Last Time

The Successful Jump Frequency as an Activated Process

Energy Distributed among Particles in an Ensemble of Fixed Energy

The Square Well Approximation

The Harmonic Well Approximation

3.21 Spring 2001: Lecture 15

Many-Body Theory of Activated Processes at Constant Pressure

In a real system, an atom or a vacancy does not make a successful hop without affecting (or getting effected by) its neighbors—all of the particles are vibrating and saddle point energy is an oscillating target produced by the random vibrations of all the atoms. The energy-surface that an atom, interstitial, or vacancy travels upon is a complicated and changing surface. If there are N spherical particles, then there are $6N$-degrees of freedom to this surface, but it will be assumed that the momentum variables can be averaged out so that only a $3N$-dimensional potential surface remains:

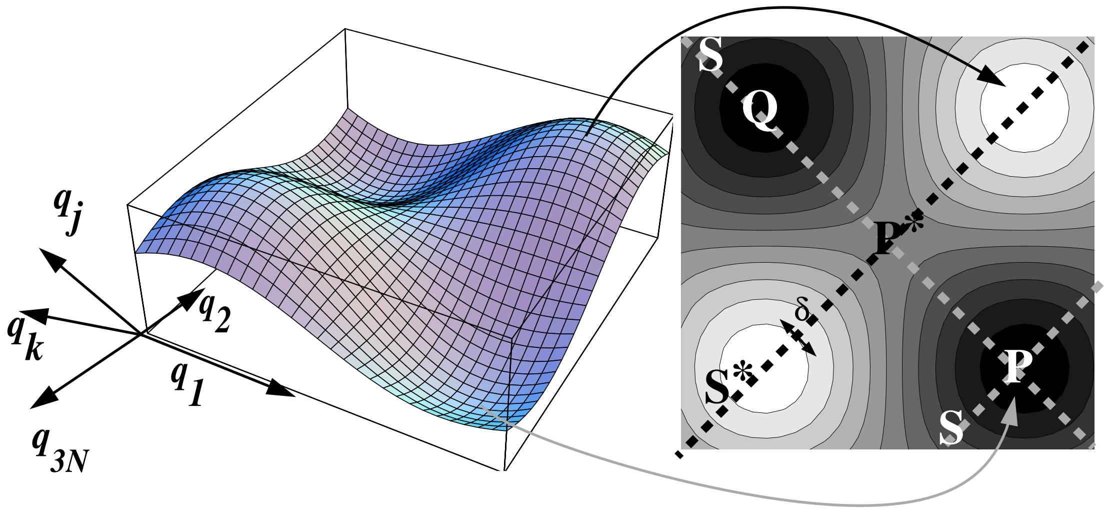

Figure 15-1: A schematic representation of the $3N$-dimensional (positions) surface for a crystal with N sites. The minima are located at P and Q and it may be supposed, for simplicity, that a particle that jumps from P to Q does so along the trajectory S crossing through a maximum of width δ at the saddle point A^* which is located at the minium along the ridge S^*.

Effectively, the average over the momentum variables is supposed to account for events such as increased probability of a hop by an interstitial or vacancy when the oscillations of nearby host atoms cooperate to create an enlarged path (or reduced activation barrier).

The minima, or equilibrium values of momenta and positions, can be approximated by harmonic wells:

$$E(q_i) = E_{min} \sum_{i=1}^{3N} \frac{m_i \omega_i^2}{2} q_i^2 \tag{15-1}$$

where ω_i is the characteristic harmonic frequency of a particle oscillating near the ith minimum.

Considering the process of a single hop, consider the trajectory of the particle as illustrated in Figure 15-1. It can be supposed that trajectory $P \to Q$ is along the positive direction of the coordinate q_1. This effectively turns the many-body problem into a one-dimensional problem along the line S in Figure 15-1. Therefore, the rate of crossing can be related to the average velocity in the activated state and the "effective width" in the activated state.[28]

Let the first coordinate be in the direction of the crossing (parallel to S), then the average (rms) momentum p_1 in that direction is related to the an average rate of attempts. The result that was derived for the harmonic potential can be re-used in this case:

[28] Recall from the simulations in class that the particle spends most of its time in the well and most of the stime near the saddle points where the net velocity is small.

$$\Gamma = \sqrt{\frac{kT}{m}}\frac{1}{L_A}\text{(fraction of particles in activated state)} \qquad (15\text{-}2)$$

where L_A is recognized to be the width δ in Figure. 15-1.

However, in this case, the particle may have a different volume in the activated state compared to the equilibrium state:[29]

$$\Delta V_{part}^{mig} = V_{part}^{A} - V_{part}^{eq} \qquad (15\text{-}3)$$

For the case where the volume may vary, but pressure is constant, the canonical constant pressure partition function must be used:

$$Z_P = \sum_{energies,\, volumes} e^{-\frac{(E+PV)}{kT}} \qquad (15\text{-}4)$$

Therefore Γ_{part} picks up an additional factor:

$$\Gamma_{part} = \sqrt{\frac{kT}{m}}\frac{1}{L_A} e^{\frac{-P\Delta V_{part}^{mig}}{kT}} \frac{Z_A}{Z_{min}} \qquad (15\text{-}5)$$

It remains to evaluate the partition functions by summing over all energies: $Z = \sum_i^{3N} e^{-E(p_i,q_i)/kT}$. The usual strategy in evaluating the sum for a partition function is to replace it with an integration over a continuous variable: $\sum_i \exp[-E_i/kT] \rightarrow \int \exp[-E(\zeta)/kT]d\zeta$, where ζ is a continuous variable that mimics the index i. However, because the atoms are part of a lattice, the positions and momenta are quantized. Therefore, a trick must be employed to convert the sum over quantized values to continuous values. The trick involves degeneracy and the Heisenberg uncertainty principle. The partition function is evaluated by passing to the classical limit by dividing up the quantum phase space into cells of side-length equal to Planck's constant, h:

[29] This is certainly important for the case for migrating particles that have a large compliance (low stiffness) such as vacancies.

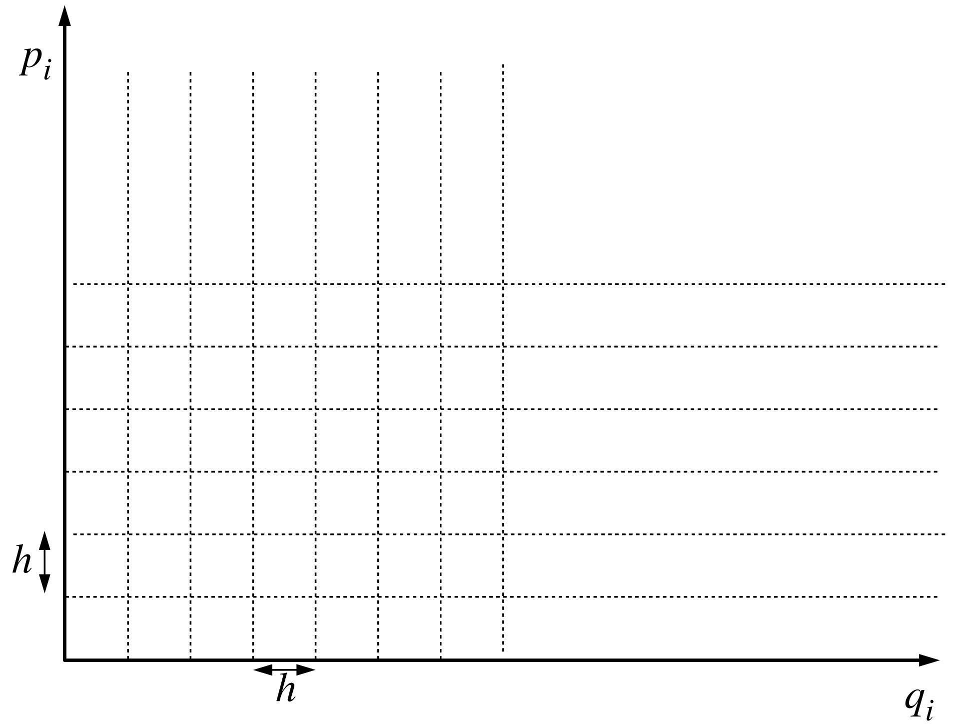

Figure 15-2: Illustration of the trick used to evaluate the partition function by counting degeneracy in quantum phase space with the uncertainty principle.

Because of the uncertainty principle:

$$\Delta p_i \Delta q_i \geq h \tag{15-6}$$

Each elementary volume, $(\Delta p \Delta q)_i$, in phase space must be considered to have degeneracy:

$$\frac{\Delta p_i \Delta q_i}{h} \tag{15-7}$$

Therefore, in the classical limit, each elementary box $dpdq$ will have a degeneracy of at least $1/h$.

$$Z = \sum_i e^{-\frac{E_i}{kT}} \approx \frac{1}{h^{3N}} \int \int \ldots \int_{-\infty}^{\infty} e^{-\frac{E(p_i, q_i)}{kT}} dp_1 dp_2 \ldots dp_{3N} dq_1 dq_2 \ldots dq_{3N} \tag{15-8}$$

or

$$Z = \frac{1}{h^{3N}} \int \int \ldots \int_{-\infty}^{\infty} e^{-\frac{\sum_i p_i^2/(2m_i) + \phi(q_1, q_2, \cdots, q_{3N})}{kT}} dp_1 dp_2 \ldots dp_{3N} dq_1 dq_2 \ldots dq_{3N} \tag{15-9}$$

Using the Harmonic approximations (Equation 15-1) for the minima and carrying out the integration over the momenta independently:[30]

[30]Note that $\int_{-\infty}^{\infty} e^{-\frac{p_1^2}{2m_1 kT}} dp_1 = \sqrt{2\pi m_1 kT}$.

$$Z_{min} = \left(\frac{2\pi kT}{h}\right)^{3N} \left(\prod_{i=1}^{3N} \frac{1}{\omega_i}\right) e^{-\frac{E_{min}}{kT}} \tag{15-10}$$

where each of the ω_i is the natural frequency near the potential ith well in Equation 15-1.

Carrying out the same process for the activated state (which has one less degree of freedom) except for the momentum p_1 that will have the slow mode as it traverses the saddle point, there are $3N-1$ natural frequency and one averaged velocity near the saddle point.

$$Z_A = L_A e^{-\frac{E_A}{kT}} \left(\frac{2\pi kT}{h}\right)^{3N-1} \left(\sqrt{\frac{m}{2\pi kT}}\right) \left(\prod_{i=2}^{3N-1} \frac{1}{\omega_i^A}\right) \tag{15-11}$$

The products over the vibrational modes can be related to the entropies of the states, i.e.,

$$\left(\prod_{i=2}^{3N-1} \omega_i^A\right) = \left(\frac{2\pi kT}{h}\right)^{3N-1} e^{-\frac{S^A}{k}} \tag{15-12}$$

Putting this all back into the expression for the rate of jumps,

$$\Gamma_{part} = \frac{kT}{h} e^{-\frac{(E_{part}^{mig} + P\Delta V_{part}^{mig} - TS_{part}^{mig})}{kT}} = \Gamma_{part} = \frac{kT}{h} e^{-\frac{G_{part}^{mig}}{kT}} \tag{15-13}$$

Advanced Topic: Variational Flows

Suppose that the free energy for the entire system can be written as an integral over the local volumes, to simplify the discussion consider one dimension:

$$F(c) = \int f(c, \partial c/\partial x, x) dx \tag{15-14}$$

where $f(c, c', x)$ represents an expression for the free energy density that might be a function of the local concentration $c(x, t)$, its spatial derivative $\partial c/\partial x$ and possibly on position. $F(c)$ is a *functional*—it takes a function as an argument and returns a scalar quantity, the free energy of the entire system at some time t. In other words, $F(c)$ is a recipe for calculating the energy for an arbitrary function $c(x, t)$.

Recall the discussion in the first few lectures about the gradient and directional derivative. One might consider if the field $c(x, t)$ is changing or *flowing* with velocity $v(x, t)$, how would this affect the total energy F? The recipe is:

$$F(c + vt) = \int f(c + vt, \partial(c + vt)/\partial x, x)dx \tag{15-15}$$

The instantaneous change of F due to the flow v can be obtained by taking the derivative with respect to t and evaluating at time $t = 0$:

$$\left.\frac{\partial F}{\partial t}\right|_{t=0} \equiv \frac{\delta F}{\delta c} \cdot v = \int \left[\frac{\partial f}{\partial c} v + \frac{\partial f}{\partial \partial c/\partial x}\frac{\partial v}{\partial x}\right] dx \tag{15-16}$$

Where $\frac{\delta F}{\delta c} \cdot v$ defines the "functional gradient" projected onto the velocity v—it is a directional derivative.

Integrating by parts[31]

$$\left.\frac{\partial F}{\partial t}\right|_{t=0} \equiv \frac{\delta F}{\delta c} \cdot v = \int \left[\frac{\partial f}{\partial c} - \frac{\partial}{\partial x}\frac{\partial f}{\partial \partial c/\partial x}\right] v dx \tag{15-17}$$

The part inside the brackets represents the gradients contribution local change of the field. If this acts like a directional derivative, then the energy changes the fastest when v is "antiparallel" to the local functional gradient:

$$v \propto -M\left[\frac{\partial f}{\partial c} - \frac{\partial}{\partial x}\frac{\partial f}{\partial \partial c/\partial x}\right] \tag{15-18}$$

This is a rule for how to choose the flow so that the free energy deceases as quickly as possible. Consider some examples that apply to diffusion. For a free energy density with a simple minimum:

$$f(c) = \frac{f''(c_{min})}{2}(c - c_{min})^2 \tag{15-19}$$

Since composition is locally conserved, then the flux must be antiparallel to the gradient of local functional gradient:

$$J(x, t) = -M\nabla\left[\frac{\partial f}{\partial c} - \frac{\partial}{\partial x}\frac{\partial f}{\partial \partial c/\partial x}\right] = -M\nabla f''(c_{min})(c - c_{min}) \tag{15-20}$$

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[31] The boundary conditions may be chosen to make the "$\left. uv \right|_{BC}$" part vanish, or the surface term may be considered to be small compared to the volume.

The conservation principle implies:

$$\frac{\partial c}{\partial t} = \nabla \cdot M f''(c_{min}) \nabla c \tag{15-21}$$

which is the diffusion equation with the thermodynamic factor.

Alternatively, one could consider the local energy density as being composed of the penalty for being inhomogeneous, in this case the local free energy penalty goes like:

$$f(c) = \kappa \left(\frac{\partial c}{\partial x} \right)^2 \tag{15-22}$$

where κ is a gradient energy coefficient.

In this case, the gradient is not conserved, so the linear kinetic approximation for the change in concentration field is:

$$\frac{\partial c}{\partial t} = -M \left[\frac{\partial f}{\partial c} - \frac{\partial}{\partial x} \frac{\partial f}{\partial \partial c / \partial x} \right] = M \frac{\partial^2 c}{\partial x^2} \tag{15-23}$$

which is another way to derive the diffusion equation. More details on this method can be found in Appendix D of KPIM.