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 specfic conditions/constraints of sysem , these limit the numebr 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 $N \to N_A$.

- 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 contraint back in, the system would not go back to the original state! (irreverssible 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 $S(E)$:

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

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.

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

4. If f is very large

$$\ln \Omega = (f - 1) \ln \Omega(\epsilon) + \ldots$$
$$\approx f \ln \Omega(\epsilon)$$

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:

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

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

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' = $ maximum at equilibrium

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

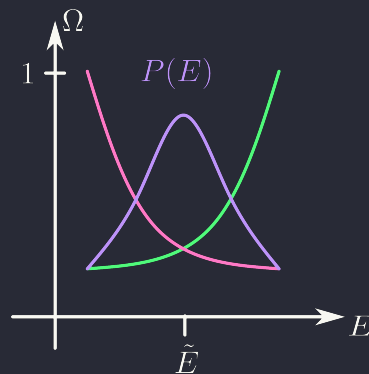Figure 1.1: Graph of $P(E), \Omega(E)$ (green), $\Omega'(E')$

What is kT?

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

$$\frac{1}{kT} = \beta = \frac{\partial \ln \Omega}{\partial E} \approx f \frac{\partial \ln E}{\partial E} = \frac{f}{\bar{E}}$$

$$\implies kT \approx \frac{\bar{E}}{f}$$

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 $kT \approx 1/40$ eV = 25 meV

- A superconducting qubit of energy (usually in GHz) 25 μeV 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

$$\bar{E}_f = \tilde{E}$$
$$\bar{E}'_f = \tilde{E}' = E^{(0)} - \tilde{E}$$

The heat exchange is

$$Q = \bar{E}_f - \bar{E}_i$$
$$Q' = \bar{E}'_f - \bar{E}'_i$$

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:

- $T \to T'$

- 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:

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

Simply,

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

If one assumes an infinitesimal amount of heat $đQ$

$$\boxed{dS' = \frac{đQ'}{T'}}$$

which is the 2nd law of thermodynamics.

The first law of thermodynamics is (as we discovered)

$$dE + đW = đQ$$

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

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

Review

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

$$ds = \frac{dQ}{T}, \quad S = k \ln \Omega$$

1.7 Density of states on external parameters

When a parameter $x \to x + dx$ the energy of each microstate r changes by

$$\frac{\partial E_r}{\partial x} dx$$

where

$$X = -\frac{\partial E_r}{\partial x}$$

is the generalized force.

- $\Omega(E, x)$: external parameter x for the # of states in $[E, E + \delta E]$.

- $\Omega_Y(E, x)$: # of states in $[E, E + \delta E]$ *with* $Y = \frac{\partial E_r}{\partial x}$ in $[Y, Y + \delta Y]$

The total number of states is now

$$\Omega(E, x) = \sum_Y \Omega_Y(E, x)$$

Consider energy E when $x \to x + dx$:
some states r originally with energy $< E$ Can now aquire energy $> E$:

- $\sigma(E)$: # of state of originally

- $\sigma_Y(E)$: \$ of states ... with $Y = \frac{\partial E_r}{\partial x}$ in $[Y, Y + \delta Y]$

For a given E, Y; the work done is the generalized force times the change in the parameter $Y\,dx$ which is like the width of the rectangle below the energy E.

Above the energy $[E, E + \delta E]$ we can treat the total area as the total # of states $\Omega_Y(E, x)$, and dividing by the width δE kind of gives us a linear density of states per unit energy. Finally we can find σ_Y by getting the area

$$\sigma_Y(E) = \frac{\Omega_Y(E, x)}{\delta E} Y\,dx$$

and thus

$$\sigma(E, x) = \sum_Y \sigma_Y(E, x) = \sum_Y \frac{\Omega_Y(E, x)}{\delta E} Y\,dx$$

$$= \frac{\Omega(E, x)}{\delta E} \bar{Y}\,dx$$

$$\bar{Y} = \frac{1}{\Omega(E, x)} \sum_Y Y \Omega_Y(E, x)$$

The change of the DoS is

$$\frac{\partial \Omega(E, x)}{\partial x} dx = \sigma(E) - \sigma(E + \delta E) = -\frac{\partial \sigma(E)}{\partial E} \delta E$$

on the RHS

$$\frac{\partial \sigma(E, x)}{\partial E} = \frac{dx}{\delta E} \frac{\partial \Omega \bar{Y}}{\partial E}$$

and thus

$$\frac{\partial \Omega(E,x)}{\partial x} = -\frac{\partial \Omega \bar{Y}}{\partial E} = -\frac{\partial \Omega}{\partial E}\bar{Y} - \Omega\frac{\partial \bar{Y}}{\partial E}$$

dividing both sides by Ω

$$\frac{1}{\Omega}\frac{\partial \Omega}{\partial x} = -\frac{1}{\Omega}\frac{\partial \Omega}{\partial E}\bar{Y} - \frac{\partial \bar{Y}}{\partial E}$$

where

$$\frac{\partial \ln \Omega}{\partial x} = \frac{1}{\Omega}\frac{\partial \Omega}{\partial x}, \quad \frac{\partial \ln \Omega}{\partial E} = \frac{1}{\Omega}\frac{\partial \Omega}{\partial E}$$

and another trick: the second term is $\sim \bar{Y}/E$ and $\Omega \sim E^f$ so we can drop the second term

$$\frac{\partial \ln \Omega}{\partial x} = -\frac{\partial \ln \Omega}{\partial E}\bar{Y} = \beta\bar{X}$$

Recap: For a system with states $\Omega(E,x)$ we are give

$$\boxed{\frac{\partial \ln \Omega}{\partial E} = \beta}, \quad \boxed{\frac{\partial \ln \Omega}{\partial x} = \beta\bar{X}}$$

The second equation tells us that doing work will obviously increase Ω.

The rubber band example: Stretching the rubber band (work done) adds energy or heat to the system.

1.8   Equilibrium of interacting systems

$\Omega^{(0)}(E,x)$ will be maximum at $\tilde{E}, \tilde{x}$.

Consider an infinitesimal quasi-static process where A and A' are brought from equiilibrium to another state $\tilde{E} + d\tilde{E}, \tilde{x} + d\tilde{x}$.

The differential of the log Dos is (using math)

$$\begin{aligned}
d\ln\Omega(E,x) &= \frac{\partial \ln \Omega}{\partial E}d\tilde{E} + \frac{\partial \ln \Omega}{\partial x}d\tilde{x} \\
&= \beta(d\tilde{E} + Xd\tilde{x}) \quad Xd\tilde{x} = đW \\
&= \beta đQ \\
kd\ln\Omega(E,x) &= \frac{đQ}{T}
\end{aligned}$$

where $S = k\ln\Omega$ or equivalently

$$dS = \frac{đQ}{T}$$

Case 1 : Thermally isolated and quasi-static process

$$đQ = 0 \implies \Delta S = 0$$

thus a **reversible process**

Worksheet   A gas with N atoms confined to half a box is released to fill the whole container:
Given

- Ideal gas: $PV = NkT$

- Average energy: $\bar{E}(T) = \frac{3}{2}NkT$

(i) Change in entropy $S = k \ln \Omega$: Originally we have only 1 macrostate or Ω_0 microstates, and now the total number of arrangements is $\Omega_0 2^N$ so

$$\Delta S = k \ln \Omega_0 2^N - k \ln \Omega_0 = Nk \ln 2$$

where we have a volume independence $\Omega \sim V^N X(E)$.

(ii) Defining a quasi-static process where energy doesn't change from initial to final state: We can now use

$$dS = \frac{đQ}{T}$$

and for a quasi-static process

$$đQ = \cancel{d\bar{E}} + đW$$
$$đQ = đW = PdV$$

So

$$\Delta S = \int ds = \int_{V_0}^{2V_0} \frac{PdV}{T} = \int_{V_0}^{2V_0} \frac{Nk}{V}dV = Nk \ln 2$$

1.9   Fundamental Results

1.9.1   Thermodynamic laws

0th law   If two systems are in equilibrium with a 3rd system, they're in equilibrium with each other. (allows us to compare temp of systems via thermometer)

1st law   Energy is conserved: $đQ = d\bar{E} + đW$

2nd law   An equilibrium macrostate can be characterized by S (entropy), whichhas properties that

a. In any thermally isolated process goes from one macrostate to another, entropy tends to increase

$$\Delta S \geq 0$$

b. If the system is not isolated and undergoes a quasi-static process (absorbs heat),

$$dS = \frac{đQ}{T}$$

3rd law   The entropy S of a system has the limiting properties that

$$T \to 0, \quad S \to S_0 \quad \text{(Absolute entropy)}$$

Remarks   All four laws are *macroscopic*. In the context of three parameters $\bar{E}, S, T$.

1.9.2   Statistical calculation of thermodynamic quantities

Statistical Relations (Microscopic nature)

- $S = k \ln \Omega$

- $\beta = \frac{\partial \ln \Omega}{\partial E}, \quad X_\alpha = \frac{1}{\beta} \frac{\partial \ln \Omega}{\partial x_\alpha}$

For the free expansion of an idea gas:

$$\Omega \propto V^N X(E)$$

where the log of the DoS is

$$\ln \Omega = N \ln V + \ln X(E) + C$$

So from the mean pressure

$$P = \frac{1}{\beta} \frac{\partial \ln \Omega}{\partial V} = \frac{1}{\beta} \frac{\partial \ln V^N}{\partial V} = \frac{1}{\beta} \frac{N}{V} = \frac{NkT}{V}$$
$$PV = NkT$$

From the beta relation

$$\beta = \frac{\ln X(E)}{E}$$

thus it is only a function of energy and not volume V:

$$\beta(\bar{E}) = E \implies \bar{E}(T) = \bar{E}$$

Extensive vs Intensive parameters　For macroscopic parameters y_1, y_2 we have two cases:

- Case 1: Extensive if $y_1 + y_2 = y$

- Case 2: Intensive if $y_1 = y_2 = y$

Extensive	Intensive
Volume	T
Energy	Pressure
entropy	specific heat
mass	
heat capacity	

1.10　Heat capacity and specific heat

Suppose we add dQ to the system while other parameters are fixed, the system temperature raised by dT

$$\text{``Heat capacity''}\quad \left(\frac{dQ}{dT}\right)_y = C_y$$

In general　The heat capacity is defined by temperature and the parameter

$$C_y = C_y(T, y)$$

We can also relate it to the entropy change $ds = \frac{dQ}{T}$:

$$C_y = \left(\frac{dQ}{dT}\right)_y = T\left(\frac{ds}{dT}\right)_y$$

Specific heat:　Intensive parameter

$$C_y = \frac{C_V}{V}\quad \text{per mole}$$

$$C_y = \frac{C_P}{\text{mass}}\quad \text{per gram}$$

or the "specific heat/heat capacity per mole/gram"

Defining some units:

- Calorie: Heat required to raise temperature of 1 g of water @ 1 atm from $14.5 \to 15.5$ °C.

- Joule: Applied work

$$1\,\text{cal} = 4.1840\,\text{J}$$

Worksheet

1. Increase in entropy of a cup of water as it is heated from room temp to boiling:

$$\Delta S = \int dS = \int \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{C_P}{T} dT$$

$$= C_P \ln \frac{T_2}{T_1} = C_P \ln \frac{373}{298}$$

where $q = mC_P \Delta T$