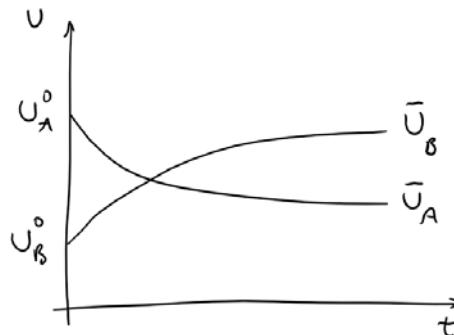


Lecture 23 – Kinetic theory

PREVIOUSLY: So far we've dealt with systems at equilibrium (e.g. two systems in thermal contact), but said very little about how equilibrium is reached over time.

There are 3 mechanisms of heat transfer:

- Radiation – interaction of light with matter (Lect. 24)
- Conduction – interaction of matter with matter (e.g. molecular collisions) (Lect. 25)
- Convection – bulk flow (not covered in Phys. 427)



TODAY: Kinetics

Recall from Lect. 1-2 that the notion of a statistical ensemble is that a system can explore all its accessible microstates*, subject to some constraints (e.g. constant total energy U in isolated system, constant temperature T in a system in thermal equilibrium with a reservoir)

$$N = n_{\uparrow} + n_{\downarrow}$$

Ex: in isolated paramagnetic system with N independent spins, we considered all possible spin configurations that have the same total energy, i.e. the multiplicity $\Omega(U, N)$.

For all microstates to be accessible, transitions between microstates must occur (in this example, spin flips) over a reasonable time period.

Transitions between microstates are essential for a system to reach equilibrium.

*Note: we may ask whether a single system can explore the same number of microstates over time as an ensemble of independently prepared systems. The assumption that they do is called the ergodic hypothesis. The property that the ensemble average = time average is called ergodicity.

KEY CONCEPT: Master equation

How do we quantify transitions between states?

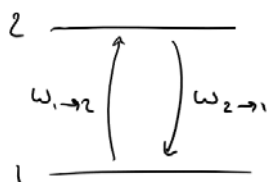
Define $P_i(t)$ as the probability that the system is found in state i at time t .

- $P_i(t)$ will increase with time if transitions are made into state i from other states,
- $P_i(t)$ will decrease with time if transitions are made out of state i into other states.

Define $w_{i \rightarrow j}$ as the transition probability per unit time between states i and j

Consider a 2-state system for simplicity

For state 1:



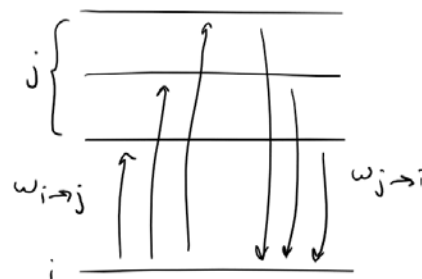
$$\frac{dP_1}{dt} = w_{2 \rightarrow 1}P_2 - w_{1 \rightarrow 2}P_1$$

The first term on the right is the rate from state 2 to 1, which must be proportional to the probability of being in state 2, $P_2(t)$. The second term is the rate out of state 1 into state 2, which is proportional to $P_1(t)$.

A similar expression for state 2 can be obtained

For an arbitrary number of states:

$$\frac{dP_i}{dt} = \sum_j \underset{\substack{\uparrow \\ \text{transition rate} \\ \text{into state } i}}{w_{j \rightarrow i}P_j} - \sum_j \underset{\substack{\uparrow \\ \text{transition rate} \\ \text{out of state } i}}{w_{i \rightarrow j}P_i}$$



This is called the master equation. It is one of the most important equations in non-equilibrium statistical mechanics.

KEY CONCEPT: the principle of detailed balance

Let's consider that state occupancies have become stationary so $dP_i/dt = 0$, i.e. steady-state is reached

We can satisfy the steady-state condition by:

$$\sum_j w_{j \rightarrow i}P_j = \sum_j w_{i \rightarrow j}P_i$$

where the sum of transitions into state i are balanced by transitions out of state i

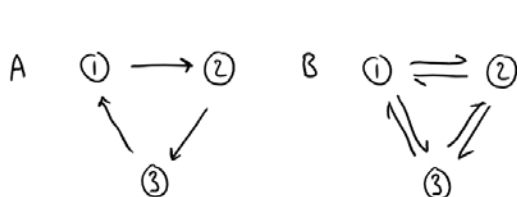
However, there is a stronger statement that satisfies the steady-state condition:

$$w_{j \rightarrow i}P_j = w_{i \rightarrow j}P_i$$

where each individual transition is balanced, i.e. the number of transitions per time from a state j to i = the number of transitions per time from i to j . This is called detailed balance.

To illustrate steady-state with detailed balance and without, consider a three-state system:

Question 1: Write the master equation for state 1 in case A, where detailed balance is violated, and B, where it is satisfied



In case A: $\frac{dP_1}{dt} = -w_{1 \rightarrow 2}P_1 + w_{3 \rightarrow 1}P_3,$

Steady-state is satisfied by $w_{1 \rightarrow 2}P_1 = w_{3 \rightarrow 1}P_3$ (also $= w_{2 \rightarrow 3}P_2$). Note that there is a circulating “current” or flux around the cycle from $1 \rightarrow 2 \rightarrow 3$.

In case B: $\frac{dP_1}{dt} = (-w_{1 \rightarrow 2}P_1 + w_{2 \rightarrow 1}P_2) + (-w_{1 \rightarrow 3}P_1 + w_{3 \rightarrow 1}P_3)$

With detailed balance, $w_{1 \rightarrow 2}P_1 = w_{2 \rightarrow 1}P_2$, $w_{1 \rightarrow 3}P_1 = w_{3 \rightarrow 1}P_3$ (also $w_{2 \rightarrow 3}P_2 = w_{3 \rightarrow 2}P_3$). Note that there is no net current around the cycle.

KEY CONCEPT: steady-state vs. equilibrium

At equilibrium, a system is at steady-state, i.e. the system no longer evolves vs. time. Steady-state is necessary but NOT sufficient for equilibrium. Equilibrium also must satisfy detailed balance, i.e each transition is balanced by its reverse.

Ultimately, this is because microscopic reversibility—i.e. microscopic dynamics (governed by Newton or Schrödinger equation) being symmetric with respect to time reversal—ensures that an individual transition is balanced by its reverse.

A couple other points about equilibrium:

1. For a closed (or isolated) system, the fundamental assumption (Lect. 1) states that each microstate is equally likely, i.e. $P_i = P_j$, so

$$w_{j \rightarrow i} = w_{i \rightarrow j}$$

Transitions between states of equal energy have identical transition probabilities

2. For a system in thermal equilibrium with a reservoir, the probability of a microstate is given by the Boltzmann factor (Lect. 5): $P_i = e^{-\epsilon_i/k_B T} / Z$, so detailed balance means

$$\frac{w_{j \rightarrow i}}{w_{i \rightarrow j}} = \frac{P_i}{P_j} = e^{-(\epsilon_i - \epsilon_j)/k_B T}$$

Transition probability from high to low energy > transition probability from low to high energy

(For more on this read Reif Ch. 15)

Ex: Einstein A and B coefficient

Consider a gas of atoms at equilibrium with thermal photons in a cavity at temperature T

We'll assume that the electronic energy levels are such that we can consider two levels E_1 and E_2 and ignore all others

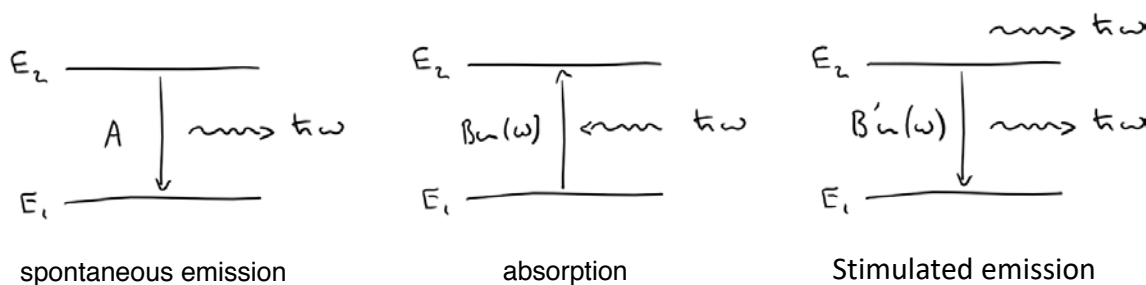
Interactions between the atoms and the photons allow transitions between energy levels. There are 3 mechanisms for transitions:

1. Spontaneous emission. Electrons in state 2 spontaneously decay to 1. By conservation of energy, the photon energy is: $\hbar\omega = E_2 - E_1$. Let A = transition probability
2. Absorption. Electrons in state 1 absorb a photon of energy $\hbar\omega = E_2 - E_1$ and transition to 2. The transition depends on the availability of photons at the appropriate energy, which is given by the energy spectrum $u(\omega)$ from the Planck distribution (Lect. 13):

$$u(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\beta\hbar\omega} - 1}$$

The transition probability = $Bu(\omega)$

3. Stimulated emission. Electrons in state 2 can be stimulated to emit a photon of energy $\hbar\omega = E_2 - E_1$ by the presence of other photons of that energy (equivalent to negative absorption; this is the principle of the laser). The transition again depends on the photon energy spectrum $u(\omega)$. The transition probability = $B'u(\omega)$



Question 2: Write a) the detailed balance condition for this system, and b) use the fact that the system is at equilibrium to find a relation between A , B and B' in terms of constants.

a) Writing the master equation for state 1:

$$\frac{dP_1}{dt} = 0 = (A + B'u(\omega))P_2 - Bu(\omega)P_1$$

b) At equilibrium, the state probabilities are proportional to Boltzmann factors. (Note: we assume there is no degeneracy to worry about).

$$\frac{P_1}{P_2} = e^{-\beta(E_1 - E_2)} = e^{\beta\hbar\omega} \quad \text{so} \quad \frac{A + B' u(\omega)}{B u(\omega)} = \frac{P_1}{P_2} = e^{\beta\hbar\omega}$$

which simplifies to:

$$A(e^{\beta\hbar\omega} - 1) = \frac{\hbar\omega^3}{\pi^2 c^3} (B e^{\beta\hbar\omega} - B')$$

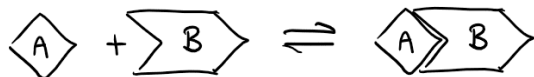
This relation must be true for all temperatures, so the only solution is that:

$$A = B \frac{\hbar\omega^3}{\pi^2 c^3} \quad \text{and} \quad B' = B$$

These Einstein relations (1917) show that any one constant determines the others. Note that there is no way to achieve detailed balance at all T without all three processes.

Ex: chemical kinetics

We can use the master equation to quantify the kinetics of a chemical reaction



Consider a simple chemical reaction: $A + B \rightleftharpoons AB$
(Recall that $[A]$, $[B]$, and $[AB]$ are concentrations of the chemical species)

The probability of being in species AB, $P_{AB} \propto N_{AB} \propto [AB]$, so the rate out of AB is also $\propto [AB]$

The rate into AB depends on molecules of species A and B simultaneously encountering. This will be proportional to both $[A]$ and $[B]$

Putting it all together, the master equation for the product AB has the form:

$$\frac{d[AB]}{dt} = k_+ [A][B] - k_- [AB]$$

k_+ and k_- are called rate constants for the forward (+) and reverse (−) reactions.

k_- has units of $1/[\text{time}]$ (usually s^{-1}) and is referred to as a first order rate constant.

k_+ has units of $1/([\text{concentration}] \times [\text{time}])$ (usually $\text{M}^{-1} \text{s}^{-1}$, where 1 molar = 1 M = 1 mol/L) and is referred to as a second order rate constant. It describes the rate of a bimolecular collision.

At equilibrium $\frac{d[AB]}{dt} = 0$, and $\frac{[AB]}{[A][B]} = \frac{k_+}{k_-}$

Compare this to the law of mass action (Lect. 11)*:

$$\frac{[AB]n_0}{[A][B]} = e^{-\Delta G^0/k_B T} = K(T)$$

where n_0 is a reference concentration (standard is 1 M), so

$$\frac{k_+}{k_-} = K(T) = e^{-\Delta G^0/k_B T}$$

(customarily, the n_0 is dropped since it is equal to 1. As long as we express all concentrations in M, the numbers will be correct)

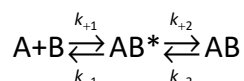
*Recall chemical equilibrium (Lect. 11):

The reaction can be written as $-1 \cdot A - 1 \cdot B + 1 \cdot AB = 0$, so $-\mu_A - \mu_B + \mu_{AB} = 0$

For a dilute solution, the chemical potential is $\mu_i = \mu_i^0 + k_B T \ln \frac{n_i}{n_0}$, so

$$k_B T \ln \left(\frac{[A][B]}{[AB]n_0} \right) = \underbrace{-\mu_A^0 - \mu_B^0 + \mu_{AB}^0}_{\Delta G^0(T, p_0)} \quad \text{or} \quad \frac{[AB]}{[A][B]} n_0 = e^{-\Delta G^0/k_B T} = K(T)$$

Question 3: Consider the following two-step chemical reaction below with an intermediate state AB^* . Write the law of mass action $[AB]/[A][B]$ in terms of rate constants of the reaction:



(Hint: write down the master equation for the reactants and product)

$$\frac{d[A]}{dt} = 0 = k_{-1}[AB^*] - k_{+1}[A][B] \quad \text{and} \quad \frac{d[AB]}{dt} = 0 = k_{+2}[AB^*] - k_{-2}[AB]$$

At steady-state: $\frac{[AB^*]}{[A][B]} = \frac{k_{+1}}{k_{-1}}$ and $\frac{[AB]}{[AB^*]} = \frac{k_{+2}}{k_{-2}}$

Multiplying the two: $\frac{\cancel{[AB^*]}}{[A][B]} \frac{[AB]}{\cancel{[AB^*]}} = \frac{[AB]}{[A][B]} = \frac{k_{+1}k_{+2}}{k_{-1}k_{-2}} = K(T)$

Note that since $K(T)$ is a function of T , it follows that the rate constants must be as well.