

Lecture 3 From Vacancy Diffusion to Cavity Growth

The Phenomenological Definition of Diffusivity

In the previous lecture, we have adopted a continuum picture of vacancy diffusion. Let C be the vacancy concentration (i.e., the number of vacancies per unit volume), and J_i be the vacancy flux (i.e., the number of vacancies across a plane per unit area per unit time). These quantities are functions of spatial coordinates (x_1, x_2, x_3) and time t . Following Fick, we have asserted that the vacancy flux is proportional to the gradient of the vacancy concentration:

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

This equation defines the coefficient of diffusion, D .

Diffusivity Can Be Determined Experimentally

If we can set up a vacancy concentration gradient in a crystal, and measure the vacancy flux, we can experimentally measure the coefficient of diffusion of vacancies. D is found to be independent of the vacancy concentration and vary with the temperature as

$$D = D_0 \exp\left(-\frac{q}{kT}\right),$$

where D_0 and q are constants fitting the experimental data. Measure the diffusivity at several temperatures, and plots $\ln D$ as function $1/kT$. The data points typically fall on a straight line:

$$\ln D = \ln D_0 - \frac{q}{kT}$$

The intercept of the line with the vertical axis gives $\ln D_0$, and the slope of the line gives q .

Typically, q is on the order of 1 eV. Thus, $kT \ll q$.

Atomic Picture of Vacancy Diffusion

The vacancy concentration is low, so that individual vacancies are far apart. Atoms vibrate. Each vacancy undergoes the Brownian motion. Imagine that the number of vacancies per unit volume, C , has a *gradient* in the x direction. Focus on two neighboring atomic layers of a crystal lattice lying normal to the x axis. Layer 1 has C_1 vacancies per volume, and layer 2 has C_2 vacancies per volume. If $C_1 > C_2$, more vacancies jump from layer 1 to layer 2 than the other way around. This gives rise to a net vacancy flux.

Atoms vibrate at a frequency ν , on the order $\nu \sim 10^{13} \text{s}^{-1}$. But not every jiggle is energetic enough to move a vacancy from one lattice site to another. To change site, the vacancy must overcome the *energy barrier* imposed by its neighboring atoms. Denote this migration energy by ε_m . Typically, $\varepsilon_m \approx 1 \text{ eV}$, much larger than the average vibration energy kT . A vacancy changes $\nu \exp(-\varepsilon_m / kT)$ number of sites per unit time.

Layer 1 has $C_1 a$ vacancies per unit area, so that $C_1 a \nu \exp(-\varepsilon_m / kT)$ vacancies per area per time are energetic enough to change site. Some jump to another site in layer 1, some jump to layer 2, and some to another neighboring layer. We'll ignore this detail and simply say all the energetic vacancies on layer 1 jump to layer 2. Similarly, layer 2 has $C_2 a$ vacancies per unit area, so that $C_2 a \nu \exp(-\varepsilon_m / kT)$ vacancies per area per time are energetic enough to change site. Consequently, the net vacancy flux is the difference, namely,

$$J \approx (C_1 - C_2) a \nu \exp(-\varepsilon_m / kT).$$

Recall the definition for the concentration gradient, $\partial C / \partial x \approx (C_2 - C_1) / a$, and for the diffusivity, $J = -D \partial C / \partial x$. The diffusivity is

$$D \approx a^2 \nu \exp(-\varepsilon_m / kT).$$

Models like this should never be taken literally; for numerical values of diffusivities, experiments are called for. But such models develop our intuition into things that we don't have direct experience—things that are too large, too small, run too fast, too slow. (Have you ever sat near an atom, counting how many times it jiggles in a second?) This model really has this kind of quality. It tells us a number of things.

- The diffusivity really should have the kind of temperature-dependence observed in experiments, $D = D_0 \exp(-q / kT)$.
- The pre-exponential factor scales as $D_0 \approx \nu a^2 \approx (10^{13} \text{ s}^{-1})(10^{-10} \text{ m})^2 = 10^{-7} \text{ m}^2/\text{s}$. There is a dimensionless coefficient that we have dropped.
- The activation energy q has the physical meaning of the migration energy. An atomistic simulation may compute this quantity.
- The diffusivity is indeed independent of the concentration.

Cavity Growth Is Caused by a Series of Tiny Effects

- A *tiny* fraction of lattice sites are vacant.
- The tensile stress increases the vacancy concentration at the external surface by a *tiny* fraction.
- The *tiny* nonuniformity in the vacancy concentration drives diffusion.
- A *tiny* fraction of vacancies change site, by an atomic distance.

From Atomic Time Scale to Cavity Growth Time Scale

Atoms vibrate at a huge frequency, $\nu \sim 10^{13} \text{ s}^{-1}$, but cavity grows slowly. How does the atomic time scale get slow down at the macroscopic scale? The time scale for cavity growth is

$$t_0 \sim \frac{kTR_0^2}{\sigma\Omega D} \exp\left(\frac{\varepsilon_f}{kT}\right)$$

A combination with the atomistic formula for diffusion coefficient gives

$$t_0 \sim \frac{1}{\nu} \left(\frac{kT}{\sigma\Omega}\right) \left(\frac{R_0}{a}\right)^2 \exp\left(\frac{\varepsilon_m}{kT}\right) \exp\left(\frac{\varepsilon_f}{kT}\right).$$

The small atomic time scale, $1/\nu$, amplifies to the macroscopic time scale, t_0 , by

- the Boltzmann factor $\exp(+\varepsilon_f/kT)$ (Only a tiny fraction of lattice sites are vacant.)
- the Boltzmann factor $\exp(+\varepsilon_m/kT)$ (Only a tiny fraction of vacancies jump over the energy barrier.)
- the length ratio $(R_0/a)^2$ (The nonuniformity of the vacancy concentration is over the length scale R_0 . The vacancy jump is over atomic distance a .)