

# Phase transition of a triple line; shape of the drops of a nonwetting liquid

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(Submitted 30 December 1987)

Pis'ma Zh. Eksp. Teor. Fiz. **47**, No. 5, 254–256 (10 March 1988)

An edge line separating liquid, gas, and crystalline solid phases is shown to undergo a phase transition from a rough state into a smooth state.

Despite the indisputable practical importance of wetting phenomena and despite the nearly two centuries of research on these phenomena, many questions in this field seem to have received little attention (see, for example, the review by de Gennes<sup>1</sup>).

We wish to examine one of these phenomena in the present letter. We will show that a triple line separating regions of liquid, gas, and crystalline solid phases may, as the temperature is raised, undergo a phase transition from a localized (smooth) state to a delocalized (rough) state. Macroscopically, these two states will be distinguished by the respective presence or absence of a hysteresis in the edge angles (see Ref. 1 regarding the determination of the hysteresis) and by a “faceting” of the perimeter of a drop.

Let us consider a triple line separating solid, liquid, and gas phases. We denote by  $\gamma_{SV}$ ,  $\gamma_{SL}$ , and  $\gamma$  the surface-tension coefficients of the solid-gas, solid-liquid, and gas-liquid interfaces, respectively. These coefficients are related to the edge angle  $\theta$  by Young's law<sup>1</sup>:

$$\gamma \cos \theta = \gamma_{SV} - \gamma_{SL} \quad (1)$$

We denote by  $f$  the displacement of the triple line from some position. The elastic energy associated with such distortions is expressed in terms of the Fourier components of the displacements,  $f(k)$ , by<sup>1,2</sup>

$$H = \frac{1}{4} \gamma \sin^2 \theta L \sum_k |k| |f(k)|^2, \quad (2)$$

where  $L$  is the length of the line. The unusual dependence on the wave number  $k$  is the reason for the phenomena listed above. There is a simple explanation for the linearity in the wave number<sup>1</sup>: When a line with a wave number  $k$  is distorted, the liquid-gas interface is perturbed over a distance on the order of  $1/k$ . The ordinary capillary energy, proportional to  $k^2$ , must therefore be multiplied by the size of the region in which this energy is concentrated. Let us calculate the mean square fluctuation of a line, using the expression<sup>2</sup>

$$\langle f^2 \rangle = \frac{2T}{\gamma \sin^2 \theta} \int \frac{dk}{2\pi} \frac{1}{|k|} \sim \frac{T}{\gamma \sin^2 \theta} \ln L,$$

where  $T$  is the temperature, and we have set the microscopic length scale along the line equal to unity. The logarithmic divergence of the mean square is interesting. Precisely the same situation arises for a surface separating bulk phases, e.g., a crystal-liquid interface. We know (see, for example, Ref. 3 and the bibliography there) that incorporating the discrete nature of a crystal leads to a roughness phase transition in this case. Let us assume that the triple line lies at the surface of a crystal. We first consider a one-dimensional periodicity perpendicular to the line. Instead of (2) we would then have to study the Hamiltonian

$$H = \frac{1}{4} \gamma \sin^2 \theta L \sum_k |k| |f(k)|^2 - y \int dx \cos \frac{2\pi}{a} f. \quad (3)$$

Here  $y$  is a measure of the amplitude of the crystallographic relief with a period  $a$ . The renormalization of Hamiltonian (3) is standard.<sup>3</sup> In first order in  $y$  we have

$$\frac{dy}{dl} = \left( 1 - \frac{4\pi T}{a^2 \gamma \sin^2 \theta} \right) y, \quad (4)$$

where  $l$  is an ordinary renormalization parameter. There is no renormalization of  $\gamma \sin^2 \theta$  (i.e., its temperature dependence due to the proximity to the transition point) in any order in  $y$ . The reason is that a periodic analytic perturbation cannot lead to a renormalization of a nonanalytic term  $|k| |f(k)|^2$ . We need go no higher than second order in  $y$  to find contributions of the type  $k^2 |f(k)|^2$ , as well as higher harmonics. They can be ignored, however, since the corresponding renormalization-group eigenvalues of such perturbations are negative on the fixed line corresponding to Hamiltonian (2).

If the factor in parentheses in (4) is negative, the periodic relief will be unimportant, and the line will be rough. If, on the other hand, this factor changes sign, the surface will localize, and  $\langle f^2 \rangle$  will become finite at  $L \rightarrow \infty$ . The transition point corresponds to the expression

$$T_c = \frac{\gamma a^2 \sin^2 \theta}{4\pi}.$$

If we are just slightly below  $T_c$ , the expression describing the growth of  $y$  determines the dependence of the correlation length  $\xi$  on the reduced temperature  $t = (T - T_c)/T_c$ . From (4) we find

$$\xi \sim \exp(\text{const} / |t|).$$

It can be shown that the corresponding contribution to the free energy is proportional to  $\xi^{-1}$ . Since the second term in Hamiltonian (3) is essentially a periodic variation imposed on the right side of Young's law (1), the hysteresis of the edge angles vanishes as  $\xi^{-1}$  as  $T_c$  is approached from below. As in the case of a roughness transition,<sup>3</sup> the coefficient of the logarithm in the correlation function of the fluctuations of the line,  $\langle (f(x) - f(0))^2 \rangle$ , is universal at the transition point, having the value  $a^2/\pi^2$ .

Up to this point we have been talking about a one-dimensional periodicity of a

crystalline potential. We now move on to the properties of a macroscopic drop of a nonwetting liquid. The orientation dependence is contained in the second term in Hamiltonian (3). Each "crystallographic" orientation of the triple line corresponds to a particular distance between the minima of the periodic relief and thus a particular transition temperature; above this temperature, the periodicity in the given direction becomes inconsequential. At the same time, it is substantial for other directions with large values of  $a$ . If the temperature is zero (and in this case we would have to be talking about a drop of superfluid helium), the entire perimeter of the drop will be "faceted." Indeed, for any part of a line which does not have a "crystallographic" orientation there will always exist some arbitrarily close "crystallographic" direction which has a lower energy (3). At some temperature, which differs from zero by an arbitrary amount, rounded regions will appear in the faceting of the perimeter of the drop. As the temperature is raised, these rounded regions will cover a greater relative area, and at some temperature corresponding to the fundamental period, or to one of several fundamental periods, the last smooth regions will disappear.

Quantum effects can also be taken into account by the approach of Ref. 4. It turns out that all the results described above remain the same, except that the region with a critical behavior contracts—to a progressively greater extent as the temperature is lowered. At absolute zero, the perimeter is completely faceted.

Our conclusions remain in force if there are no defects in the system. In the opposite case, a triple line is always rough.<sup>1,2</sup>

Liquid helium is a natural candidate as a system for testing the effects described above.

There are several other interesting questions: How does the curvature disappear (continuously or abruptly)? How does the size of a smooth region depend on the proximity to the transition point? How do smooth and rounded regions join together?

I wish to thank A.P. Levanyuk, S. A. Minyukov, A. A. Sorokin, and E. M. Terent'ev for useful discussions.

<sup>1</sup>P. G. de Gennes *Usp. Fiz. Nauk* **151**, 619 (1987) [*Sov. Phys. Usp.* **30**, *Rev. Mod. Phys.* **57**, 827–863 (July 1985)].

<sup>2</sup>M. O. Robbins and J. F. Joanny, *Europhys. Lett.* **3**(6), 729 (1987).

<sup>3</sup>P. Nozieres and F. Gallet, *J. Phys. (Paris)* **48**, 353 (1987).

<sup>4</sup>D. S. Fisher and J. D. Weeks, *Phys. Rev. Lett.* **50**, 1077 (1983).

Translated by Dave Parsons