Last Time

Strategies for Solving Problems

Numerical Methods

Random Walks

A Puzzle: Why for a random walk is $\nabla\mu = 0$?

3.21 Spring 2002: Lecture 10

The Successful Jump Frequency as an Activated Process

The treatment of diffusion as a statistical process permitted a physical correspondence between the macroscopic diffusivity and microscopic parameters for, average jump distance $\langle r \rangle$, jump correlation f, and the average frequency at which a jumper makes a finite jump Γ.

In this lecture, the statistical evaluation of microscopic process will be applied to the successful jump frequency Γ. A physical correspondence for Γ that is related to microscopic processes of attempt or natural atomic vibration frequency and the difference in energy between the potential energy of site and the maximum value of the minimum potential energy (the saddle energy) as the atom moves from one equilibrium site to the next.

The result that will be obtain, that the frequency of successful hops,

$$\Gamma = \nu e^{-\frac{E_{saddle} - E_{equil.}}{kT}} \tag{10-1}$$

is related to the natural frequency multiplied by a Boltzmann factor has remarkable general application.

Distribution of Energy among Particles

A fundamental result from statistical mechanics is that for an ensemble of atoms at a fixed temperature T, that the energies of the atoms has a characteristic probability distribution:

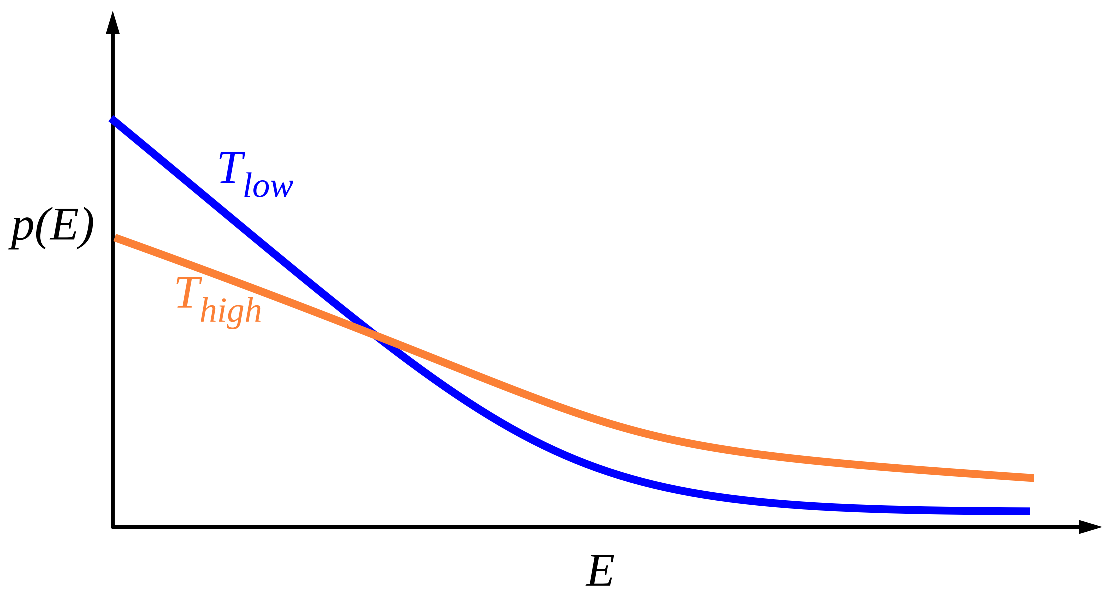

Figure 10-1: Schematic illustration of the distribution of energies at a fixed temperature, plotted for two different temperatures. $P(E) = \exp(-E/kT)/Z$ where Z is the normalizing factor (partition function) Z, such that $1 = \sum_E P(E)$.

Below, the rate of successful jumps for simple models of activated processes will be derived. Each derivation will depend on the distribution of energies given above. It will be supposed that a single atom will assume all possible values of energy with probabilities given by the Boltzmann distribution over time (the ergodic assumption). In other words, the distribution is considered to apply to the atoms at a time scale that is rapid compared to the natural frequency of the atoms—no correlation is made for the loss (or gain) of energy as an atom hops from one equilibrium site to the next.

Activation Processes in Square Wells

Consider an ensemble of particles with distributed energies moving about on the following energy landscape:

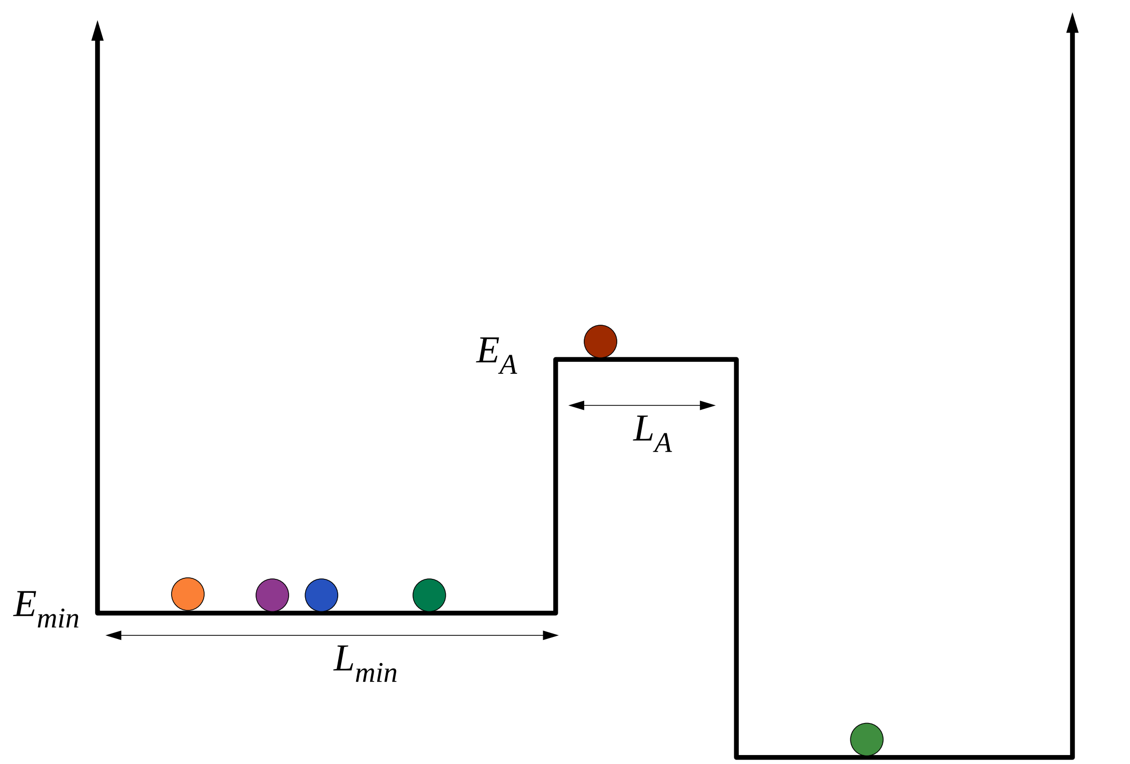

Figure 10-2: Simple model of activated process occurring between two square wells with an activation barrier of height E_A.

The characteristic time it takes a particle to cross the activated state is

$$\tau_{cross} \approx \frac{L_A}{v_{rms}} \approx L_A \sqrt{\frac{m}{kT}} \tag{10-2}$$

where $v_{rms} = \sqrt{\langle v^2 \rangle}$ and m is the mass of the particle with characteristic thermal energy kT.

The total rate, R_{cross}, that particles cross the barrier is

$$\begin{aligned} R_{cross} &= \frac{\text{(number of particles in activated state)}}{\tau_{cross}} \\ &= \frac{N_{tot}\,\text{(probability of being in activated state)}}{\tau_{cross}} \\ &= N_{tot}\sqrt{\frac{kT}{m}}\frac{1}{L_A}\frac{Z_A}{Z_{min}} \end{aligned} \tag{10-3}$$

where Z_A and Z_{min} are the partition functions for the activated and minimum states.

The rate that single particle crosses, Γ, is:

$$\Gamma = \sqrt{\frac{kT}{m}}\frac{1}{L_A}\frac{Z_A}{Z_{min}} \tag{10-4}$$

$$\frac{Z_A}{Z_{min}} = \frac{\int_{L_A} e^{-\frac{E(x)}{kT}} dx}{\int_{L_{min}} e^{-\frac{E(x)}{kT}} dx} = \frac{L_A}{L_{min}} e^{-\frac{E_A - E_{min}}{kT}} \tag{10-5}$$

Therefore,

$$\Gamma = \sqrt{\frac{kT}{m}} \frac{1}{L_{min}} e^{-\frac{E_A - E_{min}}{kT}} \tag{10-6}$$

The term that multiplies the Arrhenius factor (the 1/T exponential) is the characteristic time it takes a particle to make an attempt at the activated state.

Activation Processes in Harmonic Wells

Consider the following modification of the above simple case, the minima are treated as harmonic wells:

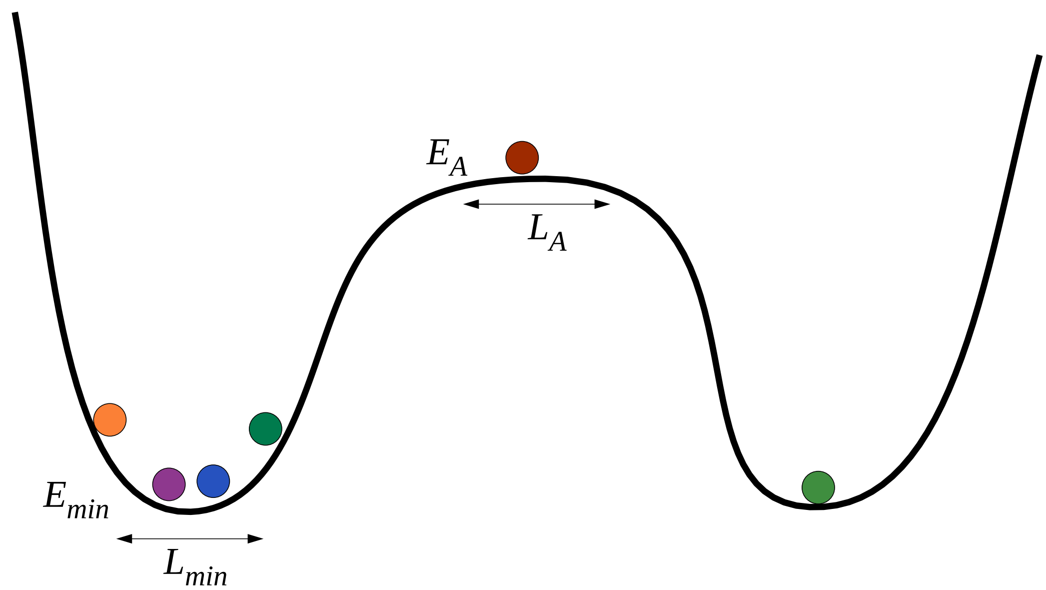

Figure 10-3: Modification to the simple square wells activated process by a harmonic potential for the equilibrium and saddle points.

The minima can be approximated by

$$E(x) = E_{min} + \frac{\beta}{2}(x - x_{min})^2 \tag{10-7}$$

The analysis is similar to the case of the square wells, but for the ratio of the partition functions:

$$\frac{Z_A}{Z_{min}} = \frac{\int_{L_A} e^{-\frac{E(x)}{kT}} dx}{e^{-\frac{E_{min}}{kT}} \int_{\frac{-L_{min}}{2}}^{\frac{L_{min}}{2}} e^{-\frac{\beta(x-x_{min})^2}{kT}} dx} \tag{10-8}$$

Approximating,

$$\int_{\frac{-L_{min}}{2}}^{\frac{L_{min}}{2}} e^{-\frac{\beta(x-x_{min})^2}{kT}} dx \approx \int_{-\infty}^{\infty} e^{-\frac{\beta(x-x_{min})^2}{kT}} dx \tag{10-9}$$

and carrying out the integration,

$$\Gamma = \sqrt{\frac{\beta}{m}} \frac{1}{\sqrt{2\pi}} e^{-\frac{E_A - E_{min}}{kT}} = \omega_o e^{-\frac{E_A - E_{min}}{kT}} \tag{10-10}$$

where ω_o is the characteristic oscillating frequency at the minima of a particle with mass m sitting in a well of curvature β.

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:

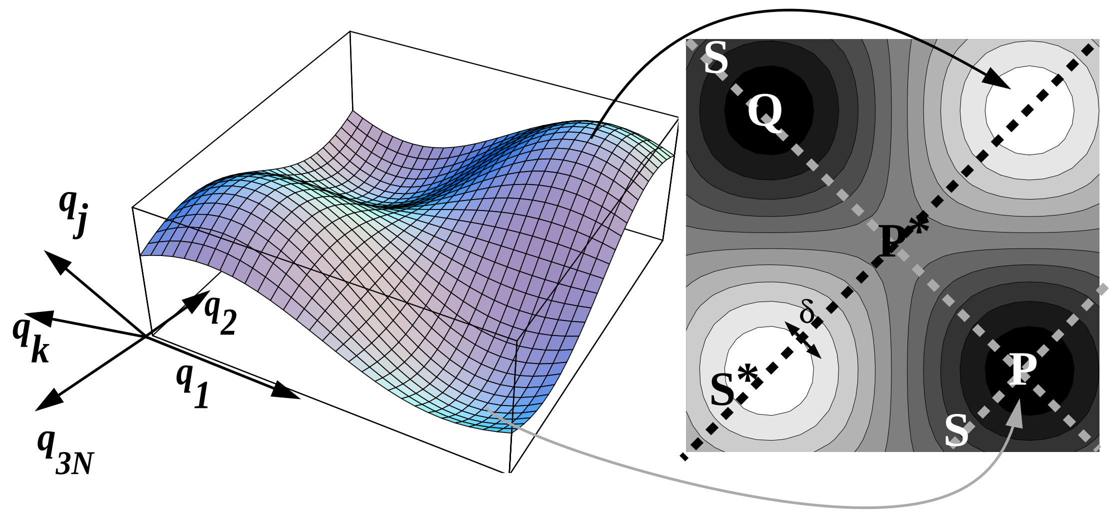

Figure 10-4: A schematic representation of the $3N$-dimensional (positions) surface for a crystal with N sites. The minima are located at P and Q and it may be supposed, for simplicity, that a particle that jumps from P to Q does so along the trajectory S crossing through a maximum of width δ at the 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:

$$E(q_i) = E_{min} \sum_{i=1}^{3N} \frac{m_i \omega_i^2}{2} q_i^2 \qquad (10\text{-}11)$$

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 10-4. It can be supposed that trajectory $P \rightarrow Q$ 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 10-4. Therefore, the rate of crossing can be related to the average velocity in the activated state and the "effective width" in the activated state.[23]

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

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:

$$\Gamma = \sqrt{\frac{kT}{m}}\frac{1}{L_A}\text{(fraction of particles in activated state)} \tag{10-12}$$

where L_A is recognized to be the width δ in Figure. 10-4.

However, in this case, the particle may have a different volume in the activated state compared to the equilibrium state:[24]

$$\Delta V_{part}^{mig} = V_{part}^{A} - V_{part}^{eq} \tag{10-13}$$

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

$$Z_P = \sum_{energies,\ volumes} e^{-\frac{(E+PV)}{kT}} \tag{10-14}$$

Therefore Γ_{part} picks up an additional factor:

$$\Gamma_{part} = \sqrt{\frac{kT}{m}}\frac{1}{L_A}e^{\frac{-P\Delta V_{part}^{mig}}{kT}}\frac{Z_A}{Z_{min}} \tag{10-15}$$

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:

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

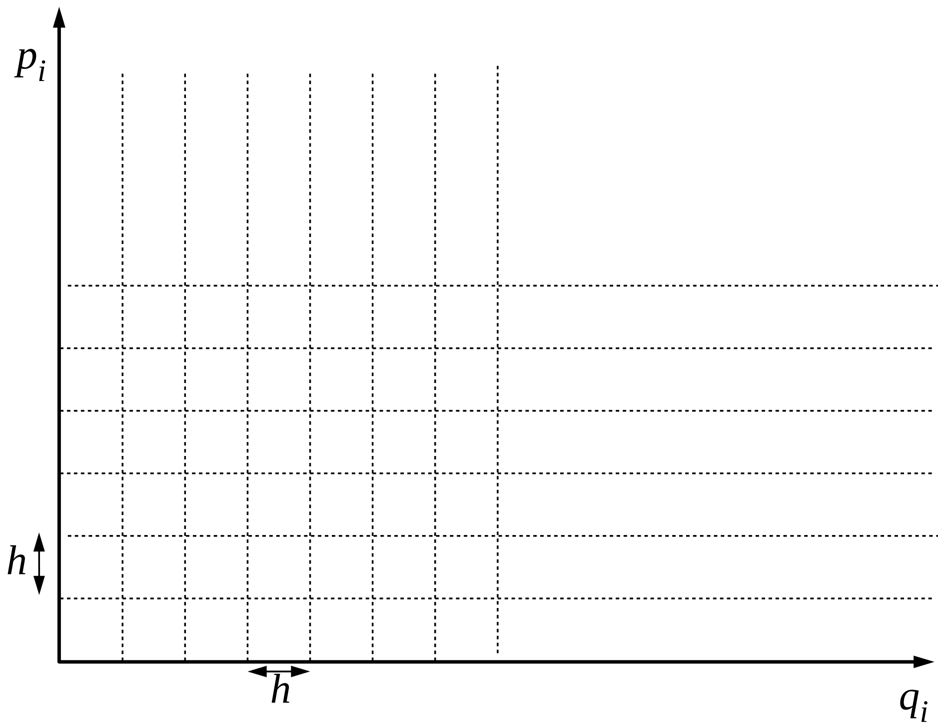

Figure 10-5: Illustration of the trick used to evaluate the partition function by counting degeneracy in quantum phase space with the uncertainty principle.

Because of the uncertainty principle:

$$\Delta p_i \Delta q_i \geq h \tag{10-16}$$

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

$$\frac{\Delta p_i \Delta q_i}{h} \tag{10-17}$$

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

$$Z = \sum_i e^{-\frac{E_i}{kT}} \approx \frac{1}{h^{3N}} \int \int \ldots \int_{-\infty}^{\infty} e^{-\frac{E(p_i,q_i)}{kT}} dp_1 dp_2 \ldots dp_{3N} dq_1 dq_2 \ldots dq_{3N} \tag{10-18}$$

or

$$Z = \frac{1}{h^{3N}} \int \int \ldots \int_{-\infty}^{\infty} e^{-\frac{\sum_i p_i^2/(2m_i) + \phi(q_1, q_2, \cdots, q_{3N})}{kT}} dp_1 dp_2 \ldots dp_{3N} dq_1 dq_2 \ldots dq_{3N} \tag{10-19}$$

Using the Harmonic approximations (Equation 10-11) for the minima and carrying out the integration over the momenta independently:[25]

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

$$Z_{min} = \left(\frac{2\pi kT}{h}\right)^{3N} \left(\prod_{i=1}^{3N} \frac{1}{\omega_i}\right) e^{-\frac{E_{min}}{kT}} \tag{10-20}$$

where each of the ω_i is the natural frequency near the potential ith well in Equation 10-11.

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.

$$Z_A = L_A e^{-\frac{E_A}{kT}} \left(\frac{2\pi kT}{h}\right)^{3N-1} \left(\sqrt{\frac{m}{2\pi kT}}\right) \left(\prod_{i=2}^{3N-1} \frac{1}{\omega_i^A}\right) \tag{10-21}$$

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

$$\left(\prod_{i=2}^{3N-1} \omega_i^A\right) = \left(\frac{2\pi kT}{h}\right)^{3N-1} e^{-\frac{S^A}{k}} \tag{10-22}$$

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

$$\Gamma_{part} = \frac{kT}{h} e^{-\frac{(E_{part}^{mig} + P\Delta V_{part}^{mig} - TS_{part}^{mig})}{kT}} = \Gamma_{part} = \frac{kT}{h} e^{-\frac{G_{part}^{mig}}{kT}} \tag{10-23}$$