Relation between $F(T)$ and $S(E)$

(1)

$Z(T) = \int dE\, \omega(E) e^{-\beta E}$ ⇒ Z is the Laplace transform of $\omega(E)$

$Z(T) \underset{N\to\infty}{\asymp} e^{-\beta[E^* - TS(E^*)]}$ where $E^* = \text{argmax}[E - T\underset{m}{S}(E)]$

$$e^{-\beta F} \asymp e^{k^{-1}\underset{m}{S}(E^*) - \beta E^*}$$

* $\boxed{F(T) = -kT \ln Z = E^* - T\underset{m}{S}(E^*)}$

This is exactly the definition of F in thermodynamics $F = U - TS$

From hereon, I will use equivalently $E^* = \langle E \rangle = U$.

* $-\beta F = \sup_E [k^{-1}\underset{m}{S}(E) - \beta E]$ ⇒ $-\beta F$ is the Legendre transform of $-k^{-1}\underset{m}{S}(E)$ with respect to E. Again, the signs & factor of $-\beta$ are somewhat unfortunate... ($\Psi = -\frac{F}{T}$ is called the Massieu function)

Legendre: $\psi(x) = \sup_y [xy - \phi(y)]$ $\begin{cases} \psi = -\beta F \\ \phi = -S \\ x = E \\ y = -\beta \end{cases}$:-(

* So far, micro $\underset{m}{S}(E)$ ⟶ macro $F(T)$

Q: can we come back & compute $\underset{m}{S}(E)$ from $F(T)$?

Yes, if $\underset{m}{S}(E)$ is convexe and we have complete equivalence of ensembles:

$-k^{-1}\underset{m}{\tilde{S}}(E) = \sup_\beta[\beta F(\beta) - \beta E]$ then $\tilde{S}_m(E) = \underset{m}{S}(E)$ if $S_m(E)$ concave

[Touchette H, arxiv: 0804.0327, The large deviation approach to stat Mech.]

Gibbs entropy: So far $S(E) = S_m(E) = k \log \Omega(E)$

But we could also define $S_c(T) = -k \sum_q p_c(q) \ln p_c(q)$ ↳ canonical distrib.

$$\Rightarrow S_c(T) = -\frac{k}{Z} \sum_q e^{-\beta E(q)} \left[-\beta E(q) - \ln Z\right]$$

$$= \frac{1}{T} \langle E(q) \rangle + k \ln Z \underbrace{\frac{\sum_q e^{-\beta E(q)}}{Z}}_{1} = \frac{\langle E \rangle}{T} - \frac{F}{T}$$

$$\boxed{S_c(T) = \frac{\langle E \rangle}{T} - \frac{F}{T}} \qquad \left(\neq k_B \ln \Omega(E) \right)$$

A priori different from S_m. Not surprising $\Rightarrow$ not even the same argument!

But large N: $\langle E \rangle = E^*$ & $TS_c = E^* - F = E^* - (E^* - TS_m)$
$= TS_m$

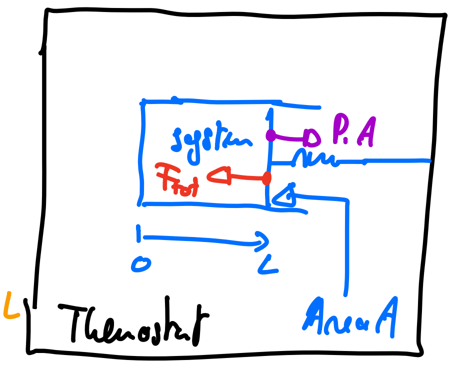
$\Rightarrow$ In the thermodynamic limit S_c & S_m agree, provided

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

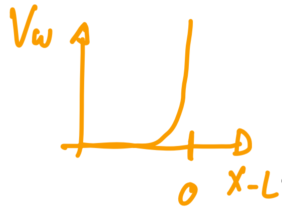
More broadly, if microcanonical & canonical ensembles are equivalent at large N, we should be able to construct the same thermodynamics from each of them.

3.2.3) Thermodynamics from the canonical ensemble perspective

Pressure: let us show that the mechanical pressure exerted by the system is $P = -\frac{\partial F}{\partial V}\Big|_T$.



Walls ↔ repulsive potential that diverges at L:



$$H_{tot} = H_0 + \sum_{i=1}^{N} V_w(x_i - L)$$

The force exerted by the piston on the particles is $F_w = \sum_{i=1}^{N} -\partial_x V(x_i - L)$

At equilibrium $\langle F_w \rangle + P \times A = 0 \Rightarrow P = \frac{1}{A}\sum_{i=1}^{N} \langle \partial_x V(x_i - L)\rangle$

[side remark, $P = \frac{1}{A}\int d\vec{q}\, d\vec{p}\, f_1(\vec{q},\vec{p})\, \partial_x V(q_x - L)$]

$V = AL \Rightarrow -\frac{\partial F}{\partial V}\Big|_T = -\frac{1}{A}\frac{\partial F}{\partial L}\Big|_T$ since A is fixed.

$$\Rightarrow -\frac{\partial F}{\partial V}\Big|_T = \frac{k_BT}{A}\frac{\partial \ln Z}{\partial L}\Big|_T = \frac{k_BT}{AZ}\frac{\partial Z}{\partial L} = \frac{k_BT}{AZN!}\frac{\partial}{\partial L}\int \prod_{i=1}^{N}\frac{d^3\vec{q}_i\, d^3\vec{p}_i}{h^3}\, e^{-\beta H - \beta\sum_i V_w(x_i - L)}$$

$$= \frac{1}{AZN!\, h^{3N}}\int \prod_i d\vec{q}_i\, d\vec{p}_i \sum_i \partial_x V_w(x_i - L)\, e^{-\beta H - \beta\sum_i V_w(x_i - L)}$$

$$\boxed{-\frac{\partial F}{\partial V}\Big|_T = \frac{1}{A}\left\langle \sum_{i=1}^{N} \partial_x V(x_i - L)\right\rangle = P}$$

Q: Is this consistent with the microcanonical result?

We had shown $dU = TdS - p\,dV$ and we know that $F = \underbrace{U}_{E^*(T,V,N)} - TS$

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$$\Rightarrow \frac{\partial F}{\partial V}\Big|_T = \frac{\partial U}{\partial V}\Big|_T - T\frac{\partial S}{\partial V}\Big|_T \quad (\Delta)$$ but the 1st law says $dS = \frac{1}{T}dU + \frac{P}{T}dV$

$$\Rightarrow dS = \frac{P}{T}dV + \frac{1}{T}\left(\frac{\partial U}{\partial V}dV + \frac{\partial U}{\partial T}dT\right)$$

$$\Rightarrow T\frac{\partial S}{\partial V} = P + \frac{1}{T}\frac{\partial U}{\partial V} \quad (\Delta\Delta)$$

(Δ) & $(\Delta\Delta) \Rightarrow \frac{\partial F}{\partial V}\Big|_T = -P$, as expected $\Rightarrow$ consistent!

We know that $F(V,T)$ & $\frac{\partial F}{\partial V}\Big|_T = -P \Rightarrow$ what about $\frac{\partial F}{\partial T}\Big|_V$?

Proceed exactly:

$$\frac{\partial F}{\partial T}\Big|_V = \frac{\partial}{\partial T}(-kT\ln Z) = -k\ln Z - kT\frac{\partial}{\partial T}\ln Z$$

$$\frac{\partial}{\partial T} = \frac{\partial \beta}{\partial T}\cdot\frac{\partial}{\partial \beta} = -\frac{1}{kT^2}\frac{\partial}{\partial\beta} \Rightarrow \frac{\partial F}{\partial T}\Big|_V = \frac{-kT\ln Z}{T} + \frac{1}{T}\underbrace{\frac{\partial}{\partial\beta}\ln Z}_{-\langle E\rangle} = \frac{F}{T} - \frac{\langle E\rangle}{T}$$

$$\Rightarrow \frac{\partial F}{\partial T}\Big|_V = -S_c(T,V) \underset{N\to\infty}{=} -S_m(U,V) \quad \text{if} \quad \frac{\partial S}{\partial E}\Big|_V = \frac{1}{T}$$

1st law: Is this consistent with what we know?

$$dF = \frac{\partial F}{\partial T}\Big|_V dT + \frac{\partial F}{\partial V}\Big|_T dV = -S\,dT - P\,dV \quad (1)$$

Since $F = U - TS$, $dF = dU - TdS - SdT \quad (2)$

(1) & $(2) \Rightarrow dU = TdS - pdV$ consistent.

Summary: In the large N limit, the concentration of the measures in the statistical ensemble lead to ensemble equivalence (when the thermodynamic potentials are strictly concave or convex). The saddle point induces a (one-to-one) mapping between the control parameters, here T & E.

As a consequence, we can choose our favorite ensemble to compute thermodynamic functions, they will give the correct value everywhere.

Sometimes canonical is easier; e.g. S for ideal gas.

——— microcanonical is easier; e.g. $P = T \frac{\partial S}{\partial V}$

Check on ideal gas

In microcanonical, we had computed

$$S_c = N k_B \ln\left[\frac{Ve}{N}\left(\frac{4\pi m e E}{3 N h^2}\right)^{3/2}\right]$$

Canonical: $F = -N k_B T \ln\left[\frac{Ve}{N\Lambda^3}\right] = -N k_B T \ln\left[\frac{Ve}{N}\right] + \frac{3}{2} N k_B T \ln\left[\frac{h^2}{2\pi m k T}\right]$

$$S_c = -\frac{\partial F}{\partial T} = N k_B \ln \frac{Ve}{N} - \frac{3}{2} N k_B \ln\left[\frac{h^2}{2\pi m k T}\right] + \frac{3}{2} N k_B \ln e$$

$$S_c = N k_B \ln\left[\frac{Ve}{N}\left(\frac{2\pi m k_B T e}{h^2}\right)^{3/2}\right] \quad \text{vs} \quad S_m = N k_B \ln\left[\frac{Ve}{N}\left(\frac{4\pi m e E}{3 N h^2}\right)^{3/2}\right]$$

then $\frac{\partial S_m}{\partial E} = \frac{3}{2} N k_B \times \frac{1}{E} = \frac{1}{T} \Rightarrow E = \frac{3}{2} N k_B T \Rightarrow k_B T = \frac{2E}{3N}$

$$\Rightarrow S_c = N k_B \ln\left[\frac{Ve}{N}\left(\frac{4\pi m e E}{3 N h^2}\right)^{3/2}\right] = S_m \quad \text{as expected.}$$

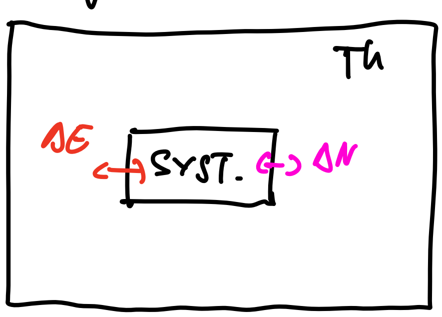
<u>Pressure</u>: $P = -\frac{\partial F}{\partial V} = \frac{N k_B T}{V} \Rightarrow PV = N k_B T$ as expected

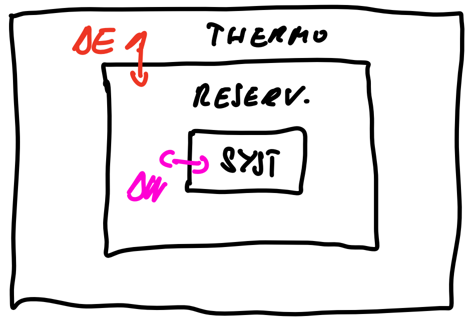
$\Rightarrow$ Same physics in both ensemble in the thermodynamic limit

3.3) The grand canonical ensemble

3.3.1) Changing ensemble

Let us now consider open systems, that can exchange particles and energy with a reservoir.

① 

② 

①	②
System + Thermostat isolated	System + Reservoir exchange ΔE with reservoir
$\left.\begin{matrix} E(q_{th}) + E(q_s) = E \\ N(q_{th}) + N(q_s) = N \end{matrix}\right\}$ microcanonical ensemble	$\left.\begin{matrix} \text{Temperature } T_{th} \\ N(q_s) + N(q_{res}) = N \end{matrix}\right\}$ canonical ensemble
Microstate $\{q_s, q_{th}\}$	Microstate $\{q_s, q_{res}\}$
$P(q_s, q_{th}) = \frac{1}{\Omega(E,N)} \delta_{N_{th}+N_s, N}\, \delta_{E_{th}+E_s, E}$	$P(q_s, q_{res}) = \frac{1}{Z(T,N)} e^{-\beta[E(q_s) + E(q_{res})]}$
Thermostat $\gg$ syst	Thermostat $\gg$ reservoir $\gg$ syst

Macro state: fixing q_{syst} & computing $P(q_s)$

* Route ① & ② are equivalent in the limits of large thermostat & reservoirs, with <u>finite</u> systems (still large enough to neglect interaction energy). Here: follow ①