One-dimensional phase transition and epitaxy

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The kinetics of a one-dimensional phase transition and the average thickness of the layer of an unstable phase at a boundary promoting the formation of this phase are studied as functions of the deviation from equilibrium.

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In this letter is it shown that in a one-dimensional system, under certain boundary conditions, a layer (more precisely, a filament) of an unstable phase forms near a boundary at which the condition for the existence of this one unstable phase is rigidly imposed. The average thickness (or length) of this layer (or filament) increases toward the transition point in proportion to $(\alpha_t - \alpha)^{-1}$, where α is the order parameter, and α_t is the value of this parameter corresponding to the equilibrium transition.

We consider a model of molecules arranged in a straight line at a uniform spacing δ; with n as the index of the particular site, the coordinate is $x = n\delta$. Each molecule can be in one of two states: A or B.

The probability for the conversion $A \rightarrow B$ for a molecule A which is at the end of a chain, i.e., which has (for example) a neighbor A to its left and a neighbor B to its right, is denoted by $w\alpha$. The probability for the inverse conversion, $B \rightarrow A$, for the boundary molecule B^* in the chain $AAAB^*BB$ is denoted by $w(1 - \alpha)$. We find the following equation for the probability $p(x,t)$ for the boundary between B and A to be at the point x:

$$\frac{\partial p}{\partial t} = -u\frac{\partial p}{\partial x} + D\frac{\partial^2 p}{\partial x^2}, \quad u = w(1 - 2\alpha); \; D = w\delta^2. \tag{1}$$

We consider the problem of the transition on an infinite line with an initial condition A^* at the origin of coordinates; i.e., we have exclusively A at $x \leqslant 0$ and exclusively B at $x > 0$. For p this situation means $p(x,0) = \delta(x)$.

It is a trivial matter to solve the equation for p:

$$p = \frac{1}{\sqrt{2\pi D t}} \exp\left[-(x - ut)^2/4Dt\right]. \tag{2}$$

This result means that the average position of the boundary, $\bar{x}$, moves at a velocity u, and fluctuations in the position of the boundary, with a magnitude on the order of $\sqrt{Dt}$, arise simultaneously. The direction of the motion depends on the sign of $(1 - 2\alpha)$, so that $\alpha = \alpha_t = 1/2$ is a critical value.

Why has this kinetic analysis led us to a complete transition $B \rightarrow A$ at $\alpha < 1/2$ and, correspondingly, a complete transition $A \rightarrow B$ at $\alpha > 1/2$, i.e., a sharp phase transition, in contradiction of the well-known theorem on the properties of one-dimensional sys-

tems? The answer is that we have ignored the possible appearance of an isolated molecule in one state flanked on both sides by molecules in the other state, e.g., ...*AABAA*... in a chain ...*AAAAA*.... . A fluctuation of this sort in an infinitely long chain ...*AAA*... can then, with a certain probability, give us a *B* "island" of infinite size inside the *A* phase. It is thus the spontaneous appearance of a nucleus of the *B* phase inside a solid *A* phase (and the inverse process) which causes a state at thermodynamic equilibrium, regardless of the value of α, to have certain *A* and *B* fractions which are neither 0 nor 1. These fractions change continuously as α crosses its critical value α_t.

The nucleation of *B* within *A* described above is, however, a "difficult" process. In a normal situation we could speak in terms of a contact point energy $\Delta = 2E(AB) - E(AA) - E(BB)/2$, as a one-dimensional analog of surface tension in the three-dimensional case.

The formation of an isolated molecule *B* inside a solid *A* chain requires an energy 2Δ in addition to that required for the conversion of *A* into *B* at the edge of the chain. For this reason, fluctuations which begin with the formation of isolated nuclei of the new phase are far rarer than the conversions $A \rightleftarrows B$ at an existing boundary between two phases. Here we have a "smallness parameter"

$$\nu = \exp\left(-\Delta / kT\right).$$

The transition is effectively blurred, but over only a narrow interval.

At equilibrium ($\alpha = 0.5$), the regions into which an infinite chain decomposes each contain, on the average, ν^{-1} molecules of each phase.

If we replace the problem of an infinite sequence of *A*, *B* molecules by the problem of a finite number (N) of molecules, then the transition ceases to be sharp even in the limit $\nu \to 0$. Fifty years ago, Sorokin and the present author[1] pointed out that a sharp phase transition occurs only in the limit $N \to \infty$, and the dimensionality of the space does not modify this conclusion. In the one-dimensional problem with a finite N there are two quite different situations: 1) $N > \nu^{-1}$, in which case the situation is similar to an infinite sequence; 2) $N < \nu^{-1}$. In this second situation the most probable case is that in which the entire set of molecules consists of a single phase, regardless of the value of α.

A realistic, observable situation arises when we consider epitaxy, i.e., the events which occur on a line segment bounded by another substance. Let us assume $\alpha > 0.5$, i.e., that the equilibrium sequence is *BBB*..., but at the origin of coordinates we put a wall which holds the molecule in state *A* in a determinate manner.

Let us find the steady-state solution $P(x)$ with $\alpha > 0.5$ which arises, working in the approximation of the first part of this study, i.e., without ν-phase nuclei ($\nu = 0$):

$$P(x, t \to \infty) = \frac{u}{D} \exp\left(-ux/D\right) = \text{const} \exp\left[-x\left(\alpha - 0, 5\right)/2\delta\right].$$

Although we are considering only the interaction between neighbors, the average distance over which the wall makes its presence known is large. The quantity $\bar{x}$ increases in inverse proportion to the deviation of α from its critical value $\alpha_t = 0.5$.

The A layer which results from the presence of the wall is large, but so are its fluctuations, $\overline{(x - \bar{x})^2} \sim (\bar{x})^2$.

This solution is meaningful only as long as $\bar{x} < \delta v^{-1}$, i.e., only as long as we can ignore the appearance of isolated fluctuations. The question of the depth to which surface effects extend in a phase transition has been taken up previously. Kaganov[2] studied the problem involving a minimization of the free energy $u(\phi)$. He introduced a term proportional to the square of the gradient, $S(\nabla\phi)^2$, in connection with magnetic problems. A first-order phase transition corresponds to the simple model

$$u = \frac{A}{4}(\phi^2 - \phi_0^2)^2 - \gamma\phi.$$

There are two states, $\phi = \pm\phi_0$, of which (under the condition $\gamma > 0$) $\phi = +\phi_0$ is stable and $\phi = -\phi_0$ is metastable.

A variation of the free energy gives us the following equation in the steady state:

$$S\frac{d^2\phi}{dx^2} = -A\phi(\phi^2 - \phi_0^2) + \gamma.$$

With $\gamma = 0$ this equation has a well-known solution which describes the boundary between coexisting phases at equilibrium:

$$\phi = \phi_0 \operatorname{th}(x\sqrt{A/S}).$$

We set $\phi = -\phi_0$ at $x = 0$ with $\gamma > 0$; i.e., $\phi = \phi_0$ is stable, so that at the boundary we have specified an unstable (metastable) state. Solving the equation under these boundary conditions, we find that the thickness of the metastable layer is determined by an integral of the type $(\phi + \phi_0 = -\psi)$

$$x = \int_0^{\phi_0} \frac{\sqrt{S}\,d\psi}{\sqrt{2\gamma\phi_0 + A\phi_0^2\psi^2}} \cong x_0 \ln b,$$

where $x_0 = \sqrt{S/A}$ and $b = \sqrt{A\phi_0^3/\gamma}$.

As we approach equilibrium, i.e., at a small value of γ, the thickness of the layer of nonequilibrium phase thus increases only logarithmically as $\gamma \to 0$—more slowly than in the case discussed above. Chernov[3] has evaluated the possible thickness of the nonequilibrium layer on the basis of energy considerations. The expenditure of (free) energy on the creation of the layer is proportional to the layer thickness $\bar{x}$ and to the deviation from equilibrium, γ or $(\alpha - \alpha_t)$. The interaction of a solid surface leads to the formation of metastable phase, accompanied by the evolution of a certain amount of energy E, which does not depend on the deviation from equilibrium. Equating the two energies, we find

$$\gamma x = E.$$

These simple arguments thus lead to the same result which was found above, $x \sim \gamma^{-1} \sim (\alpha - \alpha_t)^{-1}$.

We note, however, that arguments based on energy considerations are not always correct. If we increase the energy E we first increase the probability for the surface to be covered with an A layer, but at $E > kT$ (per molecule) saturation sets in, and a further increase does not increase the average thickness of the layer.

It would be more accurate to assert that the orientation of the molecules in the surface layer gives us an amount of "information" no greater than one bit per molecule; i.e., there is a decrease in entropy. The subsequent orientation of the following layers is caused not by the energy but by the entropy of the first layer. The two- and three-dimensional problems are vastly more complicated[4,5] and beyond the scope of this letter.

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