

Lecture 6 Surface Diffusion Driven by Surface Energy

Examples

Flattening a surface.

Spherodizing.

Rayleigh instability.

Grain boundary grooving.

Sintering

Self-assembled quantum dots

Atomic Flux and Surface Velocity

Atoms can arrive to the surface in many ways. Atoms in the vapor can condense to the surface. Or conversely, atoms on the solid surface can evaporate. Atoms can diffuse in the volume of the solid. The body can also change shape by creep. In this lecture, we assume atoms can only move on the surface by diffusion, and all other modes of transport are negligibly slow. This situation happens for crystals at relatively low temperature, in a low vapor pressure environment.

Define the atomic flux on a solid surface by

$$\mathbf{J} = \frac{\text{number of atoms}}{(\text{length})(\text{time})}$$

Note that this flux is a vector tangent to the surface, and has a different dimension from that in the bulk. The flux is a *vector field* on the solid surface

Consider a small element of the surface of the body. Let v_n be the velocity of the solid surface, taken to be positive when the surface element gains atoms. The velocity is normal to the solid surface. The velocity is a *scalar field* on the solid surface.

The surface element extends when it gains atoms, and recedes when it loses atoms. Let Ω be the volume per atom in the solid. Thus, v_n/Ω is the number of atoms gained per unit area and per unit time. The flux divergence $\nabla \cdot \mathbf{J}$ is the number of atoms diffusing out of the surface element per unit area and per unit time. The divergence is taken on the surface. Because there are no other modes of transport, atoms gained by the surface element come solely from those diffuse into the element, namely,

$$v_n = -\Omega \nabla \cdot \mathbf{J}.$$

If we know how to calculate the diffusion flux, we can calculate the surface velocity, and thereby evolve the surface.

The Free Energy

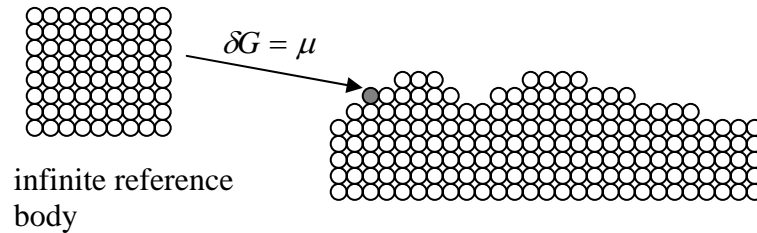
Whenever we talk about energy, we must specify a reference. Since the reference is arbitrary, results of physical significance must be independent of the reference. By specifying a reference, we avoid a common error of using different references in the middle of thinking (i.e. using double standard). To study phenomena involving a small body of identical atoms, we will use atoms of an infinite crystal as the reference. Define the free energy of a body under study as the difference between the body and the same number of atoms in the infinite crystal.

In this lecture, we are interested only in the surface energy. We assume that the surface energy is the same in all crystal orientation, and neglect the effect of crystalline anisotropy. The free energy of the body is the surface energy γ times the surface area S :

$$G = \gamma S$$

The Chemical Potential

Consider the body and the infinite crystal as a composite system. *Define the chemical potential of the surface as the free energy change associated with transferring one atom from the reference to the body.* The chemical potential of atoms in the infinite crystal is zero.



Let's first look at several simple situations. First consider a spherical particle of radius R . The sphere is large compared to individual atom. When an atom is transferred from the infinite crystal to the sphere, the sphere is larger, the surface area increases, and the surface energy increases. Consequently, the free energy of the composite system increases. Adding one atom to the sphere increases its volume by $4\pi R^2 dR = \Omega$, and therefore increases its radius by $dR = \Omega / (4\pi R^2)$. Consequently, the area of the sphere increases by $d(4\pi R^2) = 8\pi R dR = 2\Omega / R$. The chemical potential of an atom on the surface of the sphere is

$$\mu = \Omega \frac{2\gamma}{R}.$$

The chemical potential of the spherical particle is positive. Recall our reference, the infinite crystal, has a zero chemical potential. Consequently, the composite system reduces its free energy when an atom transfers from the sphere to the infinite crystal. This can be observed experimentally. If you place a small crystal near a large crystal, allowing atoms to transfer, the small crystal will disappear.

Similarly, one can show that when an atom is transferred from the infinite crystal to a cylinder of radius R , the free energy of the combined system increases by

$$\mu = \Omega \frac{\gamma}{R}.$$

When an atom is transferred from the infinite crystal to the surface of the spherical cavity of radius R , the surface area *decreases*, so that the free energy of the combined system decreases. The chemical potential of an atom on the spherical cavity surface is

$$\mu = -\Omega \frac{2\gamma}{R}.$$

If the body has an arbitrary surface, the curvature depends on position, and so does the chemical potential μ . Imagine that the body gains a hump, so that a surface area element dA moves by a distance δr_n . The body gains $\delta r_n dA / \Omega$ number of atoms from the infinite crystal, and the composite system gains

$$\delta G = \mu \frac{\delta r_n}{\Omega} dA$$

amount of free energy.

Let K_1 and K_2 be the two principal curvatures at a given position of the surface. Each curvature is taken to be positive if the particle is convex (like a solid sphere), and negative if the particle is concave (like a spherical cavity). A geometric consideration shows that when the surface element dA extends by a distance δr_n , the surface area of the body increases by

$$\delta S = (K_1 + K_2) \delta r_n dA$$

Recall that $G = \gamma S$. When an atom is transferred from the large crystal to this particular position on the surface of the given system, the free energy of the composite system increases by

$$\mu = \Omega \gamma (K_1 + K_2).$$

This is the chemical potential due to isotropic surface energy, valid for a body of an arbitrary shape. The chemical potential is a *scalar field* on the surface of the body.

The Driving Force for Surface Diffusion

For simplicity, consider a two dimensional body, so that its surface is a curve. The position of a point on the surface is specified by the curve length L . Denote $\mu(L)$ as the free energy increase as one atom is transferred from the reference system to the given system at location. The chemical potential at position $L + \delta L$ is $\mu(L + \delta L)$. When an atom relocate from position L to position $L + \delta L$, the free energy of the body changes by $\mu(L + \delta L) - \mu(L)$.

Recall that the driving force F is the free energy reduction when an atom moving a unit distance. When the atom moves on the surface by distance δL , the free energy of the system changes by $-F\delta L$. Equating the two expressions of the free energy change, $-F\delta L = \mu(L + \delta L) - \mu(L)$, we obtain that

$$F = -\frac{\partial \mu}{\partial L}.$$

The driving force relates to the gradient of the chemical potential. The gradient is taken on the surface.

For a body in three dimensions, the driving force is a vector tangential to the surface, and is the gradient of the chemical potential in the surface:

$$\mathbf{F} = -\nabla \mu.$$

The driving force is a *vector field* on the surface of the body.

Surface Diffusion

The atomic flux on the surface is taken to be linearly proportional to the driving force:

$$\mathbf{J} = M\mathbf{F},$$

where M is the mobility.

The mobility relates to the coefficient of self-diffusion on the surface as

$$M = \frac{D_s \delta_s}{\Omega k_B T}.$$

This relation arises from the analogy with self-diffusion in the bulk, and δ_s is introduced to fix dimension. This relation serves to define δ_s if all other quantities can be independently measured.

Two kinds of experiments have been used to study surface diffusion. In the first kind, we observe a macroscopic phenomenon caused by surface diffusion, such as the healing rate of a scratched surface, and then use a theoretical model to reduce the measured healing rate to diffusivity. This kind of experiments gives the product $D_s \delta_s$. Swinkels and Ashby (1981) have compiled data obtained by this kind of experiments.

In the second kind of experiments, we observe atomic motion on the solid surface, by field ion microscope, or scanning tunneling microscope. We image the positions of an individual adatom at different times. The adatom performs the random walk on the surface. From the distance λ traveled in the time t , we can obtain the diffusivity of the adatom:

$$D_a \sim \frac{\lambda^2}{t}.$$

Kellogg (1994) and Barth (2000) have compiled data obtained from such experiments.

If we assume that self-diffusion is entirely facilitated by adatoms, then the mobility is given by the Einstein relation:

$$M = \frac{C_a D_a}{k_B T},$$

where C_a is the number of adatom per unit area. Like vacancies in a crystal lattice, the adatom concentration can reach an equilibrium value dictated by its formation energy relative to the

temperature. We usually assume that adatoms reach Local equilibrium, unless there is a flux impinging on the surface, such as during deposition.

The Algorithm to Evolve the Shape of a Body

The main equations are collected as follows.

$$\mu = \Omega\gamma(K_1 + K_2)$$

$$\mathbf{F} = -\nabla\mu$$

$$\mathbf{J} = M\mathbf{F}$$

$$v_n = -\Omega\nabla \cdot \mathbf{J}$$

The algorithm to evolve the surface is as follows. Start with a given surface shape. Calculate the curvatures at all points on the surface. The curvatures give the chemical potential, the gradient of which gives the atomic flux on the surface. The divergence of the atomic flux gives the velocity of the normal surface. This velocity updates the surface shape for a small time increment. Repeat the above steps for the new surface shape.

A combination of the above equations gives that

$$v_n = B\nabla^2(K_1 + K_2)$$

The parameter

$$B = \Omega^2\gamma M = \frac{\Omega\gamma\delta_s D_s}{k_B T}$$

has the dimension $(\text{length})^4/(\text{time})$. To use this equation to evolve the surface, one has to do three things: (1) for a given surface, calculate the curvature, (2) calculate the velocity from the above equation, and (3) update the surface for a small time step using the velocity v_n . We discuss step (1) and (3) for specific problems.

Flattening of a Nearly Flat Solid Surface

Governing Equation. Represent a surface by writing its height h as the function $h(x, y, t)$. The surface is assumed to be a small perturbation from the plane $h = 0$. For this nearly flat surface, the curvatures are given by

$$K_1 \approx -\frac{\partial^2 h}{\partial x^2}, \quad K_2 \approx -\frac{\partial^2 h}{\partial y^2},$$

and the surface velocity is given by

$$v_n \approx \frac{\partial h}{\partial t}.$$

Consequently, the governing equation becomes

$$\frac{\partial h}{\partial t} = -B \left(\frac{\partial^4 h}{\partial x^4} + 2 \frac{\partial^4 h}{\partial x^2 \partial y^2} + \frac{\partial^4 h}{\partial y^4} \right).$$

This partial differential equation evolves the surface profile $h(x, y, t)$, once an initial profile is prescribed.

Evolution of a Fourier Component. For the nearly flat surface, the partial differential equation is linear. Consequently, if two functions $h_1(x, y, t)$ and $h_2(x, y, t)$ satisfy the PDE, so is their sum $h_1(x, y, t) + h_2(x, y, t)$. Any function $h(x, y, t)$, at a given time, is a sum of its Fourier components. Consider a particular Fourier component of amplitude q and period λ :

$$h(x, y, t) = q(t) \cos(kx)$$

The wave number is defined as $k = 2\pi / \lambda$. Insert this expression into the partial differential equation, and we obtain that

$$\frac{dq}{dt} = -Bk^4 q.$$

This is an ordinary differential equation for the amplitude $q(t)$. The solution is,

$$q(t) = q(0)\exp(-Bk^4t)$$

where $q(0)$ is the wave amplitude at $t = 0$ (i.e., the amplitude of the initial imperfection).

For a general Fourier component,

$$h(x, y, t) = q(t)\exp(ik_1x + ik_2y),$$

the same procedure also shows that its amplitude evolves according to $q(t) = q(0)\exp(-Bk^4t)$,

where $k = \sqrt{k_1^2 + k_2^2}$.

Fourier Synthesis. Let the initial surface profile be given as $h(x, y, 0)$. Define the Fourier transform by

$$h(x, y, 0) = \int \hat{h}(k_1, k_2, 0)\exp(ik_1x + ik_2y)dk_1dk_2.$$

The surface profile will evolve according to

$$h(x, y, t) = \int \hat{h}(k_1, k_2, 0)\exp(-Bk^4t)\exp(ik_1x + ik_2y)dk_1dk_2.$$

An Experimental Method to Determine Surface Diffusivity. We can scan the surface profile by using many instruments, and convert the profile into their Fourier components. Modern instruments usually come with this software feature. There is no need for you to learn how to do Fourier transform. However, it is important for you to understand what the Fourier transform can do for you. (In the same spirit, there is no need to learn how to multiply big numbers, so long as you know what multiplication means, and how to formulate your thoughts in terms of this idea.)

The ratio of the Fourier components at two different times is

$$\frac{\hat{h}(k_1, k_2, t)}{\hat{h}(k_1, k_2, 0)} = \exp(-Bk^4t).$$

Rearranging, we obtain that

$$\frac{1}{t} \ln \left[\frac{\hat{h}(k_1, k_2, t)}{\hat{h}(k_1, k_2, 0)} \right] = -Bk^4$$

Experimentally, we can start with a nearly flat but otherwise arbitrary surface profile. Determine the quantities on the left-hand side of the equation by measuring the surface profiles at two or more different times. Plot the measured values as a function of k , and we can determine the parameter B . This method determines the product $\gamma\delta_s D_s$. To determine $\delta_s D_s$, one must independently measure the surface energy. Note that the surface energy of a metal or a ceramic is typically on the order of 1J/m^2 .

Reading

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