

1 Statistical thermodynamics

Irreversibility and attainment of equilibrium

1.1 Equilibrium conditions and constraints

Equilibrium condition: The system is equally likely to be found in any accessible states.

“accessible states”: some specific conditions/constraints of system, these limit the number of states the system can be possibly found.

Furthermore, how does the change of constraints change the number of accessible states?

Examples:

- Box divided (partition) into two equal parts: left half is filled with gas, and the right half is empty. After removing the partition (constraint), the gas spreads, but the probability of the gas being in the left half is much smaller, $\frac{1}{2^N}$. Rather, we would expect an equal number of particles on each side for $N \rightarrow N_A$.
- Box with insulating wall constrained to move: If the barrier freely moves, we would expect the Pressures to equalize $P = P'$
- Box with noninsulating wall (can't move): We would expect temperature to be equal $T = T'$

After the states reach equilibrium, if we added the constraint back in, the system would not go back to the original state! (irreversible process)

But what is temperature???

- Kinetic energy? Heat transfer?
- Perhaps macroscopically: flow of heat from one system to another by touch (thermal contact)

1.2 Distribution of energy between systems via heat

Consider two systems A and A' :

- A : Energy E , Number of states $\Omega(E)$
- A' : Energy E' , Number of states $\Omega(E')$

where $\Omega(E)$ is the # of states in A with energy range $(E, E + \delta E)$

The total combined system $A^{(0)}$, with number of states $\Omega^{(0)}$, has a constant total energy,

$$E^{(0)} = E + E' = \text{constant}$$

where we define: $\Omega^{(0)}(E)$: # of states accessible to $A^{(0)}$ when the subsystem A has energy $(E, E + \delta E)$.

When $A^{(0)}$ is in equilibrium the probability is proportional to the number of accessible states:

$$P(E) \propto \Omega^{(0)}(E), \quad \text{or} \quad P(E) = \frac{\Omega^{(0)}(E)}{\sum_E \Omega^{(0)}(E)} = C \Omega^{(0)}(E)$$

where C is a constant.

Multiplicity

$$\Omega^{(0)}(E) = \Omega(E) \Omega'(E^{(0)} - E)$$

Now, the probability $P(E)$ with E is

$$P(E) = C \Omega(E) \Omega'(E^{(0)} - E)$$

Graphically, we would expect E vs. $\Omega(E)$ to increase (as E increases, $\Omega(E)$ increases), and same with E' vs. $\Omega'(E')$. But E vs. $\Omega'(E^{(0)} - E)$ would decrease. In addition, the probability $P(E)$ as a function of E would have a sharp peak near the equilibrium \tilde{E} .

Finding maximum Take the derivative (of the log because multiplication becomes addition):

$$\frac{\partial \ln P(E)}{\partial E} = 0, \quad \ln P(E) = \ln C + \ln \Omega(E) + \ln \Omega'(E^{(0)} - E)$$

hence

$$\frac{\partial \ln P(E)}{\partial E} = \frac{\partial \ln(\Omega(E))}{\partial E} - \frac{\partial \ln(\Omega'(E'))}{\partial E'} = 0$$

Thermodynamic beta (Wikipedia) Define β :

$$\beta = \frac{\partial \ln \Omega(E)}{\partial E}$$

where at equilibrium, $\beta(\tilde{E}) = \beta'(\tilde{E}')$

Then we introduce a *dimensionless* parameter T such that

$$\boxed{kT = \frac{1}{\beta}}$$

where k (k_B everywhere else) is the Boltzmann constant. Therefore, temperature characterizes the variation of density of state with energy.

Entropy From temperature and defining entropy $S(E)$:

$$\begin{aligned} \frac{1}{T} = k\beta &= \frac{\partial k \ln \Omega(E)}{\partial E}, \quad S(E) = k \ln \Omega(E) \\ &= \frac{\partial S}{\partial E} \end{aligned}$$

Worksheet

1. # of energy levels $\Phi_1(\epsilon) \leq \frac{\epsilon}{\Delta\epsilon} = C\epsilon$
2. Average energy per molecule is $\epsilon = E/f$ (f molecules)

$$\Phi(E) = (\Phi_1(\epsilon))^f$$

3.

$$\begin{aligned} \Omega(E) &= \Phi(E + \delta E) - \Phi(E) \\ &= \frac{\partial \Phi(E)}{\partial E} \delta E, = \Phi_1^{f-1} \frac{\partial \Phi_1}{\partial \epsilon} \delta E \end{aligned}$$

4. If f is very large

$$\begin{aligned} \ln \Omega &= (f-1) \ln \Omega(\epsilon) + \dots \\ &\approx f \ln \Omega(\epsilon) \end{aligned}$$

5. So

$$\Omega \propto \phi_1(\epsilon)^f \propto E^f$$

Review of last time: What is temperature?

For two systems A and A' that present heat exchange:

- $E^{(0)} = E + E'$: total energy is constant
- At thermal equilibrium, the temperature of the systems are the same.
- $P(E) \propto \Omega^{(0)}(E)$: probability of finding system A to have energy E is proportional to the number of accessible states in the total system A^0 .
- $\Omega^{(0)}(E) = \Omega(E)\Omega'(E^{(0)} - E)$: multiplicity
- To find the maximum, take the derivative to zero:

$$\begin{aligned} \frac{\partial \ln P(E)}{\partial E} &= 0 \\ \Rightarrow \frac{\partial \ln \Omega(E)}{\partial E} &= \frac{\partial \ln \Omega'(E^{(0)} - E)}{\partial E'} \end{aligned}$$

where

$$\beta = \frac{\partial \ln \Omega(E)}{\partial E} \quad \text{and} \quad kT = \frac{1}{\beta}$$

and at equilibrium, $\beta(\tilde{E}) = \beta'(\tilde{E}')$ Finally, we define entropy $S(E)$ as

$$S(E) = k \ln \Omega(E)$$

where $S + S' = \text{maximum at equilibrium}$

[insert figure graph of $P(E), \Omega(E), \Omega'(E')$]

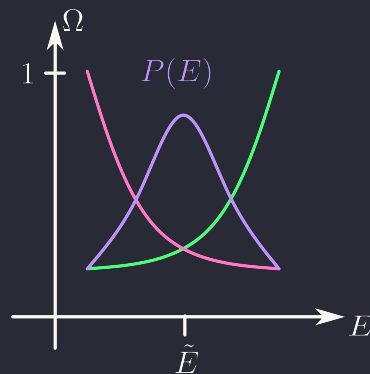


Figure 1.1: Graph of $P(E), \Omega(E)$ (green), $\Omega'(E')$

What is kT ?

We replace $\Omega \sim E^f$ so

$$\begin{aligned} \frac{1}{kT} = \beta &= \frac{\partial \ln \Omega}{\partial E} \approx f \frac{\partial \ln E}{\partial E} = \frac{f}{E} \\ \Rightarrow kT &\approx \frac{\bar{E}}{f} \end{aligned}$$

so kT roughly represents energy per atom. Or

kT is a measure of the mean energy above the ground state per atom

- In the hydrogen atom, if $kT \geq \Delta$ (energy difference between the ground state and the first excited state), then the atom can be excited.

- Room temperature (300 K) is roughly $kT \approx 1/40 \text{ eV} = 25 \text{ meV}$
- A superconducting qubit of energy (usually in GHz) $25 \mu\text{eV}$ uses temperature in the magnitude of 15 mK: Backwards calculation: Going from 300K to 25 meV means we need to go to 0.3 K, but 0.03 K for the precision, to be in the range of the qubit.

1.3 Approach to equilibrium

Given A, A' we have average initial energy \bar{E}_i, \bar{E}'_i : At equilibrium

$$\begin{aligned}\bar{E}_f &= \tilde{E} \\ \bar{E}'_f &= \tilde{E}' = E^{(0)} - \tilde{E}\end{aligned}$$

The heat exchange is

$$\begin{aligned}Q &= \bar{E}_f - \bar{E}_i \\ Q' &= \bar{E}'_f - \bar{E}'_i\end{aligned}$$

where the total heat is constant, $Q + Q' = 0$.

- The system that absorbs heat is “colder”
- The system that releases (gives off) heat is “hotter”

1.4 Temperature

Properties of T :

- If the two systems have same T , they will remain in equilibrium when brought together.
- Zeroth Law of Thermodynamics: If two systems are in thermal equilibrium with a 3rd system, then they must be in equilibrium with each other.

This allows us to use a test system as a “thermometer”: a small system that has a macroscopic parameter that varies when brought into contact with another system.

1.5 Heat Reservoir

A heat reservoir A' with temp T' transfers heat to a smaller system A with temp T :

- $T \rightarrow T'$
- T' does not change!

Using the parameter $\beta' = \beta'(E')$ (where it is inversely related to temp),

$$\left| \frac{\partial \beta'}{\partial E'} Q' \right| \ll \beta'$$

which pretty much tells us that $\Delta \beta' \ll \beta'$, so the temperature of the reservoir does not change.

The change of the density of states of the reservoir is

$$\ln \Omega'(E' + Q') - \ln \Omega'(E')$$

where the Taylor expansion gives us

$$= \frac{\partial \ln \Omega'}{\partial E'} Q' = \beta' Q'$$

This is proportional to the change of entropy:

$$\begin{aligned}\Delta S' &= k(\ln \Omega'(E' + Q) - \ln \Omega'(E')) \\ \beta' Q' k &= \frac{Q'}{T'}\end{aligned}$$

Simply,

$$\Delta S' = \frac{Q'}{T'} \quad (\text{for a heat reservoir})$$

If one assumes an infinitesimal amount of heat dQ

$$dS' = \frac{dQ'}{T'}$$

which is the 2nd law of thermodynamics.

The first law of thermodynamics is (as we discovered)

$$dE + dW = dQ$$

1.6 Dependence on Density of States (DoS) on external parameters

$\Omega(E, x)$ where x is an external parameter. The change of energy is

$$\frac{\partial E}{\partial x} dx \quad \text{where} \quad X = -\frac{\partial E}{\partial x} \quad \text{“generalized force”}$$