Physics of surfaces and interfaces

5. Thermodynamic aspects of physics of surfaces and interfaces

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Outline of current lecture

- Introduction
- Equilibrium shape of crystals and Wulff theorem
- Phase transition from atomically flat terraces into a state with rough surface
- Phase separation in binary alloys. Ising model
- Wetting, Young formula and regimes of growth of solid-state nanostructures

Introduction

Simple and constrained optimization problems (1)

1. Finding the extrema for a function of two variables without additional conditions

$$F(x, y) \to min/max$$

Solution

$$\frac{\partial F}{\partial x} = 0 \quad \text{and} \quad \frac{\partial F}{\partial y} = 0.$$

2. Determination of extrema for a function of two variables with additional conditions

$$F(x, y) \to min/max \quad \text{provided that} \quad \varphi(x, y) = 0.$$

Solution of the constrained problem by method of Lagrange multipliers: we introduce an auxiliary function

$$G(x, y, \lambda) = F(x, y) \pm \lambda \cdot \varphi(x, y),$$

where λ is a constant, and then test it for extremal values

$$\frac{\partial G}{\partial x} = 0, \quad \frac{\partial G}{\partial y} = 0 \quad \text{and} \quad \frac{\partial G}{\partial \lambda} = 0.$$

Simple and constrained optimization (2)

Problem: There is a rectangle of length a and width b. Assume that the perimeter of this rectangle $P = 2(a + b)$ is fixed. At what ratio a/b the area of this rectangle $S = a \cdot b$ is maximal?

Solution:

The constrain function is $\varphi(a, b) = 2a + 2b - P$.

We introduce an auxiliary function

$$G = S - \lambda \cdot \varphi(a, b) = a \cdot b - \lambda \cdot (2a + 2b - P).$$

The criteria of the unconditioned extremum of three-parameter function G are

$$\frac{\partial G}{\partial a} = b - 2\lambda = 0, \quad \frac{\partial G}{\partial b} = a - 2\lambda = 0 \quad \text{and} \quad \frac{\partial G}{\partial \lambda} = 2a + 2b - P = 0.$$

The first and second equalities gives

$$a = b = 2\lambda,$$

therefore, the rectangle of the maximal area should be a square. From the last equation we get

$$a = b = \frac{P}{4}.$$

Thermodynamic potential (internal) energy (1)

According to the first law of thermodynamics, the differential of internal energy dU for a system with non-fixed number of particles can be written as follows

$$dU = dQ - dA + \mu dN = T\,dS - p\,dV + \mu\,dN,$$

where dQ denotes the quantity of energy supplied to the system as heat, dA denotes the quantity of energy supplied to the system as mechanic work, T is absolute temperature, S is entropy, p is pressure, V is volume, μ is chemical potential, N is number of particle.

Natural variables for the internal energy are S, V и N. It means that dU is zero for closed system (zero heat transfer) at fixed volume (zero work) and number of particles (zero mass flow).

Total internal energy can be written in the following form

$$U = TS - pV + \mu N.$$

Note: the chemical potential μ is equal to the energy that can be absorbed or released due to a change of the particle number by one in the system:

$$U\Big|_{S,V,N+1} - U\Big|_{S,V,N} = \mu(N+1) - \mu N = \mu.$$

Thermodynamic potential (internal) energy (2)

For system at fixed temperature it is convenient to introduce the Helmholtz free energy

$$F = U - TS$$

instead of the internal energy.

The differential of the free energy dF for a system with non-fixed number of particles can be written as follows

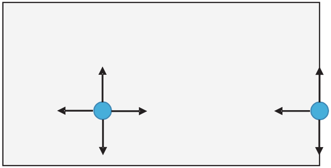
$$dF = d(U - TS) = TdS - pdV + \mu dN - SdT - TdS = -SdT - pdV + \mu dN.$$

Natural variables for the Helmholtz free energy are T, V и N. It means that $dF = 0$ for systems at constant temperature at fixed volume and number of particles, when $dT = 0$, $dV = 0$ and $dN = 0$.

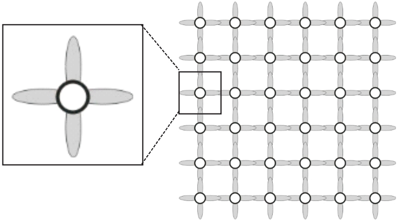
The term $(-TS)$ is sometimes referred to as entropic contribution and it reflects the tendency of open systems for increasing its entropy.

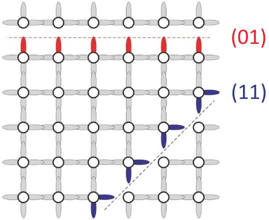
Surface tension

Isotropic system



Anisotropic system (crystal)





The differential of the internal/free energy

$$dU = \sigma\, dS \quad \text{and} \quad dF = \sigma\, dS,$$

where dS is the change in the surface between two phases. The parameter $\sigma > 0$ is called surface tension coefficient.

Part I

Equilibrium shape of crystals and Wulff theorem

Equilibrium shape of crystals (1)

Let $z(x,y)$ be the surface of the crystal in equilibrium. We assume that the surface tension coefficient σ for each closely-packed terrace, characterized by the unit normal vector $\boldsymbol{n}$, is known either from calculations or experiments.

The unit vector $\boldsymbol{n}$ of the local normal can be presented in the form

$$\boldsymbol{n} = \frac{p}{\sqrt{1+p^2+q^2}}\,\boldsymbol{e}_x + \frac{q}{\sqrt{1+p^2+q^2}}\,\boldsymbol{e}_y - \frac{1}{\sqrt{1+p^2+q^2}}\boldsymbol{e}_z,$$

where the following notations for the partial derivative are introduced for brevity

$$p \equiv \frac{\partial z}{\partial x} \quad \text{and} \quad q \equiv \frac{\partial z}{\partial y}.$$

The equilibrium shape of crystals should corresponds to the minimum of the surface energy

$$E_s = \iint \sigma(\boldsymbol{n})\, dS$$

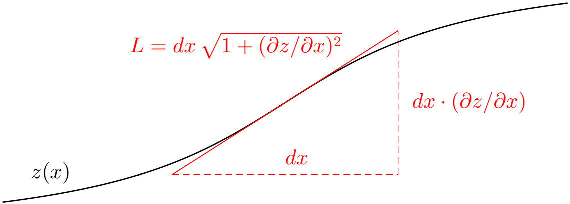
at additional constrain accounting the constancy of the volume of the crystal

$$V = \iint z(x,y)\, dxdy = const.$$

Equilibrium shape of crystals (2)

We take into account that $\sigma(\boldsymbol{n}) = \sigma(p, q)$ and the element of curved surface is equal to

$$dS \simeq \sqrt{1+p^2}\,dx \cdot \sqrt{1+q^2}\,dy \simeq \sqrt{1+p^2+q^2}\,dxdy \quad \text{at} \quad |p| \ll 1 \quad \text{and} \quad |q| \ll 1.$$



Thus, we formulate the following constrained-optimization problem

$$I = \iint \mathcal{F}(p, q)\,dxdy + 2\lambda \iint z\,dxdy,$$

where

$$\mathcal{F}(p, q) \equiv \sigma(p, q)\,\sqrt{1+p^2+q^2}$$

is the auxiliary function, and λ is a Lagrange multiplier.

Equilibrium shape of crystals (3)

Let us assume that the surface $z_0(x,y)$ corresponds to the minimum of the energy, therefore the auxiliary functional is equal to

$$I_0 = \iint \mathcal{F}_0 \, dxdy + 2\lambda \iint z_0 \, dxdy.$$

For the modified surface $z(x,y) = z_0(x,y) + \delta z(x,y)$ using standard rules of calculus of variations and integration by parts, we have

$$I = \iint (\mathcal{F}_0 + \delta\mathcal{F}) \, dxdy + 2\lambda \iint (z_0 + \delta z) \, dxdy =$$

$$= I_0 - \iint \delta z \left(\frac{\partial}{\partial x} \frac{\partial \mathcal{F}}{\partial p} + \frac{\partial}{\partial y} \frac{\partial \mathcal{F}}{\partial q} \right) dxdy + 2\lambda \iint \delta z \, dxdy,$$

therefore

$$\delta I = I - I_0 = \iint \left(2\lambda - \frac{\partial}{\partial x} \frac{\partial \mathcal{F}}{\partial p} - \frac{\partial}{\partial y} \frac{\partial \mathcal{F}}{\partial q} \right) \cdot \delta z \, dxdy.$$

Thus, the minimum of the surface energy of crystal corresponds to zero variational derivative

$$2\lambda - \frac{\partial}{\partial x} \frac{\partial \mathcal{F}}{\partial p} - \frac{\partial}{\partial y} \frac{\partial \mathcal{F}}{\partial q} = 0 \quad \Longrightarrow \quad \mathcal{F}(p,q) = \lambda \cdot (p\,x + q\,y - z)$$

Equilibrium shape of crystals and Wulff theorem (1)

Combining two expressions

$$\mathcal{F}(p,q) \equiv \sigma(p,q)\sqrt{1+p^2+q^2} \qquad \text{and} \qquad \mathcal{F}(p,q) = \lambda \cdot (p\,x + q\,y - z),$$

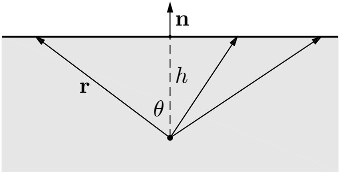
we arrive at the Wulff theorem (1901) for the equilibrium shape of crystal of given volume and minimal surface energy

$$\sigma(p,q) = \lambda\,\frac{(p\,x + q\,y - z)}{\sqrt{1+p^2+q^2}} = \lambda\,\frac{(p\,\boldsymbol{e}_x + q\,\boldsymbol{e}_y - \boldsymbol{e}_z)\cdot(x\,\boldsymbol{e}_x + y\,\boldsymbol{e}_y + z\,\boldsymbol{e}_z)}{\sqrt{1+p^2+q^2}}$$

or

$$\sigma(p,q) = \lambda\,(\boldsymbol{n}\cdot\boldsymbol{r}) \quad \text{or} \quad \sigma(p,q) = \lambda\cdot h,$$

where $\boldsymbol{n}$ is the unit normal vector and $\boldsymbol{r} = x\,\boldsymbol{e}_x + y\,\boldsymbol{e}_y + z\,\boldsymbol{e}_z$ is radius-vector running from the origin to arbitrary points at the surface of crystal, and θ is the angle between $\boldsymbol{n}$ and $\boldsymbol{r}$, and h is the distance from the origin to the cutting plane.



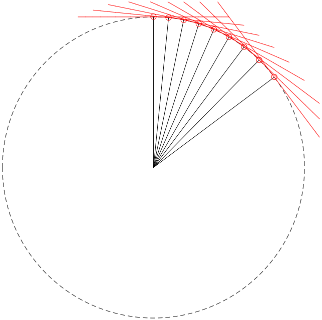
Equilibrium shape of crystals and Wulff theorem (2)

The Wulff theorem for isotropic surface tension $\sigma(p,q)=\sigma_0$

$$\sigma_0=\lambda\left(\boldsymbol{n}\cdot\boldsymbol{r}\right)\qquad\Longrightarrow\qquad\sigma_0=\lambda\,|\boldsymbol{n}|\,|r|\,\cos\theta\qquad\Longrightarrow\qquad h\equiv|r|\,\cos\theta=\frac{\sigma_0}{\lambda},$$

where θ is the angle between the normal vector and the radius vector to any point at the surface.

Since the distance h from the center of the crystal to any points at an arbitrary plane limited the inner part of the crystal does not depend on the choice of the cutting plane, we conclude that a sphere is the equilibrium surface with minimal surface energy.

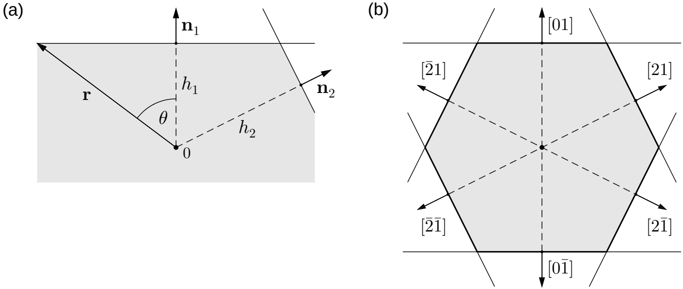


Equilibrium shape of crystals and Wulff theorem (3)

Now assume that the surface tension coefficient depends on the direction: $\sigma = \sigma(p, q)$.

If two arbitrary planes in the crystal are characterized by the vectors $\boldsymbol{n}_1$ and $\boldsymbol{n}_2$, and the surface tension coefficients σ_1 and σ_2, then

$$h_1 = \frac{\sigma_1}{\lambda} \quad \text{and} \quad h_2 = \frac{\sigma_2}{\lambda}.$$



After considering all possible directions and plotting all cutting planes one can find the smallest area enclosed by the planes – this area corresponds to the crystal of minimal surface energy.

Equilibrium shape of crystals and Wulff theorem (4)

Alternative presentation – the Wulff plot

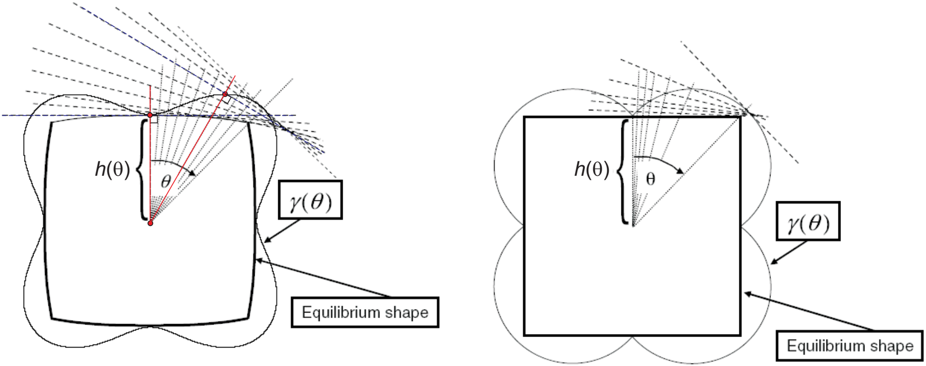


Fig. 4.12. Wulff plot and equilibrium shapes when $\gamma(\theta)$ has no cusp (upper panel) and when $\gamma(\theta)$ has a cusp at $\theta = 0$ (lower panel).

H. Ibach, *Physics of Surfaces and Interfaces*, Springer-Verlag Berlin Heidelberg (2006)

Equilibrium shape of crystals and Wulff theorem (5)

All typical cusps at the surface will disappear at increasing temperature, therefore at high temperatures all 2D islands will looks like disks:

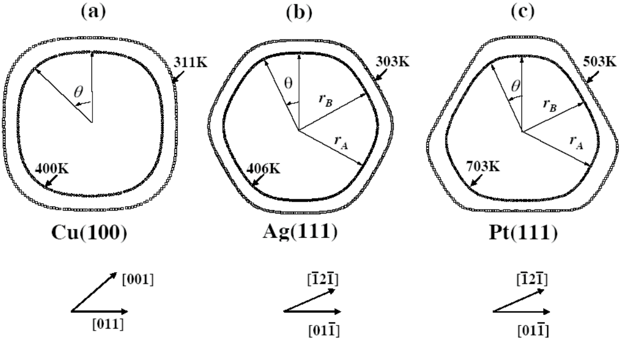


Fig. 4.18. Experimentally determined equilibrium island shapes on **(a)** Cu(100), **(b)** Ag(111), and **(c)** Pt(111) [4.27, 28]. The higher the temperature the rounder is the shape, eventually approaching a circle. For Ag(111), and also for Cu(111) A- and B-steps have nearly identical step line tensions, for Pt(111) the line tensions for A- and B-steps differ.

H. Ibach, *Physics of Surfaces and Interfaces*, Springer-Verlag Berlin Heidelberg (2006)

Part II

Phase transition into a state with developed surface roughness

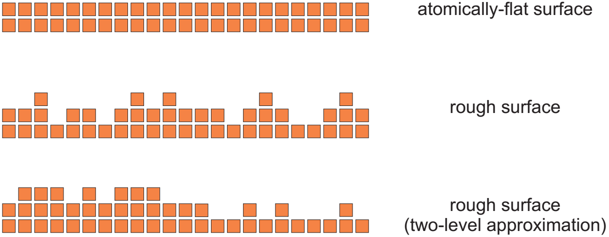
Free energy functional (1)

We consider the effect of temperature on microscopic structure of the surface of crystal and demonstrate that there is a second-order phase transition corresponding to a spontaneous formation of surface roughness at temperature exceeding some critical value T_c.

We assume that the flat surface of a crystal has N sites (places) potentially available for adsorbed atoms (so called adatom) and N_1 is the number of adatoms (i.e. excited atoms which leave their positions in the close-packed terrace). The coverage is defined as follows

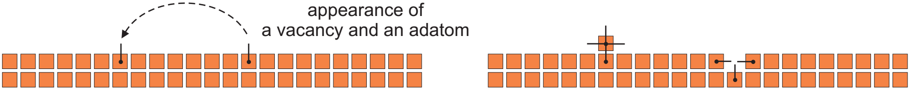
$$\theta \equiv \frac{N_1}{N}$$

and it varies from zero to unity. Atomically-flat surface corresponds to $\theta = 0$ and 1, while surface with the maximal surface roughness corresponds to $\theta = 1/2$.



Free energy functional (2)

Thermally-assisted formation of vacancy-adatom pairs increases the number of dangling bonds and thus increases the internal energy of the system:



We estimate the internal energy of the crystal, associated with the surface. This energy should be proportional to the number of broken chemical bonds

$$U \simeq \varepsilon_0 \, N_1 \, Z \, (1-\theta) \simeq \varepsilon_0 \, N \, Z \, \theta \, (1-\theta),$$

where ε_0 is a typical energy of a single broken bond, Z is the difference of coordination numbers for the atom inside the close-packed surface and the atom on top of the surface, and factor $1-\theta$ determines probability to find the broken bond on the surface of the crystal.

It is clear that the internal energy defined above is minimal for the ideal flat surface ($\theta = 0$ and $\theta = 1$) and maximal for the surface with developed roughness ($\theta = 1/2$).

Free energy functional (3)

In order to analyze equilibrium properties of the system at constant temperature, we need to introduce the Helmholtz free energy $F = U - T \cdot S$ and estimate the entropy S.

Entropy depends on the number of combinations W – i.e. the number of possible combinations to arrange N_1 particles for N sites

$$W = \frac{N!}{N_1!\,(N - N_1)!},$$

assuming that any site can adsorb no more than one atom. This vale can be also called the number of *micro*-states corresponding to the same *macro*-state.

If we know the number of microstates W, then we can calculate the entropy based on the Boltzmann's formula $S = k_B \ln W$, where $k_B = 1.38 \cdot 10^{-23}$ J/K is the Boltzmann constant. Using an approximate Stirling's formula $\ln N! \simeq N\, ln\, N$, we get

$$S = k_B \ln \frac{N!}{N_1!\,(N - N_1)!} \simeq k_B\, N \left\{ \ln N - \frac{N_1}{N} \ln N_1 - \left(1 - \frac{N_1}{N}\right) \ln (N - N_1) \right\} \simeq$$

$$\simeq -k_B\, N \left\{ \theta \ln \theta + (1 - \theta) \ln (1 - \theta) \right\}.$$

The entropy is zero for the ordered atomically-flat surface ($\theta = 0$ and $\theta = 1$) and maximal for the state with maximal roughness ($\theta = 1/2$).

Phase transition into state with surface roughness (1)

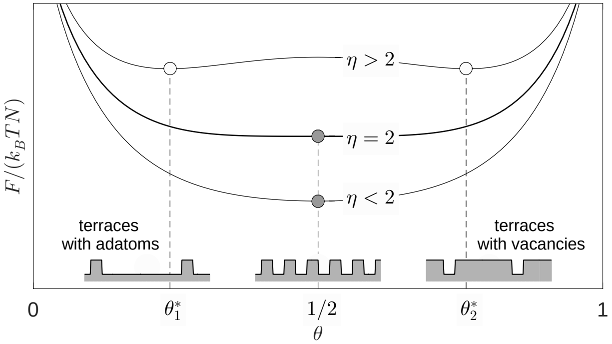
Combining the expressions for the internal energy U and the entropy S, we get the expression for the normalized free energy

$$F' \equiv \frac{U - TS}{k_B T N} = \eta\,\theta\,(1-\theta) + \theta \ln\theta + (1-\theta)\ln(1-\theta),$$

where

$$\eta \equiv \frac{Z\varepsilon_0}{k_B T}$$

is the effective activation energy.



Phase transition into state with surface roughness (2)

One extremum of $F'(\theta)$ is always located at $\theta^* = 1/2$ and depending on the η value this extremum is a local minimum (at $\eta < 2$) or local maximum (at $\eta > 2$). This solution corresponds to the surface with the maximal roughness.

Provided $\eta > 2$ there are two minima at θ_1^* и θ_2^*, symmetrically positioned with respect to $\theta = 1/2$. These solutions correspond to the surface with wide flat terraces with adatoms or vacancies.

Thus, the critical value of the effective activation energy corresponding to the phase transition is $\eta_c = 2$. We can define the critical temperature of the phase transition

$$\eta_c = 2 \quad \Longrightarrow \quad T_c \equiv \frac{Z\varepsilon_0}{k_B \eta_c} = \frac{Z\varepsilon_0}{2k_B}.$$

One can rewrite the expression for the normalized free energy

$$F' = \frac{2T_c}{T} \cdot \theta\,(1-\theta) + \theta\,\ln\,\theta + (1-\theta)\,\ln\,(1-\theta).$$

From the condition $dF'/d\theta = 0$ we determine the equilibrium coverage θ^*

$$\frac{2T_c}{T} \cdot (1 - 2\theta^*) + \ln\left(\frac{\theta^*}{1-\theta^*}\right) = 0.$$

Phase transition into state with surface roughness (3)

1. Limit of low temperature: $T \ll T_c$

In this case $\theta_1^* \to 0$, therefore

$$\frac{2T_c}{T}(1-2\theta_1^*) + \ln\left(\frac{\theta_1^*}{1-\theta_1^*}\right) = 0 \quad \Longrightarrow \quad \frac{2T_c}{T} + \ln\theta_1^* = 0,$$

$$\theta_1^* \simeq e^{-2T_c/T} \simeq e^{-Z\varepsilon_0/(k_B T)} \quad \text{and} \quad \theta_2^* \simeq 1-\theta_1^* \simeq 1 - e^{-Z\varepsilon_0/(k_B T)}.$$

It means that there are unavoidable structural defects (adatoms and vacancies) at the surface of the crystal at any finite temperature even for ideal conditions.

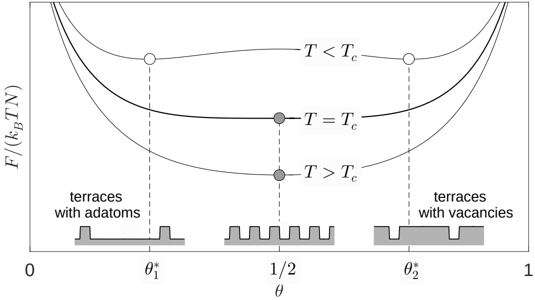
2. Limit of high temperature: $T \to T_c$.

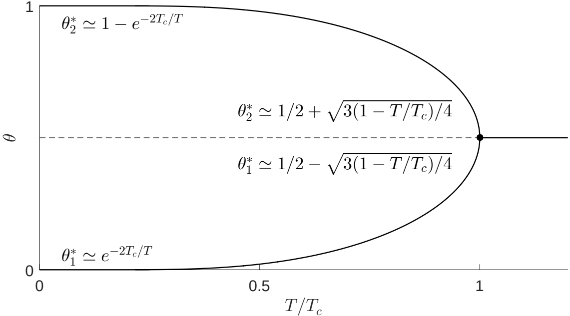
In this case $\theta_1^* = 1/2 - \varepsilon$ and $\theta_2^* = 1/2 + \varepsilon$, where $\varepsilon \to 0$. After the expansion of logarithmic function into a Taylor series, we come

$$\ln\left(\frac{\theta_1^*}{1-\theta_1^*}\right) = \ln\left(\frac{1-2\varepsilon}{1+2\varepsilon}\right) = \ln(1-2\varepsilon) - \ln(1+2\varepsilon) \simeq -4\varepsilon - \frac{16}{3}\varepsilon^3,$$

$$4\left(1-\frac{T_c}{T}\right) + \frac{16}{3}\varepsilon^2 = 0 \quad \Longrightarrow \quad \varepsilon \simeq \sqrt{\frac{3}{4}\left(1-\frac{T}{T_c}\right)} \quad \Longrightarrow \quad \theta_{1,2}^* \simeq \frac{1}{2} \pm \sqrt{\frac{3}{4}\left(1-\frac{T}{T_c}\right)}.$$

Phase transition into state with surface roughness (4)



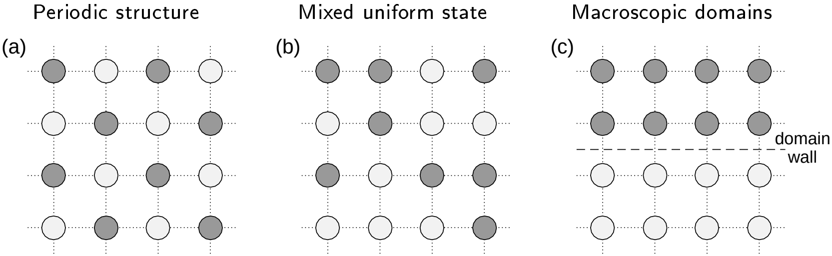


Part III

Phase separation in binary alloys. Ising model for ferromagnetic transition

Functional of internal energy for binary alloys (1)

We consider a binary alloy (solid-state mixture), consisting on equal amounts of atoms A and B. Which state corresponds to the minimum of internal/free energy?



For simplicity we will take into account the interaction only between neighbor atoms:
$-E_{AA}$ and $-E_{BB}$ is the energy of interaction between two atoms of the same type,
$-E_{AB}$ is the energy of interaction between two different atoms.

Ising model: assume that cites A and B correspond to the magnetic atoms with spin-up and spin-down magnetic states. It is clear that the same model will describe magnetic phase transition between non-magnetic state and ferromagnetic state with developed magnetic domains.

Functional of internal energy for binary alloys (2)

The total internal energy of interatomic interaction for the binary alloy in the mean field approximation is equal to

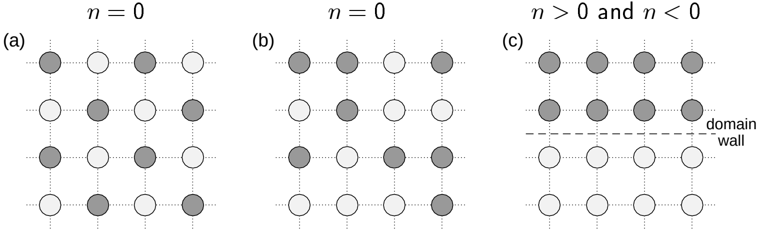
$$U = -\frac{N}{2}\left\{E_{AA}\cdot p_{AA} + E_{BB}\cdot p_{BB} + 2E_{AB}\cdot p_{AB}\right\},$$

where N is number of all atoms; $p_{X,Y}$ is a probability to find two atoms of types X and Y next to each other. If C is the local concentration of the atoms of type A, then $p_{AA} = C^2$, $p_{BB} = (1-C)^2$ и $p_{AB} = C(1-C)$.

We introduce the parameter

$$\eta \equiv C - \frac{1}{2},$$

which characterizes the difference of the local concentration of the atoms of type A from the concentration for ideally mixed system.



Functional of internal energy for binary alloys (3)

The difference between the interaction energy of the different atoms and the mean interaction energy of the same atoms can be called a mixing energy

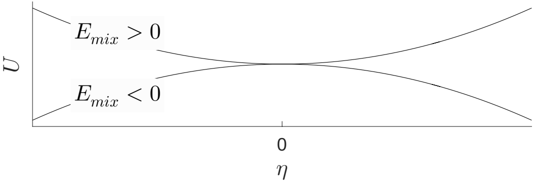
$$E_{mix} \equiv E_{AB} - \frac{(E_{AA} + E_{BB})}{2}.$$

We rewrite the expression of the total internal energy using the parameters η and E_{mix}

$$U = -\frac{N}{2}\left\{E_{AA}\left(\frac{1}{4} + \eta + \eta^2\right) + E_{BB}\left(\frac{1}{4} - \eta + \eta^2\right) + 2E_{AB}\left(\frac{1}{4} - \eta^2\right)\right\} =$$

$$= U_0 + N\,\frac{(E_{BB} - E_{AA})}{2}\,\eta + N\,E_{mix}\,\eta^2,$$

where $U_0 = -N\,(E_{AA} + E_{BB} + 2E_{AB})/8$ is a constant independent on η.



$E_{mix} > 0$: tendency to a spontaneous mixing

$E_{mix} < 0$: tendency to a phase separation and a formation of domains

Functional of free energy for binary alloys (1)

We focus on the binary systems $E_{mix} < 0$, which demonstrate tendency to a phase separation. For simplicity we assume that $E_{AA} = E_{BB}$.

To describe thermodynamic properties of the system with fixed number of particle and fixed volume at given temperature, one should consider the free energy functional $F = U - TS$ and calculate entropy S.

To calculate entropy of binary alloy, we use the Boltzmann's formula $S = k_B \ln w$, where k_B is the Boltzmann's constant and w is the number of microstates, corresponding to the same macrostate.

Using school-level combinatorics, we find the number of possible realizations (microstates) for the system with two different sorts of atoms

$$w = \frac{N!}{N_A!\, N_B!},$$

where N_A and N_B are the number of A and B atoms, $N = N_A + N_B$ is the total number.

We use the approximate Stirling's formula ($\ln N! \simeq N \ln N$) and calculate the entropy

$$S = k_B \ln w = k_B \ln \frac{N!}{N_A!\, N_B!} \simeq k_B \left\{ N \ln N - N_A \ln N_A - N_B \ln N_B \right\} \simeq$$

$$\simeq -k_B N \left\{ C \ln C + (1 - C) \ln (1 - C) \right\}.$$

Functional of free energy for binary alloys (2)

It is easy to see that the entropy

$$S \simeq -k_B\, N \Big\{ C \,\ln\, C + (1-C)\,\ln(1-C) \Big\}$$

tends to zero for fully ordered states ($C = 0$ and $C = 1$) and it reaches maximum $S_{max} = k_B N \,\ln 2$ for fully disordered state ($C = 1/2$).

We express S via the parameter η and then expand it in Taylor series up to fourth-order terms

$$S \simeq -k_B\, N \left\{ \left(\frac{1}{2}+\eta\right) \ln\left(\frac{1}{2}+\eta\right) + \left(\frac{1}{2}-\eta\right) \ln\left(\frac{1}{2}-\eta\right) \right\} \simeq$$

$$\simeq k_B\, N \left(\ln 2 - 2\eta^2 - \frac{4}{3}\,\eta^4 \right).$$

It allows us to write the free energy in the following form

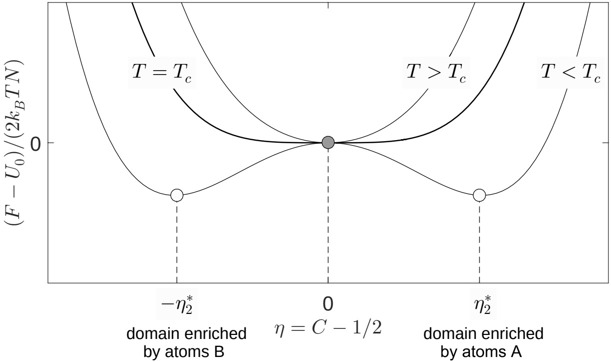
$$F = U - T\,S = (U_0 - k_B\, T\,\ln 2) + N\,E_{mix}\,\eta^2 + 2Nk_B T\,\eta^2 + \frac{4}{3}\,N\,k_B\,T\,\eta^4 =$$

$$= const + N\,(E_{mix} + 2k_B T)\,\eta^2 + \frac{4}{3} N k_B T\,\eta^4$$

Functional of free energy for binary alloys (3)

Free energy of the binary alloy

$$F = const + N\,(E_{mix} + 2k_B T)\,\eta^2 + \frac{4}{3} N k_B T\,\eta^4 .$$



The critical temperature T_c corresponds to the sign inversion for the quadratic term:

$$E_{mix} + 2k_B T_c = 0 \quad \Longrightarrow \quad T_c = -\frac{E_{mix}}{2k_B}.$$

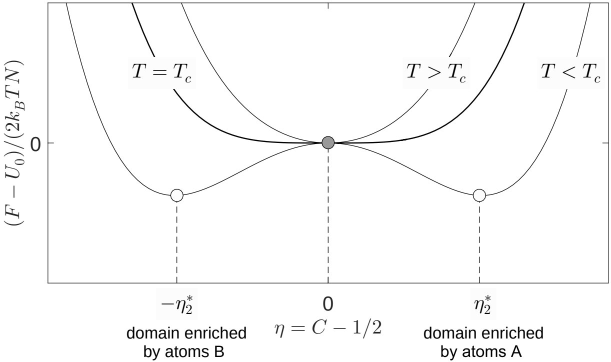
Functional of free energy for binary alloys (4)

Using the definition of the critical temperature $T_c = -E_{mix}/2k_B$, we write the free energy in the normalized form

$$F' \equiv \frac{F}{2k_B T_c N} \simeq const + \left(\frac{T}{T_c} - 1\right)\eta^2 + \frac{2}{3}\eta^4.$$

From the condition $dF'/d\eta = 0$ we find the equilibrium concentrations

$$\eta_1^* = 0 \qquad \text{и} \qquad \eta_2^* = \sqrt{\frac{3}{4}\left(1 - \frac{T}{T_c}\right)}.$$



Part IV

Wetting, Young's formula and regimes of growth of solid-state nanostructures

Contact angle and Young's formula (1)

The Wulff theorem is not applicable for heterogeneous systems.

We consider now the problem of the equilibrium shape of a droplet on a substrate. We introduce surface tension coefficients for interfaces liquid–gas σ_{13}, substrate–gas σ_{23}, and substrate-liquid σ_{12}.

We assume that the droplet has a form of the spherical segment of radius R and base angle φ. The effective free energy of the droplet of the given volume can be written as follows

$$F = \sigma_{13}\, S + (\sigma_{12} - \sigma_{23})\, S_0 - \lambda \cdot V,$$

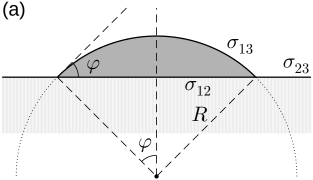
where

$$S = 2\pi R^2\,(1-\cos\varphi) \quad \text{and} \quad S_0 = \pi R^2\, \sin^2\varphi$$

are the areas of the spherical segment and its projection, respectively;

$$V = \frac{\pi R^3}{3}\Big(2(1-\cos\varphi) - \sin^2\varphi\cos\varphi\Big)$$

is the volume of the droplet, λ is Lagrange multiplier.



Contact angle and Young's formula (2)

Seeking the minimum of the free energy

$$F = \sigma_{13}\, 2\pi R^2\,(1-\cos\varphi) + (\sigma_{12}-\sigma_{23})\,\pi R^2\,\sin^2\varphi - \lambda\,\frac{\pi R^3}{3}\Big(2(1-\cos\varphi) - \sin^2\varphi\cos\varphi\Big)$$

with respect to independent variables R и φ, we get a system of nonlinear equations

$$4\,\sigma_{13}(1-\cos\varphi) + 2\,(\sigma_{12}-\sigma_{23})\,\sin^2\varphi - \lambda R\Big(2(1-\cos\varphi) - \sin^2\varphi\cos\varphi\Big) = 0,$$

$$2\,\sigma_{13}\,\sin\varphi + 2\,(\sigma_{12}-\sigma_{23})\,\sin\varphi\cos\varphi - \lambda R\,\sin^2\varphi\,\sin\varphi = 0.$$

Is it clear that this system of equation has a trivial solution

$$\sin\varphi = 0$$

regardless on the particular parameters σ_{12}, σ_{13} and σ_{23}. It corresponds to an ideal wetting and a formation of ultra-thin film on the substrate (similar to oil or benzene on water surface).

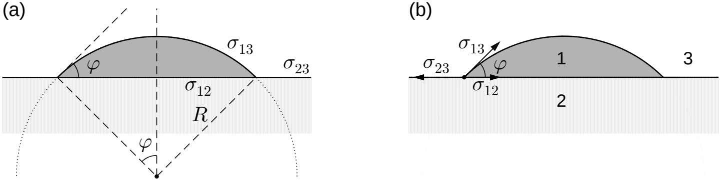
Assuming $\sin\varphi \neq 0$ and excluding all terms containing λ, we get the equation for the contact angle φ

$$4\,\sigma_{13}(1-\cos\varphi) + 2\,(\sigma_{12}-\sigma_{23})\,\sin^2\varphi - \Big(2\sigma_{13} + \\ +2(\sigma_{12}-\sigma_{23})\,\cos\varphi\Big)\left(\frac{2(1-\cos\varphi)}{\sin^2\varphi} - \cos\varphi\right) = 0.$$

Contact angle and Young's formula (3)

Thus, we get a well-known Young's formula for the contact angle

$$\cos\varphi = \frac{\sigma_{23} - \sigma_{12}}{\sigma_{13}} \qquad (*)$$



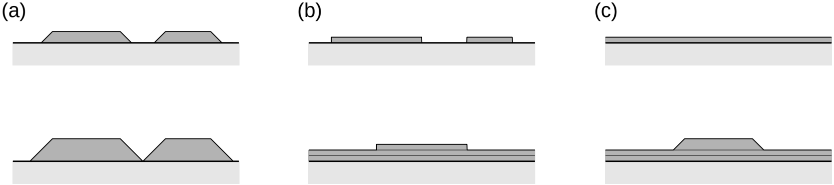
Simple mechanical interpretation: as it is known from general physics, the surface tension coefficient is equal to a tangential force, which tends to decrease the area of the surface between two media. From the balance of the forces acting at the point of contact of three media in projection on the $x-$axis, we get the equation of mechanical equilibrium

$$\sigma_{13} \cdot \cos\varphi + \sigma_{12} = \sigma_{23}$$

and then derive the Young's formula (*).

The Young's formula is very convenient for a classification of growth mechanisms.

Basic regimes of growth of solid-state nanostructures (1)



1. If $\sigma_{23} - \sigma_{12} < \sigma_{13}$, then the condition

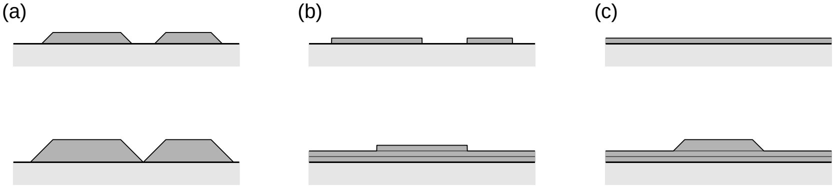
$$\cos\varphi = \frac{\sigma_{23} - \sigma_{12}}{\sigma_{13}}$$

can be fulfilled due to proper choice of the contact angle φ.

It corresponds to island or Vollmer-Weber growth mode (panel a). In this case the atoms of adsorbate are more strongly bound to each other rather than to the substrate. This mechanism is analogous to the condensation of droplets from the gaseous phase, however solid-state droplets become faceted.

It is an example of three-dimensional growth.

Basic regimes of growth of solid-state nanostructures (2)



In the opposite case $\sigma_{23} - \sigma_{12} > \sigma_{13}$ the condition $\cos\varphi = (\sigma_{23} - \sigma_{12})/\sigma_{13}$ cannot be fulfilled for any φ. It forces us to consider the independent solution

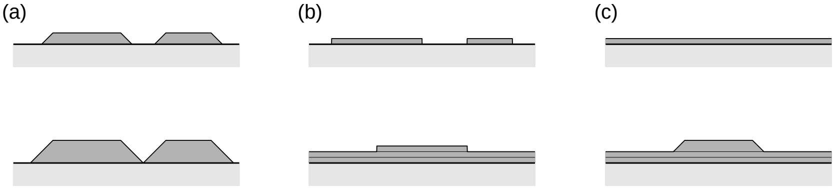
$$\sin\varphi = 0$$

There are two different scenarios.

2. The film of adsorbate can grow layer-by-layer, always covering the substrate (panel b). This regime is also called Frank–van der Merve growth mode. In this case atoms of adsorbate strongly interact with the substrate rather than to each other. As a result, in the ideal conditions each layer is fully completed before the next layer starts to grow.

It is an example of two-dimensional growth.

Basic regimes of growth of solid-state nanostructures (3)



3. In some case one can see combined layer-and-island regime, also known as Stranski-Krastanow growth mode.

At the initial stage the layer-by-layer mechanism is responsible for the formation of uniform thin film of adsorbate (single crystalline or amorphous). Upon increase in the thickness of the adsorbed film, internal mechanical stress due to mismatch of the lattice constant of substrate and adsorbate could produce the formation of dislocations and eventually leads to growth of three-dimension faceted islands.

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