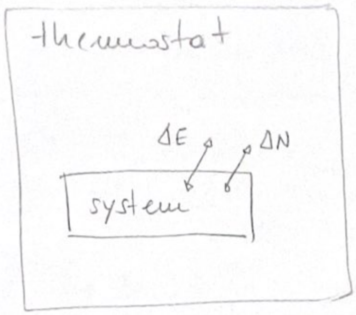
Recitation 7

Grancanonical ensemble



We allow both N and E in the system to fluctuate

What is fixed?

$$\left.\begin{aligned} E_{tot} &= E_s + E_{th} \\ N_{tot} &= N_s + N_{TOT} \end{aligned}\right\} \text{ system + thermostat is isolated}$$

microcanonical ensemble!

Microcanonical probability:

two constraints that I am imposing

$$P(\ell_s, \ell_{th}) = \frac{\delta_{E(\ell_s)+E(\ell_{th}),\, E_{tot}}\ \delta_{N(\ell_s)+N(\ell_{th}),\, N_{tot}}}{\Omega(E_{tot}, N_{tot})}$$

it's a marginalization!

As a macrostate, I choose the state of the system:

$$P(\ell_s) = \sum_{\ell_{th}} \frac{\delta_{E(\ell_{th}),\, E_{tot}-E_s}\ \delta_{N(\ell_{th}),\, N_{tot}-N_s}}{\Omega(E_{tot}, N_{tot})} = \frac{\Omega_{th}(E_{tot}-E_s, N_{tot}-N_s)}{\Omega(E_{tot}, N_{tot})}$$

using the definition of the Boltzmann entropy $\quad S_m(N,V,T) = k_B \ln \Omega(N,V,T)$

$$= \frac{e^{\frac{S_{th}(E_{tot}-E_s,\, N_{tot}-N_s)}{k_B}}}{\Omega(E_{tot}, N_{tot})} \underset{\substack{E_s \ll E_{tot} \\ N_s \ll N_{tot}}}{=} \frac{e^{\frac{1}{k_B}\left[S_{th}(E_{tot}, N_{tot}) - E_s \left.\frac{\partial S_{th}}{\partial E}\right|_{E_{tot}} - N_s \left.\frac{\partial S_{th}}{\partial N}\right|_{N_{tot}}\right]}}{\Omega(E_{tot}, N_{tot})}$$

we recognise what we defined in the μ-canonical $\left.\frac{\partial S_{th}}{\partial E}\right|_{E_{tot}, N_{tot}} =$

we introduce a new intensive parameter:

$$\mu_{th} \equiv -T \frac{\partial S_m}{\partial N}\Big|_{N_{tot}, E_{tot}}$$

$$= \frac{e^{\frac{1}{k_B}\left[S_{th}(E_{tot}, N_{tot}) - \frac{E_s}{T_{th}} + \frac{1}{T_{th}}\mu_{th} N_s\right]}}{\Omega(E_{tot}, N_{tot})}$$

$$\Rightarrow \quad P(e_s) = \underbrace{\frac{\Omega_{th}(E_{tot}, N_{tot})}{\Omega(E_{tot}, N_{tot})}}_{\frac{1}{\mathcal{Q}}} e^{-\beta_{th}\left[E(e_s) - \mu_{th} N(e_s)\right]}$$

Grancanonical distribution:

$$\boxed{P(e_s) = \frac{e^{-\beta E(e_s) + \beta\mu N(e_s)}}{\mathcal{Q}}}$$

it describe a system attached to a thermost / reservoir which fix the temperature T and the chemical potential μ

Grancanonical partition function:

$$\mathcal{Q} = \sum_{e_s} e^{-\beta E(e_s) + \beta\mu N(e_s)}$$

$$= \sum_{N,E} \Omega(N,E,V)\, e^{-\beta E + \beta\mu N} = \sum_N e^{+\beta\mu N} \sum_E \Omega(N,E,V)\, e^{-\beta E}$$

$$= \sum_N e^{+\beta\mu N} \underbrace{\sum_E e^{-\beta(E - T S_m(E))}}_{\text{it is the canonical partition function } Z(T,N,V)}$$

$S_m(E,N,V) = k_B \ln \Omega(E,N,V)$

$$\boxed{Q(T,\mu,V) = \sum_N e^{\beta\mu N} Z(T,N,V)}$$

it is a change of ensemble

$N \rightarrow \mu$

(fixed in the CANO) (fixed in the GRANCANO)

One defines the grancanonical potential as

$$\boxed{G(T,V,\mu) = -k_B T \ln Q(T,V,\mu)}$$

$P(E_s, N_s) = ?$ I am choosing the macrostate to be (E_s, N_s)

$$P(E_s, N_s) = \sum_{\substack{e_s \mid E(e_s)=E_s \\ N(e_s)=N_s}} \frac{e^{-\beta E_s + \beta\mu N_s}}{Q(T,V,\mu)}$$

$$= \frac{\Omega_s(E_s, N_s, V)}{Q(T,V,\mu)} e^{-\beta E_s + \beta\mu N_s}$$

Let's focus on the denominator:

$$Q(T,V,\mu) = \sum_{E_s, N_s} \Omega_s(N_s, E_s, V)\, e^{-\beta E_s + \beta\mu N_s}$$

$$= \sum_{E_s, N_s} e^{\beta[T S_m(N_s, E_s, V) - E_s + \mu N_s]}$$

the large parameter that I can send to infinity is V!

$$= \int dN_s \int dE_s\, e^{+\frac{V_s}{k_B T}\underbrace{\left[-\frac{E_s}{V_s} + \mu\frac{N_s}{V_s} + T\frac{S_m}{V_s}\right]}_{\sim O(1) \text{ intensive}}}$$

We can do a saddle point approximation in the $V_s \to \infty$ limit.

$$\frac{\partial}{\partial E_s}\left[-E_s + \mu N_s + T S_m(N_s, V_s, E_s)\right] = -1 + T\left.\frac{\partial S_m}{\partial E_s}\right|_{E_s^*, N_s^*} = 0$$

$$\Rightarrow \boxed{\left.\frac{\partial S_m}{\partial E_s}\right|_{E_s^*, N_s^*} = \frac{1}{T_{th}}}$$

these are two equations for E_s^*, N_s^* (μ, T are parameters of Q).

$$\frac{\partial}{\partial N_s}\left[-E_s + \mu N_s + T S_m\right] = +\mu + T\frac{\partial S_m}{\partial N_s}$$

$$\Rightarrow \boxed{-\frac{\mu_{th}}{T_{th}} = \left.\frac{\partial S_m}{\partial N_s}\right|_{N_s^*, E_s^*}}$$

$$\Rightarrow Q \underset{V\to\infty}{\simeq} e^{-\beta\left[E_s^* - \mu N_s^* - T S_m(E_s^*, N_s^*)\right]}$$

Putting all together:

$$P(E_s, N_s) = \frac{\Omega(E_s, N_s, V)\, e^{-\beta E_s + \beta\mu N_s}}{e^{-\beta\left[E_s^* - \mu N_s^* - T S_m(N^*, E^*)\right]}}$$ what we just found

$$= e^{-\beta\left[E_s - \mu N_s - T S_m(N_s, E_s, V) \overbrace{- E_s^* + \mu N_s^* + T S_m(N^*, E^*)}^{\text{this is what we have maximised}}\right]}$$

So one can say that, at equilibrium the system minimises the thermodynamic potential

$G(E_s, N_s) = E_s - \mu N_s - T S_m(E_s, N_s)$ as a function of the (fluctuating) energy E & the (fluctuating) # of particles of the system.

grand potential

This can be confusing as the equilibrium grand potential of the system is defined as $\boxed{G(\mu, T, V) \equiv -k_B T \ln Q(\mu, T, V)}$

which is a function of T, V, μ which are the parameters defining the Grancanonical ensemble.

It happens that the equilibrium grancanonical potential $G(T,\mu,V)$ is equal to the quantity minimizing

$$\min_{E,N}\left[E - TS - \mu N\right] = G(E^*, N^*)$$

So in thermodynamics: $G = \underbrace{E - TS}_{F} - \mu N$

Recap on the canonical ensemble

We have obtain it from the microcanonical ensemble by 1) considering (system + thermostat) as isolated, i.e.

$E_{tot} = E_s + E_{th} =$ fixed.

2) We focus on the system (← thermostat) and choose e_s as macrostate.

$$\Rightarrow \boxed{P(e_s) = \frac{e^{-\beta E(e_s)}}{Z}}$$ Canonical distribution function

$$\boxed{Z(T,N,V) = \sum_{e_s} e^{-\beta E(e_s)} = \sum_{E} \Omega(E,N,V)\, e^{-\beta E}}$$ Canonical partition function

the controlling parameters of the canonical ensemble are T, N, V !

Helmoltz free energy: $\boxed{F(N,T,V) = -k_B T \ln Z(N,T,V)}$

We have also seen that F is "almost" the cumulant generating function of the energy, and Z is "almost" the moment generating function of E

NB E is a fluctuating quantity in the canonical ensemble!

Since $Z = \sum_{\mathcal{C}} e^{-\beta E(\mathcal{C})}$

$$\frac{1}{Z}\frac{\partial Z}{\partial(\beta)} = \langle E \rangle = \frac{\partial}{\partial(-\beta)} \ln Z$$

$$M_E(\lambda) = \langle e^{\lambda E} \rangle = \frac{1}{Z}\sum_{\mathcal{C}} e^{-(\beta-\lambda)E} = \frac{Z(\beta-\lambda)}{Z(\beta)}$$

taking the logarithm

$$\underbrace{\Psi_E(\lambda)}_{\text{cumulant generating function}} = \ln M_E(\lambda) = \ln Z(\beta-\lambda) - \ln Z(\beta)$$

By definition of cumulants:

$$\langle E^n \rangle_c = \frac{\partial^n}{\partial \lambda^n} \ln Z(\beta-\lambda)\Big|_{\lambda=0} = (-1)^n \frac{\partial}{\partial \beta^n} \overbrace{\ln Z(\beta)}^{-\beta F}$$

We can look at the statistics of the energy, Consider for instance the variance:

$$\langle E^2 \rangle_c = \frac{\partial^2}{\partial \beta^2} \ln Z(\beta) = -\frac{\partial}{\partial \beta}\left[-\partial_\beta \ln Z(\beta)\right] = -\frac{\partial}{\partial \beta}\langle E \rangle$$

$$\beta = \frac{1}{k_B T} \qquad \frac{\partial}{\partial \beta} = \frac{\partial T}{\partial \beta}\frac{\partial}{\partial T} = \left(\frac{\partial \beta}{\partial T}\right)^{-1}\frac{\partial}{\partial T} \qquad \frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2}$$

$$\Rightarrow \langle E^2\rangle_c = +k_BT^2 \underbrace{\frac{\partial\langle E\rangle}{\partial T}}_{\equiv C_V} = k_BT^2C_V \sim E$$

In general E is not a Gaussian function, and it has non-vanishing higher cumulants. — for finite systems

In class we have looked at P(E) in the limit of large N and take the saddle point method: $\boxed{\langle E\rangle = \underset{E}{\operatorname{argmin}}\,(E - TS(E)) = E^* \qquad (**) \quad \frac{\langle E^2\rangle_c}{\langle E\rangle} \xrightarrow[N\to\infty]{} 0}$

$$P(E) = e^{-\beta[E - TS_m(E) - (\underbrace{E^* - TS(E^*)}_{\text{saddle point on the canonical partition function}})]}$$

$$Z^{(N,V,T)} \xrightarrow[N\to\infty]{} e^{-\beta(E^* - TS(E^*))}$$

And so as before $F = E^* - TS(E^*)$ is the thermodynamical potential that is minimized fixing E.

$$F(N,V,T) \overset{\text{for large } N}{=} E^* - TS(E^*, N, V) \quad \text{or equivalently } F = \langle E\rangle - T\langle S\rangle$$

(**) expanding it around E^* one gets the <u>Gaussian approximation</u>

$$P(E) \sim e^{-\frac{(E-E^*)^2}{\underbrace{2k_BT^2C_V}_{Var(E) = \langle E^2\rangle_c}}}$$ — consistent to what we have found!

All the higher order cumulants vanish as $N \to \infty$.

Recap on the microcanonical

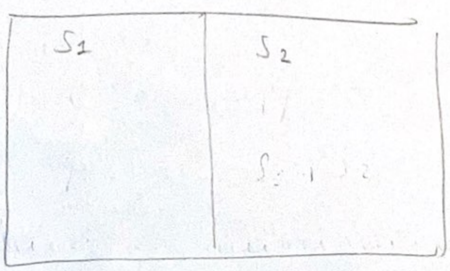
compatible with the constraints

Given fixed value of E & N $\to$ count the degeneracy of the states

thermodynamic potential $S(N,E,V) = k_B \ln \Omega(N,E,V)$

NB "Counting" requires care for continuous internal degrees of freedom like positions, momenta etc.
In practice, compute the allowed phase space volume and divide for a reasonable minimal volume, like h^3 for $d^3q\, d^3p$.

Equilibration of two subsystem:



$$\underbrace{\left.\frac{\partial S_1}{\partial E}\right|_{E_1^*} = \left.\frac{\partial S_2}{\partial E}\right|_{E-E_1^*}}$$

zeroth law of thermodynamics

it tells that two systems in contact with each other equilibrate at the temperature.

We derived it by taking a saddle point approximation of

$$\Omega(E) = \int dE_1 \; e^{\frac{N}{k_B}\underbrace{\left[s_1(E_1) + s_2(E-E_1)\right]}}$$

the system at equilibrium maximizes this quantity which is the total entropy (2nd law)

$$\Rightarrow P(E_1) \underset{N\to\infty}{\simeq} e^{\frac{1}{k_B}\left[\underbrace{S_1(E_1) + S_2(E_{tot} - E_1) - S_1(E_1^*) - S_2(E_{tot} - E_1^*)}_{<0}\right]}$$

$\longrightarrow 0$ when $E_1 \neq E_1^*$

$$P(E_1) \underset{N\to\infty}{\longrightarrow} \delta(E - E_1^*)$$

ensemble equivalence!

this is confirmed by the fact that we find

$$\langle E^2 \rangle_c \sim N$$

About thermodynamic equivalence:

MICRO: $S = S(N, V, E)$

$$dS = \frac{\partial S}{\partial V} dV + \frac{\partial S}{\partial E} dE + \frac{\partial S}{\partial N} dN$$

$$= \frac{p}{T} dV + \frac{1}{T} dE - \frac{\mu}{T} dN$$

$$\Rightarrow \boxed{dE = TdS - pdV + \mu\, dN}$$

1st law
fundamental differential of thermodynamics

internal energy (dU)

CANO: $F(N, T, V) = E^* - TS_m(N, V, E^*)$

only true in the large N limit!

Gibbs entropy: $S_c(N,V,T) = -k_B \sum_e P(e) \ln P(e)$

$$= \frac{\langle E \rangle}{T} - \frac{F(N,T,V)}{T}$$ for finite system

In the large N limit: $F(N,T,V) \longrightarrow E^* - T\,S(E^*)$

$$\langle E \rangle \longrightarrow E^*$$

$$S_G(N,V,\cancel{T}) \longrightarrow \cancel{\frac{E^*}{T}} - \cancel{\frac{E^*}{T}} + \frac{T}{T} S(E^*) \rightarrow S(E^*)$$

Gibbs entropy

Boltzmann entropy

E^* is implicitly a function of E^* (or viceversa)

$$\boxed{\frac{1}{T} = \left.\frac{\partial S_m}{\partial E}\right|_{E^*}}$$

Equivalence btw entropies !

Pressure: we have the definition of pressure from the Boltzmann entropy:

$$\boxed{P = T\,\frac{\partial S_m}{\partial V}}$$

force balance in the microcanonical ensemble

In the canonical:

$$F = -k_B T \ln Z$$

$$\frac{\partial F}{\partial V} = -\frac{k_B T}{Z}\frac{\partial Z}{\partial V} = -\frac{k_B T}{\partial Z\, A}\frac{\partial Z}{\partial L} = -\frac{1}{A}\Big\langle \underbrace{\sum_{i=1}^{N} \partial_x V(x_i - L)}_{\text{average force exerted by the gas on the wall}} \Big\rangle$$

$$= -\frac{\langle F_w \rangle}{A} = -P$$

$$\boxed{P = -\left.\frac{\partial F}{\partial V}\right|_{T,N}}$$