Thermal fluctuations of an atomically smooth crystal surface

E. B. Kolomeĭskiĭ

A. V. Shubnikov Institute of Crystallography, USSR Academy of Sciences, Moscow

(Submitted 19 December 1990)
Zh. Eksp. Teor. Fiz. **99**, 1640–1643 (May 1991)

The contribution of fluctuation-induced nucleation centers (projections and depressions on the atomically smooth interface) to the correlation functions of the surface displacements is considered. It is shown that for the surface of a three-dimensional crystal the excitations should lead to a spatial correlation function which differs from the Ornstein–Zernike one, as in the case of the two-dimensional Ising model. Due to a large lifetime, they may also determine the equilibrium dynamics of an atomically smooth surface, bringing about a nonexponential decrease of the temporal correlations. For the surface of a three-dimensional crystal the corresponding autocorrelation function for long times t is proportional to $\exp(-\mathrm{const}\cdot t^{1/2})$.

Recently the number of papers dealing both with the experimental and theoretical study of the phase transition between an atomically smooth state of a crystal surface and a rough one has substantially increased (see, e.g., Ref. 1 and references therein). Though it seems untimely to speak about a full agreement between the theory and experimental data, the existence of qualitatively different states of a crystal surface and of a phase transition between them does not raise any doubts. The properties of the rough phase are well understood and do not differ, in their essence, from those of a liquid-gas interface. As to the atomically smooth state, the situation is less definite.

The present work aims at the study of the contribution of fluctuation-induced nucleation centers (projections and depressions on an atomically smooth crystal surface) to the correlation functions of interface displacements. The idea of a dominating role of the fluctuations of this type is related to the following facts: first, such excitations exist only in the smooth phase (in the rough phase the step energy equals zero); second, as is well known,[1] the crystal growth under small supersaturations occurs via formation and propagation of two-dimensional nucleation centers; third and last, the excitations of this sort (domains of opposite sign) may determine the character of spin-spin correlations in the ordered phase of the Ising model.[2,3] The main idea of the subsequent discussion is borrowed from Ref. 3, where the authors have also pointed at a potential importance of fluctuations of this sort in any system with spontaneously broken discrete symmetry.

Let us consider a d-dimensional crystal at temperature lower than the temperature of transition to the atomically smooth state: $T < T_R$. To be definite, let us assume that the mean position of the crystal surface $\langle f \rangle = 0$ coincides with the origin. The angle brackets here and below, as always for the ordered phase, correspond to thermodynamic averaging with a chosen position of the interface. Let us consider two sites i and j on a $(d-1)$-dimensional crystal surface and belonging to a fluctuation-induced nucleation center. In the cases treated below the probability p of formation of a nucleation center is small, therefore one can neglect the interaction with other nucleation centers. When the nucleation center is formed, the positions of two surface points are shifted simultaneously. Therefore the corresponding fluctuation makes a contribution proportional to $p(1-p) \approx p$ to the equal-time correlation function

$$G_{ij} = \langle f_i f_j \rangle \tag{1}$$

between surface displacements at sites i and j belonging to the nucleation center. The fluctuation nucleation center also brings about a contribution proportional to $p(1-p)$ to the temporal autocorrelation function

$$C_i(t) = \langle f_i(0) f_i(t) \rangle \tag{2}$$

for surface positions i inside the nucleation center. The time dependence of this contribution is governed by the dynamics of the "collapse" of the nucleation center.

Let us consider first the spatial correlations and find out when one should expect deviations from the Ornstein–Zernike law[4]

$$G_{ij} \propto \exp(-r_{ij}/\xi)/r_{ij}^{(d-2)/2}, \tag{3}$$

where r_{ij} is the distance between the sites i and j, ξ is the correlation length (the characteristic step width), and $r_{ij} \gg \xi$. The maximum contribution to G_{ij} made by the fluctuation nucleation centers is proportional to the Boltzmann probability of the formation of a nucleation center of size r_{ij}. Its free energy is of order βr_{ij}^{d-2} (β is the specific step energy; below we consider, for simplicity, the isotropic case and neglect the angular dependence of β). Therefore

$$G_{ij} \propto \exp(-\mathrm{const}\,\beta r_{ij}^{d-2}/T). \tag{4}$$

The comparison of the last two formulas shows that the fluctuations of the type considered give rise to nonexponential correlations in the case of nonphysical space dimensions $2 < d < 3$; for $d > 3$ they are negligible (their probability is too small), and we have the dependence (3) brought about by the fluctuation inhomogeneities of dimension ξ; $d = 3$ is the upper critical dimensionality when the nucleation centers begin to govern the spatial correlations at large distances. It is quite natural to expect for $d = 3$ a nontrivial pre-exponential factor in (3) different from $r_{ij}^{-1/2}$ (as in the case of the two-dimensional Ising model[2,3]).

Unfortunately, in none of the exactly soluble models with a transition from the rough phase to the smooth one could the correlation function (1) be calculated for $T < T_R$ (see, e.g., Ref. 5 and references therein). At a first glance, this statement is at variance with the results of the renormalization-group analysis.[1] In fact, the latter predicts that the correlation function (1) for $r_{ij} \gg \xi$ exactly corresponds to the Ornstein–Zernike law (3). This conclusion follows from the Fourier transform

$$G(k)\propto T\xi^2/[1+(k\xi)^2]$$

calculated to the lowest order in $k\xi \ll 1$ (k is the wave vector). If we assume that the correct dependence has the form

$$G(k)\propto T\xi^2/[1+(k\xi)^2]^{\alpha} \quad (\alpha>0),$$

then, in the limit $k\xi \ll 1$, we return to the renormalization-group result

$$G(k)\propto T\xi^2/[1+\alpha(k\xi)^2].$$

The contradiction is thus removed.

Let us show now that the fluctuations concerned manifest themselves much stronger in the dynamics. As shown in Ref. 3, they determine the dynamics only in the absence of conservation laws. Therefore we discuss only a purely relaxational case.

The nucleation center containing the site i contributes to the autocorrelation function $C_i(t)$ at a time t if its lifetime is not smaller than t. The driving force of the "collapse" of a nucleation center of radius $r \gg \xi$ is the Laplace pressure β/r (see Ref. 6), therefore the equation of motion of its rear step has the form

$$\frac{dr}{dt}=-\frac{\mu\beta}{r}$$

where μ is the step mobility. Hence the lifetime of a nucleation center of initial radius r is of order $r^2/\mu\beta$, and therefore the minimum size of the nucleation center, which contributes to $C_i(t)$, is of order $(\mu\beta t)^{1/2}$. The free energy of the nucleation center of radius r is of order βr^{d-2}, therefore the greatest Boltzmann probability, contributing to $C_i(t)$, is proportional to $\exp[-(t/\tau)^{d-2/2}]$, where

$$\tau\approx T^{2/(d-2)}/\mu\beta^{d/(d-2)}$$

is the correlation time, which diverges as $T\to T_R$ (one can make sure of this by comparison with the results of the critical dynamics study[1]). Thus,

$$C_i(t)\propto \exp[-(t/\tau)^{(d-2)/2}]. \qquad (5)$$

It follows from the last relation that the nucleation centers give rise to nonexponential correlations for $2<d<4$; for $d>4$ they are negligible, and the ordinary exponential relaxation occurs. The dimensionality $d=4$ is the upper critical one, when fluctuations of the given type begin to determine the autocorrelations at long times. In this case a nontrivial preexponential factor in (5) is to be expected. In the most important case of $d=3$ we find from the last relation

$$C_i(t)\propto \exp(-\mathrm{const}\cdot t^{1/2}).$$

One may hope that the dependences found above can be observed in light-scattering experiments or in atomic-beam diffraction,[5] when the Fourier-transforms of the correlation functions (1) and (2) are measured directly.

I am grateful to A. P. Levanyuk for useful discussions.

[1] P. Nozieres and F. Gallet, J. de Phys. **48**, 353 (1987).
[2] D. B. Abragam, Phys. Rev. Lett. **50**, 291 (1983).
[3] D. A. Huse and D. S. Fisher, Phys, Rev. B **35**, 6841 (1987).
[4] L. D. Landau and E. M. Lifshitz, *Statistical Physics*, part 1, Pergamon, 1980.
[5] J. Villain, D. R. Grempel, and J. Lapujoulade, J. Phys. F: Met. Phys. **15**, 809 (1985).
[6] M. Uwaha and P. Nozieres, J. de Phys. **48**, 407 (1987).

Translated by E. Khmelnitski