{y}} = -(\tilde{y}^2 + K_\infty^2)^{1/2} \tilde{y} \approx K_\infty \tilde{y}. \quad (8)$$

Hence  $y(l^*) \propto y_0 \exp(K_\infty l^*)$  (here  $y_0$  is a quantity of the order of the initial value of  $y$ ). We have thus

$$y(l^*) \approx y_0 \exp[(2 - \pi T/J_\infty)l^*]. \quad (9)$$

We obtain  $K^*$  in similar fashion:

$$K = K^2 - K_\infty^2 \approx 2(K - K_\infty)K_\infty, \\ K^* - K_\infty - \exp(2K_\infty l^*) = -\exp[2(2 - \pi T)J_\infty/l^*]. \quad (10)$$

To find the measurable values of  $J$  and  $y$ , we must return to the initial units of length, i.e., effect an inverse scale transformation in the renormalization of the Hamiltonian (1). This does not change the value of  $J^*$ , and  $y$  is given by

$$y^* = y(l^*) \exp(-2l^*) \approx y_0 \exp(-\pi T l^*/J_\infty). \quad (11)$$

Expressing  $\exp l^*$  in terms of  $f$  from (3), and  $K$  in terms of  $J$ , we get

$$y^* \approx y_0 / f^{\pi T(1+\alpha/2)J_\infty^{-1}}, \quad (12)$$

$$J^*/T = (J_\infty/T) [1 - \text{const}(J_\infty/T) f^{-(2+\alpha)(\pi T/J_\infty^{-2})}]. \quad (13)$$

All the calculated constants in (12) and (13), and also in the equations pertaining to  $T = T_R$  (see below), are not universal, are of the order of unity, and are independent of the film thickness.

For  $T = T_R$  the equation of the trajectory is

$$\tilde{y} = -K. \quad (14)$$

Substituting it in the first equation of (6), we get

$$\dot{\tilde{y}} = -\tilde{y}^2. \quad (15)$$

This yields an asymptotic law for the decrease of  $\tilde{y}$ :

$$\tilde{y}(l^*) \approx 1/l^* \approx 1/[(1+\alpha/2) \ln f]. \quad (16)$$

The measured value of  $y$  is given by the equation

$$y^* = y(l^*) \exp(-2l^*) \approx [(1+\alpha/2) f^{\alpha+2} \ln f]^{-1}. \quad (17)$$

Similarly, the measurable quantity  $J^*/T_R$  is described by

$$J/T_R = \frac{\pi}{2} \left( 1 - \frac{\text{const}}{(2+\alpha)\ln f} \right). \quad (18)$$

Summing all the foregoing, we write down now the result of the transformation of the nongradient terms of the Hamiltonian (1) at  $T \geq T_R$  in the most important case  $\alpha = 2$ :

$$V(f) = c \left( \frac{1}{f^2} - \frac{\text{const} \cos 2\pi f}{f^4 \ln f} \right) + pf \quad \text{for} \quad T = T_R, \quad (19)$$

$$V(f) = c \left( \frac{1}{f^2} - \frac{\text{const} \cos 2\pi f}{f^{2.2\pi T/J_\infty}} \right) + pf \quad \text{for} \quad T > T_R. \quad (20)$$

Strictly speaking, it would be necessary to add in (19) and (20) nonoscillatory terms of the form  $1/f^4 \ln f$  and  $1/f^{2(2\pi T/J_\infty - 2)}$  respectively, which appear as contributions to the free energy from the excluded degrees of freedom (terms of just this kind were the subject of Ref. 4). In our case they can be neglected compared with the oscillatory ones, inasmuch as when the equilibrium film thickness is determined the differentiation of the oscillatory term will always yield a lower degree of  $1/f$ , and consequently in the limit of large  $f$  the oscillatory term will be decisive.

Expressions (19) and (20) represent the effective free energy of a film of unit area, obtained by integrating over fluctuations of surface displacements whose wave vectors lie in the range from the wave vector  $k_0$  to  $k \propto (g_0/J_\infty)^{1/2}$ . The equilibrium position of the film is determined by differentiating (19) and (20) with respect to  $f$ . When the oscillatory term is differentiated, the contribution of principal order in  $1/f$  comes from differentiating  $\cos 2\pi f$ . It is seen from (19) and (20) that the farther we are from  $T_R$  the lower the extent to which the film "gives preference" to integer values of its thickness. It is also obvious that no jumplike changes whatever occur in the thickness at  $T \geq T_R$  and at  $f \gg 1$ , i.e., the curvature of the effective potential  $V''(f)$ , calculated at the minimum of (19) and (20), is positive. Recall that the presence of layering transitions at  $t < T_R$  is connected with the fact that the second derivative  $V''(f)$  of the free energy with respect to thickness could reverse sign, and the critical points of the layering transitions were obtained from the condition  $V''(f) = 0$  (Ref. 1).

Attention is called to the remarkable fact that the temperature enters in the exponent of (20). It follows hence that all the quantities obtained from the free energy by differentiating with respect to temperature, such as the heat capacity, are also oscillating and slowly decreasing functions of the film thickness.

2. We discuss now the experimental situation, and also the possibility of verifying all the effects predicted by us. These include the dependence of the effective rigidity of the film on thickness and temperature [(13) and (18)] and all possible oscillatory dependences that follow from (19) and (20). The solution of the first problem is apparently quite realistic. The surface rigidity can be measured, for example, by determining the correlation function of the surface fluctuation, a function that determines the intensity of light scattering by a surface or, in the case of solid  $^4\text{He}$ , by investigating the spectrum of the crystallization waves (see below). In addition, it can be assumed that the quantities  $J_\infty/T$  contained in (13) and also in (20) are known from investigations of the roughening transition on the surface separating the bulk phases of  $^4\text{He}$  (Ref. 5).

The most attractive for a check on the oscillatory dependences is measurement of the heat capacity of the film as a function of thickness and temperature. In Ref. 6 was measured the heat capacity of from 2 to 13 argon layers adsorbed on graphite, in the temperature range from 60 to 90 K. In particular, one of the most interesting results is observation of a weak anomaly of the heat capacity near  $T_R$ . The authors of Ref. 6 state that they have observed a number of properties that depend on the film thickness and particularly pronounced for thinner films, but the dependence on the thickness can be separated from the alternating-sign variation of the measured quantities. It is not clear from their statement where the thickness dependence is observed—in the entire range of temperatures or only below  $T_R$ , and whether the heat capacity oscillates. Our estimate shows that the observation of the heat-capacity oscillations in an atomic period under conditions corresponding to Ref. 6 are practically within the limits of the experimental error of the heat capacity.

For  $^4\text{He}$  films, on the other hand, observation of heat-capacity oscillations is quite feasible. The main reason is that the temperatures of the roughening transitions of various faces of solid  $^4\text{He}$  are lower than the superconducting-transition temperature: for the (0001) face, according to the latest experimental data,<sup>7</sup> we have  $T_R = (1.28 \pm 0.01)$  K, and for other faces  $T_R$  is even lower.<sup>5</sup> Under such conditions the heat capacity can be measured with much higher accuracy than in the experiment of Ref. 6. Thus, the most probable object with which our predictions can be verified is a film of solid  $^4\text{He}$  in contact with a superfluid liquid (the relevant estimates are given at the end of the article).

We turn now to experiments on films of solid  $^4\text{He}$  adsorbed on graphite.<sup>8,9</sup> Layering phase transitions were first observed in Ref. 8, and the theoretical predictions [1] concerning the  $T_{c,n}(n)$  dependence were qualitatively confirmed in Ref. 9. The quantity actually measured in these studies was  $V''(f)$  taken at the minimum of  $V(f)$  (more accurately, its inverse). As follows from (20),

$$V''(f) \propto \left( \frac{1}{f^4} + \frac{\text{const} \cos 2\pi f}{f^{2.2\pi T/J_\infty}} \right). \quad (21)$$

As already stated above, for  $f \gg 1$  the only oscillatory factor need be differentiated. For  $T = T_R$  the denominator of the second term is equal to  $f^4 \ln f$ . It is clear now that near  $T_R$  the second term of (21) is practically of the same order as the first, and oscillatory phenomena should be observed. The results of Ref. 8 confirm this prediction qualitatively. Indeed, an oscillator  $V''(f)$  dependence was observed in the temperature range from  $T_R \approx 1.28$  K to a temperature 1.7 K. The oscillations became weaker with increase of temperature. We call attention to the following interesting fact: were it possible to perform an experiment in which the measured quantity were a higher derivative of  $V(f)$  (starting with the third), there would always exist a temperature range in which the Van der Waals terms could be neglected compared with the oscillatory ones.

3. Since we have concluded above that the most probable object in which our predictions can be verified is a solid  $^4\text{He}$  film in contact with a superfluid liquid, it would be of considerable interest to determine the spectrum of the melting-crystallization waves in the film compared with a surface between bulk phases. It will be shown below that the crystal-

lization-wave spectrum contains the quantity  $V''(f)$ , so that a study of the surface-oscillations spectrum is likewise capable of verifying our predictions.

The existence of melting-crystallization waves was first predicted in Ref. 2. They were observed experimentally in Ref. 10. These waves are unique for the interface between the solid and superfluid phases of  $^4\text{He}$  and can propagate at the usual acoustic frequencies<sup>10</sup> in view of the extremely rapid onset of equilibrium.

The dispersion relation of Ref. 2 was derived in fact under the assumption that the surface is atomically rough, i.e., only the gradient terms of the Hamiltonian (1) were used. The dispersion relation for surface oscillations in a film can be obtained, without repeating the calculations, by noting that the interaction between the film surface and the substrate stabilizes the surface (i.e., makes it smooth) and is analogous to the presence of a gravitational field. It follows hence that  $J_\infty k^2$  in the corresponding equation of Ref. 2 must be replaced by  $J^*(f)k^2 + V''$ .

The dispersion relation takes thus the form

$$\omega^2 = \frac{\rho_2}{(\rho_1 - \rho_2)^2} k [J^*(f)k^2 + V'']. \quad (22)$$

Here  $\rho_1$  and  $\rho_2$  are the densities of the solid and liquid phases, respectively. It is seen from the last equation that an investigation of the crystallization-wave spectrum provides a check on the effects predicted above. The damping coefficient is given as before by the equation from Ref. 2

$$\gamma = \rho_1 \rho_2 / 2m \Gamma (\rho_1 - \rho_2)^2. \quad (23)$$

Here  $m$  is the mass of the helium atom and  $\Gamma$  is the kinetic growth coefficient.<sup>2</sup> It is seen from (22) that, in contrast to the bulk case, long-wave surface oscillations in a film are similar to gravitational rather than capillary waves. The condition under which  $J^*(f)k^2$  can be neglected compared with the second (smaller) term of Eq. (21) is

$$ka \ll (a/f)^{n\tau/J_\infty a^2}. \quad (24)$$

We have neglected here the  $J^*(f)$  dependence and have introduced for clarity the lattice period  $a$ . At  $T = T_R$  the exponent in (24) is equal to two, and an additional logarithmic factor  $1/\ln(f/a)$  is present.

In the range of wave vectors satisfying the condition (24), the dispersion law is

$$\omega^2 = \frac{\rho_2}{(\rho_1 - \rho_2)^2} k V''. \quad (25)$$

Far from  $T_R$  a contribution to  $V''$  is made only by the Van der Waals term, and the condition for the applicability of (25) is given by (24) with an exponent 2.

Comparison with Eq. (23) shows that the long-wave oscillations (25) are always weakly damped. For melting-crystallization waves propagating between bulk phases, the situation is reversed. This is seen from the fact that for these waves  $\omega \propto k^{3/2}$  and  $\gamma \propto k$ . Experiment has confirmed that melting-crystallization waves are overdamped at  $T > 1$  K.<sup>11</sup>

Let us dwell, finally, on the low-temperature dependence of the surface-tension coefficient. Oscillations with a spectrum (25) are elementary excitations of the interface between a solid  $^4\text{He}$  film and a superfluid liquid. They lead to a temperature dependence of the surface tension (which, of

course, is not connected with the proximity to  $T_R$ ). Proceeding in analogy with Ref. 2, we find that the contribution to the surface tension from the surface oscillations (25) takes in the low-temperature limit the form  $T^5/V''^2$ .

We find now the temperature region in which the  $T^{7/2}$  dependence<sup>2</sup> should go over into  $T^5/V''^2$ . To this end it is necessary to compare the temperature with the energies of the elementary excitations corresponding to the first and second terms of Eq. (22). The temperature  $T^*$  at which they become of the same order is in fact the boundary between the  $T^{7/3}$  and  $T^5/V''^2$  dependences. This yields

$$T^* \sim \frac{\hbar \rho_2^{3/2}}{k_B (\rho_1 - \rho_2)} \left( \frac{V''^3}{J_\infty} \right)^{1/4}.$$

Here  $k_B$  is the Boltzmann constant. Let us calculate  $T^*$  for a film whose surface coincides with the (0001) phase and whose thickness is 20 Å (approximately 7 atomic layers). Just such films were investigated in Refs. 8 and 9. The value of the coefficient  $c$  can be expressed in terms of the Van der Waals forces constant  $\delta$  using the equation

$$c = \frac{1}{2} \frac{(\rho_1 - \rho_2)}{m} \delta.$$

The value of  $\delta$  for helium adsorbed on graphite, according to the data of Refs. 12 and 1, lies in the range  $\delta = (2.0 - 4.3) 10^{-37}$  erg·cm<sup>3</sup>. At  $\delta = 3 \cdot 10^{-37}$  erg·cm<sup>3</sup>,  $\rho_1 = 0.191$  g/cm<sup>3</sup>,  $\rho_2 = 0.173$  g/cm<sup>3</sup> (Ref. 14), and  $m = 6.6 \cdot 10^{-24}$  g we have  $c = 5 \cdot 10^{-16}$  erg. Substituting the characteristic value  $J_\infty \sim 0.24$  erg·cm<sup>2</sup> (Ref. 5) we get

$$T^* \sim 0.3 - 0.4 \text{ K}.$$

Recall that our results are valid at temperatures higher than the roughening-transition temperature, but lower than the temperature for transition to the normal liquid. For the (0001) face, the corresponding interval is 1.28–1.77 K. The value of  $T^*$  is to the left of this interval, so that the dependence predicted by the authors of Ref. 2 should be observed. One can hope to observe the  $T^5/V''^2$  dependence on films having  $T_R$  lower than 0.3 K. Note that rough surfaces of solid helium were observed when the temperature was lowered down to 0.07 K (see the literature cited in Ref. 5), so that observation of the  $T^5/V''^2$  is in no way a hopeless task.

Since we are dealing with a solid-helium film, we might ask whether we can use for it the expressions (19) and (20) calculated by the classical theory. The role of the quantum effects can be estimated by the procedure of Ref. 15. To this end we replace the classical expression for the square of the fluctuation of the film position about its mean position by its quantum variant

$$\langle \delta f_k^2 \rangle = \frac{T}{Jk^2 + V''} \frac{\hbar \omega(k)}{2T} \text{cth} \frac{\hbar \omega(k)}{2T}.$$

The condition under which the quantum contribution becomes of the order of the classical is the one that determines the limit of applicability of the classical equations (19) and (20). It is readily understood that the corresponding temperature is none other than  $T^*$ , which we have calculated above. Consequently, for a film 20 Å thick the quantum effects come into play below a temperature 0.4 K. The dependence calculated in the classical approximation should be

valid in the region 1.28–1.7 K of interest to us. Note that if the film thickness is increased tenfold, the corresponding temperature  $T^*$  becomes 1000 times lower.

We consider now the possibility of measuring the heat-capacity oscillations on a solid helium film. To this end we must compare the background part of the heat capacity with the amplitude of its oscillatory part. For a film 20 Å thick in the temperature range 1.28–1.7 K, as shown by the preceding estimates, the background part of the heat capacity is given by

$$C_b = 0,4 \frac{T^{4/3}}{\hbar^{4/3}} \left( \frac{(\rho_1 - \rho_2)^2}{J\rho_2} \right)^{3/2},$$

which follows from the results of Ref. 1. To find the amplitude of the oscillating part of the heat capacity we must write down the actual expressions for the numerical constants in Eqs. (19) and (20). This task can be performed without invoking renormalization-group equations. We express the Hamiltonian (1) in the form

$$H = \int d^2x \left( \frac{J}{2} [(\nabla \delta f)^2 + \xi^{-2} \delta f^2] - y \cos \frac{2\pi}{a} f \cos \frac{2\pi}{a} \delta f \right). \quad (26)$$

The smooth part of the potential has been expanded here about its minimum,  $\delta f$  denotes the deviation from the central position  $f$ , and the sine term is omitted, since it averages out to zero. Integration over the degrees of freedom corresponding to  $\delta f$  reduces to averaging of the cosine term with the aid of the first harmonic term of the Hamiltonian (26) (we, naturally, regard the oscillating term as a small perturbation compared with the harmonic part of (26)). As a result, the oscillatory increment to the free energy of the film takes the form

$$\delta V = -y \left( \frac{Jk_0^{-2}}{6c} \right)^{-\pi T/2Ja^2} \frac{\cos(2\pi f/a)}{(fk_0)^{2\pi T/Ja^2}}.$$

Note that we have obtained a formula that is correct for  $T \gg T_R$  (apart from logarithmic corrections at  $T = T_R$  and replacement of  $J$  by  $J_\infty$ ). The averaging is classical theory, and allowance for the quantum effects leads to an additional decrease of the common factor in the last equation. This fact will be taken into account below, since the experimental coefficient  $y$  will be used. It is seen from the last equation that the amplitude of the oscillating part of the heat capacity is given by

$$C_{osc} = Ty \left( \frac{2\pi}{Ja^2} \ln u \right)^2 \frac{1}{u^{2\pi T/Ja^2}}, \quad u = \left( \frac{Jk_0^{-2}}{6c} \right)^{1/4} fk_0.$$

To find the experimental value of  $y$  we use the results of Ref. 7. In the bulk case there are two independent quantities: the perturbation-theory parameter  $t_c = 1.26\pi^2 y k_0^{-2} / Ja^2$  and  $k_0$ . Their experimental values are  $t_c = 0.65$  and  $k_0^{-1} = 26$  Å, hence  $y = 0.014$  erg/cm<sup>2</sup>. Comparing  $C_b$  with  $C_{osc}$  at  $T = 1.3$  K we find that for a film 20 Å thick these contributions are comparable (on the order of  $10^{13}$  cm<sup>-2</sup>). It is seen from the foregoing estimate heat-capacity oscillations can be observed on a helium film. Note that measurement of the heat capacity of helium monatomic films adsorbed on graphite is quite feasible.<sup>16</sup> One can hardly expect thick films, for which the results of the present paper are valid, to create more experimental difficulties than monatomic films.

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