

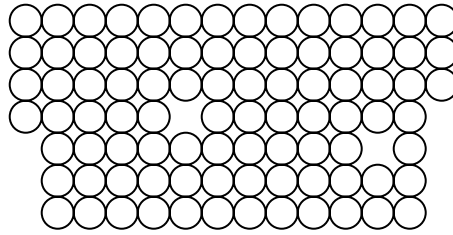
Lecture 2 The Vacancy

Imperfections in Nearly Perfect Crystals

There is a book by this title, edited by W. Shockley, J.H. Hollomon, R. Maurer, F. Seitz, published by John Wiley & Sons, in 1952. I found this book on the shelf in the Gordon McKay Library, or perhaps in the UCSB Library, in days before the internet arrived, when I spent time in libraries, browsing between shelves. The book was the proceedings of a symposium held in October 1950. Shockley and his colleagues at the Bell Labs had just invented the transistor. You might recognize some of the authors in the book: Bardeen, Herring, Guinier, Chalmers, C.S. Smith, Zener, Read... Over the years, I've returned to the book several times for illumination. The internet did do something good. A few years ago I bought a copy of the book from a book.com.

Below the melting point, a pure metal is a crystal. Each atom vibrates around its lattice site. If you look at one atom, its motion is chaotic; the atom jiggles rapidly, once in this direction and then in another. Its vibration amplitude also changes from time to time. But if you look at many atoms, they appear to be a periodic lattice. That is, if you find one atom at a point, you'll almost certainly find another atom any multiple of the lattice spacing away. Well, *almost*. The crystal is imperfect. It has defects: vacancies, dislocations and grain boundaries. They are the imperfections in the nearly perfect crystal.

Next consider the *motion* of the vacancies. A tiny fraction of lattice sites are vacant. A vacancy can switch site with a neighboring atom. The vacancy may *inject* into the crystal from one surface, *diffuse* through the crystal, and *emit* from the crystal at another surface. In this lecture we assume that vacancies are the only defects in the crystal. That is, the solid is a single crystal and has no grain boundaries or dislocations. Vacancies can only be created and annihilated at the surface of the crystal.



Cavity Growth Is an Atomic Disease

For the cavity in the crystal, the remote tensile stress motivates vacancies to inject into the crystal from the external surface. The vacancies then diffuse through the crystal, and emit from the crystal at the cavity surface. This process allows the tensile stress to enlarge the cavity. A reverse process allows the surface energy to shrink the cavity. Vacancy diffusion does not cause overall atomic bond stretch (elasticity), or any slip in the lattice (plasticity). The shape of the crystal does change over time, as the cavity enlarges or shrinks. The growth rate of the cavity depends on the diffusion rate of the vacancies. This picture links a macroscopic phenomenon (cavity growth) to an atomic process (vacancy diffusion). This lecture fills the details of this picture.

Equilibrium Vacancy Concentration is Very Small, but Finite

Why does a crystal contain vacancies? It's an outcome of a competition between probability and energy. Consider an analog first. Imagine a box of marbles, 10^4 heavy ones and 10^4 light ones. All marbles are identical in size. Shake the mixture until their average distribution doesn't change any more. What will be this *equilibrium* distribution? There will be an increasing concentration of heavy marbles toward the bottom. The mixture is a solution. The act of shaking plays the role of temperature that supplies the kinetic energy. The gravity supplies the potential energy.

Vacancy Formation Energy. Consider a crystal in equilibrium with vacuum. Use a perfect crystal as the ground state. Relocate one atom from its lattice site to the external surface. The vacancy distorts the crystal locally, increasing the internal energy of the crystal by a certain amount, ε_f , called the *vacancy formation energy*. Its magnitude is about 1 eV. Because of this energy increase, the crystal cannot have many vacancies. On the other hand, complete segregation of the atoms and vacuum is a rare event. The competition between the formation energy and the probability determines an equilibrium vacancy concentration.

Imagine a crystal made of N_a atoms and N_v vacancies. Empirically we know that $N_v / N_a \ll 1$; that is, the vacancies are far apart in the lattice, and therefore do *not* interact with one another. Consequently, the crystal containing N_v vacancies has internal energy

$$U = \varepsilon_f N_v.$$

ε_f must be positive; otherwise the crystal will be full of vacancies and you will never see a crystal.

The Entropy. Now why a crystal tolerates even a few vacancies which *increases* its internal energy? This is because the *perfect crystal* in the vacuum is itself such an intolerable state: it is perfectly ordered. The entropy of the solid *increases* if some vacancies get into the crystal.

Boltzmann defined the entropy by

$$S = k \ln g.$$

Here g is the number of ways to place the N_a atoms and the N_v vacancies on the $(N_a + N_v)$ lattice sites. The constant k has no physical significance beyond choosing a special unit system.

Computing the number g , and therefore the entropy, is a combinatorial problem. A well-known mathematical question is, given M *different* objects and M sites, how many ways are

there to place one object to each site? The answer is $M!$. The logic goes as follows. There are M ways to place the first object. After one site is taken, there are $(M - 1)$ ways to place the second object, and so on. The number ways to place all M objects is the product, $M(M - 1)(M - 2)...1 = M!$. Now our objects are not all different. All the N_a atoms are identical, and so are all the N_v vacancies. Consequently, the number of ways to place the N_a atoms and the N_v vacancies on the $(N_a + N_v)$ lattice sites is

$$g = \frac{(N_a + N_v)!}{N_a!N_v!}$$

Recall Stirling's formula for large numbers, $\ln(x!) \approx x \ln x - x$. The entropy is

$$S = k \left[(N_a + N_v) \ln(N_a + N_v) - N_v \ln N_v - N_a \ln N_a \right]$$

This expression is known as the *entropy of mixing*. When $N_v / N_a \ll 1$, the entropy increases as the number of vacancies increases.

Boltzmann's Constant and Average Thermal Energy. The value of Boltzmann constant is $k = 1.38 \times 10^{-23} \text{ J/K} = 8.63 \times 10^{-5} \text{ eV/K}$

Events	Centigrade	Kelvin	kT
Freezing Point of Water	0 °C	273 K	0.024 eV
Room Temperature	27 °C	300 K	0.026 eV
Boiling Point of Water	100 °C	373 K	0.032 eV
A High Temperature	1000 °C	1273 K	0.11 eV

Equilibrium Vacancy Concentration. The ground state is a perfect crystal with no vacancy. The free energy of a crystal with N_v vacancies is

$$U - TS = \varepsilon_f N_v - kT \left[(N_a + N_v) \ln(N_a + N_v) - N_v \ln N_v - N_a \ln N_a \right],$$

The vacancy formation energy favors fewer vacancies. The entropy favors more vacancies. The *equilibrium* number of the vacancies minimizes the free energy. Setting $d(U - TS)/dN_v = 0$, we find that the *equilibrium number of vacancies* is given by

$$\frac{N_v}{N_a + N_v} = \exp\left(-\frac{\varepsilon_f}{kT}\right).$$

We write this expression as

$$c_0 = \frac{\text{No. of Vacancies}}{\text{No. of Lattice Sites}} = \exp\left(-\frac{\varepsilon_f}{kT}\right).$$

We use c_0 to indicate the fraction of vacancies in a large crystal, under no external stress. The dimensionless ratio ε_f/kT measures the competition between the trend to segregate and the trend to mix. The crystal takes in more vacancies if each vacancy doesn't increase too much energy, or if the temperature is high. For most solids, ε_f is on the order of 1 eV, which is much larger than kT . For example, even at $T = 1000$ K, there is only one vacancy in about 10^5 lattice sites. The above formula connects something related to the interatomic forces, the vacancy formation energy ε_f , to something related to the whole solid, the equilibrium vacancy concentration c_0 .

Experimental Determination of the Vacancy Formation Energy. R.O. Simmons and R.W. Balluffi (Measurement of Equilibrium Concentration of Lattice Vacancies in Gold, *Phys. Rev.* **125**, p. 862-872, 1962) devised a method to measure the vacancy concentration in gold. They measured the thermal expansion by direct observation of the sample size change, and measured the crystal lattice parameter expansion by x-ray diffraction. The tiny volume increase of the sample in addition to that caused by the lattice expansion determined the vacancy concentration change. They then deduced the vacancy formation energy ε_f from such measurements.

Vacancy formation energy and migration energy for common metals.

	Al	Cu	Au	Ni	Fe	Mo
E_v (eV)	0.65-0.70	1.20-1.30	0.94-0.98	~1.80	1.40-1.60	3.00-3.24
E_m (eV)	0.60-0.65	0.70-0.75	0.78-0.88	~1.04	~1.20	1.30-1.60

Encyclopedia of Materials: Science and Technology (Elsevier, Online)
[Crystals: Point Defects](#), B. L. EYRE, UNIVERSITY OF OXFORD, UK

Tensile Stress Increases Vacancy Concentration in Crystal near External Surface

Now consider a crystal subject to a tensile stress, σ , normal to a surface. An atom leaves its lattice site and appends on the surface. The ground state is the crystal under stress but without the vacancy, and the current state is the crystal under stress with the vacancy. We need to know the energy difference between the two states. Because an applied stress is typically much smaller than the cohesive strength of the crystal, the value ε_f , associated with the lattice distortion due to a vacancy, is nearly unchanged by the stress. As the atom appends onto the crystal, the stress does work $\Omega\sigma$, where Ω is the volume per atom. Consequently, in creating one vacancy-atom pair, the potential energy varies by $\varepsilon_f - \Omega\sigma$. The equilibrium vacancy concentration in the crystal near the stressed surface is

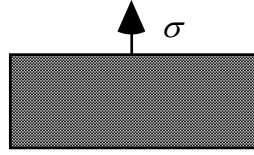
$$c = \exp\left(-\frac{\varepsilon_f - \sigma\Omega}{kT}\right) = c_0 \exp\left(\frac{\sigma\Omega}{kT}\right)$$

For representative values, $\sigma = 100$ MPa and $\Omega = 1.6 \times 10^{-29}$ m³, this work is $\Omega\sigma = 10^{-2}$ eV. Thus, typically,

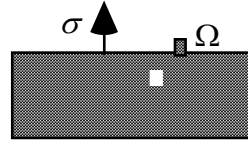
$$\Omega\sigma \ll kT \ll \varepsilon_f.$$

Note the factor $\exp(\sigma\Omega/kT) \approx 1 + (\sigma\Omega/kT)$. If $\sigma\Omega/kT = 0.1$, the tensile stress increases the equilibrium vacancy concentration by 10%. Because the equilibrium vacancy concentration in a

crystal under no stress, c_0 , is small, the vacancy concentration in a crystal under stress is still small.



reference state



atom-vacancy pair

Surface Energy Increases Vacancy Concentration in Crystal near Cavity Surface

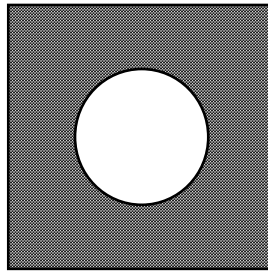
Next consider a cavity of radius R . When an atom leaves the crystal and appends on the cavity surface, the vacant lattice site increases the potential energy of the crystal by ε_f . The cavity becomes one atom smaller: the cavity volume changes by $4\pi R^2 dR = -\Omega$, and the cavity surface area changes by $8\pi R dR = -2\Omega / R$. This reduces the surface energy by $2\gamma\Omega / R$. Consequently, the creation of one atom-vacancy pair increases the potential energy of the crystal by $\varepsilon_f - 2\gamma\Omega / R$. The equilibrium vacancy concentration in the crystal near the cavity surface is

$$c = \exp\left(-\frac{\varepsilon_f - 2\gamma\Omega / R}{kT}\right) = c_0 \exp\left(\frac{2\gamma\Omega}{kTR}\right).$$

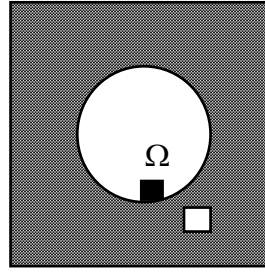
For representative values, $\gamma = 1$ N/m, $\Omega = 1.6 \times 10^{-29}$ m³, and $R = 2 \times 10^{-8}$ m, the energy change due to surface tension is this work is $2\gamma\Omega / R = 10^{-2}$ eV. Thus, typically,

$$2\gamma\Omega / R \ll kT \ll \varepsilon_f.$$

Consequently, the surface tension slightly reduces the total energy associated with creating one vacancy, and thereby slightly increases the equilibrium vacancy concentration in the crystal near the cavity surface.



Reference State



atom-vacancy pair

Will the Cavity Enlarge or Shrink?

Local equilibrium. Now return to the problem of a cavity in a crystal under a remote hydrostatic tension. Near the external surface, the vacancy in the crystal is close to the sink, so that the vacancy concentration in the crystal is in equilibrium, as dictated by the stress:

$$c = \exp\left(-\frac{\varepsilon_f - \sigma\Omega}{kT}\right) = c_0 \exp\left(\frac{\sigma\Omega}{kT}\right).$$

Near the cavity, the vacancy concentration in the crystal is in equilibrium, as dictated by the surface energy:

$$c = \exp\left(-\frac{\varepsilon_f - 2\gamma\Omega/R}{kT}\right) = c_0 \exp\left(\frac{2\Omega\gamma}{kTR}\right)$$

If the vacancy concentration in the part of crystal near the external surface is higher than that near the cavity surface, vacancies diffuse from the external surface to the cavity surface, and the cavity enlarges. The vacancy concentrations in the crystal near the two surfaces should take their respective equilibrium values, as given above. Comparing the two formulas, we see that the cavity enlarges if

$$\sigma > 2\gamma / R.$$

This is the same condition we had before.

Cavity Growth Rate

How fast does the cavity enlarge? When $\sigma > 2\gamma / R$, the vacancy concentration is higher in the crystal near the external surface than in the crystal near the cavity surface. The concentration difference drives vacancies to diffuse from the external surface to the cavity surface. It is the rate of vacancy diffusion that limits the rate of cavity growth.

The Partial Differential Equations. We assume that the only imperfection in the crystal is vacancies. There are no grain boundaries or dislocations in the crystal to inject vacancies into the crystal, or absorb vacancies from the crystal. The crystal exchanges vacancies only with the vacuum, at the external surface of the crystal. With this assumption, vacancies are conserved inside the crystal. Denote the number of vacancies per unit volume by C ($C = c/\Omega$), and the vacancy flux by \mathbf{J} (the number of vacancies across unit area in unit time). The flux divergence must be compensated by the concentration rate:

$$\frac{\partial C}{\partial t} + \frac{\partial J_i}{\partial x_i} = 0.$$

Fick's law says that the vacancy flux is proportional to the vacancy concentration gradient:

$$J_i = -D_v \frac{\partial C}{\partial x_i}.$$

Here D_v is the vacancy diffusivity. Here we accept this law as an empirical finding. We'll talk about the atomic process of vacancy diffusion in a later lecture.

The Boundary Conditions. The above partial differential equations should be solved subject to the following boundary conditions:

$$C = \frac{c_0}{\Omega} \exp\left(\frac{\sigma\Omega}{kT}\right), \text{ at the external surface,}$$

$$C = \frac{c_0}{\Omega} \exp\left(\frac{2\Omega\gamma}{kTR}\right), \text{ at the cavity surface.}$$

Solving the Boundary Value Problem. Assume the vacancy concentration has reached a steady-state, i.e., $\partial C / \partial t = 0$. Consequently, the concentration profile satisfies the Laplace equation, $\nabla^2 C = 0$. In the spherical symmetric coordinate, the Laplace equation takes the form

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dC}{dr} \right) = 0.$$

The general solution to this ODE is

$$C(r) = a + \frac{b}{r}.$$

where r is the distance from the center of the cavity, and a and b are the integration constants.

Under the local equilibrium assumption, the boundary conditions are

$$C(\infty) = \frac{1}{\Omega} \exp\left(-\frac{\varepsilon_f}{kT}\right) \exp\left(\frac{\sigma\Omega}{kT}\right), \quad C(R) = \frac{1}{\Omega} \exp\left(-\frac{\varepsilon_f}{kT}\right) \exp\left(\frac{2\gamma\Omega}{kTR}\right).$$

Consequently, the vacancy concentration in the solid distance r from the cavity center is

$$C(r) = C(\infty) + \frac{R}{r} [C(R) - C(\infty)]$$

The growth rate of the cavity radius is given by

$$\frac{dR}{dt} = -\Omega J(R).$$

$$\frac{dR}{dt} = -\Omega J(R) = \Omega D_v \left. \frac{dC}{dr} \right|_R = \frac{D_v}{R} \exp\left(-\frac{\varepsilon_f}{kT}\right) \left[\exp\left(\frac{\Omega\sigma}{kT}\right) - \exp\left(\frac{2\Omega\gamma}{kTR}\right) \right].$$

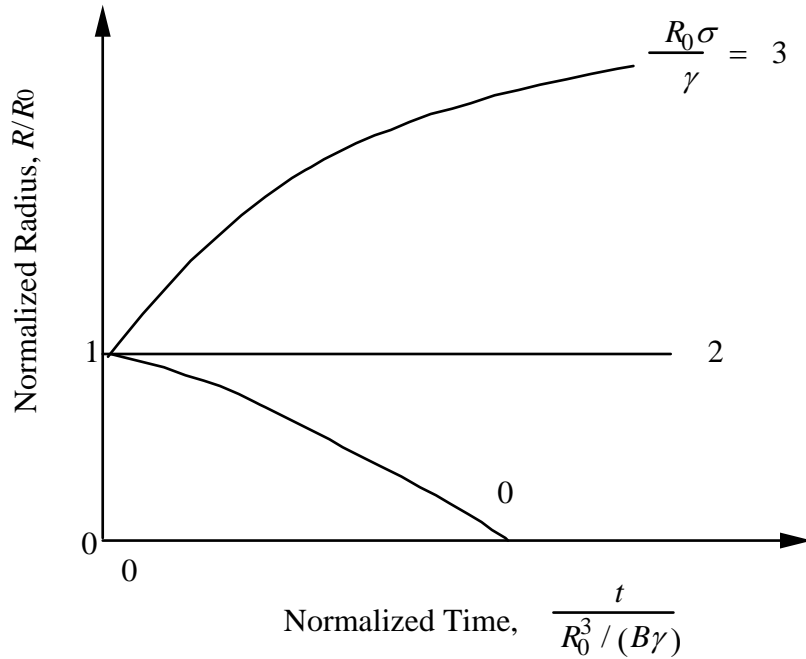
Simplify the above equation by using $\exp(x) = 1 + x$ for small x , and we have

$$\frac{dR}{dt} = \frac{B}{R} \left[\sigma - \frac{2\gamma}{R} \right],$$

with

$$B = \frac{\Omega}{kT} D_v \exp\left(-\frac{\varepsilon_f}{kT}\right).$$

After integration (do it yourself), the result looks like this (R_0 is the initial radius):



We like to present results in dimensionless form. The length is reported in units of the initial radius R_0 , and the time in $R_0^3 / (B\gamma)$.

Justification of the Steady-state Approximation

The transient diffusion occurs with the time scale of $t_1 \sim R_0^2 / D_v$. The cavity growth occurs over the time scale $t_0 \sim \frac{kTR_0^2}{\Omega\sigma D_v} \exp\left(\frac{\varepsilon_f}{kT}\right)$. A comparison shows that $t_1 \ll t_0$. It seems reasonable to neglect the transient diffusion.