S Vs E Curve

Conceptually, the hypothesis that microcanonical ensemble describes the correct equilibrium behavior often reduces the calculation of physical properties to problems in combinatorics. Most of these problems boil down to calculating $S(E)$ i.e. S as a function of total energy E of the system, perhaps subject to some additional constraints, e.g., fixed volume or fixed pressure etc. (recall $dE = TdS - PdV$)

Examples:

(a) Point like particles in box V.

Consider $H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U(\{x\})$

where $U(\{x\})$ denotes interactions between particles and also external potential (e.g. the fact that particles are confined in box V is imposed via an external potential). To illustrate basic ideas of MCE, we will set the inter-particle interactions to zero although as discussed above, this may lead to the failure of thermalization.

Infact first consider an even more drastic example where $m \to \infty$, so that

$$H = U(\{x\})$$

where $U(\{x\}) = 0$ if all $\{x\}$ inside box

$$= \infty \quad \text{otherwise}$$

Calculation of MC entropy S:

Each particle can occupy a space of volume V.

$$\Rightarrow \quad \Omega \propto V^N$$

$$\Rightarrow \quad S_{MC}(E) = \log(\Omega) + \log(\delta E)$$

$$= N \log V \quad \text{upto a constant}$$

independent of E as expected.

Two problems: (i) Not extensive!

since $N \log V$ scales faster than N at fixed density $\frac{N}{V} = \rho$.

(ii) $S_{MC}(E)$ should be dimensionless.

Problem remains even after including kinetic energy since $\int d^dx\, d^dp\, \delta E$ is <u>not</u> dimensionless.

The non-extensity also leads to the Gibbs paradox. (See Kardar e.g.)

Both of these problems are fixed by QM.

$$\Omega(E) = \frac{1}{N!} \cdot \frac{\int dp\, dq}{h^{dN}} = \text{dimensionless}$$

$N!$ ← Indistinguishable particles → Extensive entropy

h ← Planck's constant

For the above example, $\int dp$ integral diverges since $m \to \infty$, but atleast $\frac{1}{N!}$ helps in making S extensive:

$$\Omega \sim \frac{V^N}{N!} \Rightarrow S = N \log V - \underbrace{[N \log N - N]}_{\text{Sterling's approx.}}$$

$$= N \log\left[\frac{e}{\rho}\right] \qquad e = 2.718\ldots$$

$$\rho = \left(\frac{N}{V}\right).$$

The smaller the density, the larger is entropy which makes sense since more ways to arrange.

Using $dE = TdS - PdV$

$$\Rightarrow P = T \left.\frac{dS}{dV}\right|_E$$

$$= \frac{TN}{V}$$

$$\Rightarrow \boxed{PV = NT} \quad \text{or} \quad \boxed{P = \rho T}$$

Next consider finite m.

$$\Omega(E) = \frac{\int d^d x_i \int d^d p_i \; \delta\left(\sum_i \frac{\vec{p}_i^{\,2}}{2m} - E\right) \Delta E}{N!\; h^{dN}} \qquad (\Delta E \ll E)$$

$$= \frac{V^N}{N!\; h^{dN}} \frac{1}{E} (2mE)^{\frac{dN}{2}} \Delta E \int d^{dN} x_i \; \delta\left(\sum_{i=1}^{dN} x_i^2 - 1\right)$$

$$= \frac{V^N}{N!\; h^{dN}} \frac{\Delta E}{E} (2mE)^{\frac{dN}{2}} \frac{2\pi^{dN/2}}{\left[\frac{dN}{2} - 1\right]!}$$

← Surface area of dN-dim sphere.

Let's define λ via $\frac{h^2}{2m\lambda^2} = \frac{E}{N}$, λ is called thermal de Broglie length.

Using $N! \sim \left[\frac{N}{e}\right]^N$, $\Omega(E) \sim \frac{V^N}{h^{dN}\left[\frac{N}{e}\right]^N} (2mE)^{\frac{dN}{2}} \frac{2\pi^{dN/2}}{\left[\frac{dN}{2e}\right]^{\frac{dN}{2}}} \Delta E$

$$\sim \left[\frac{V}{N}\right]^N \left[\frac{2mE\pi}{h^2 \frac{dN}{2}}\right]^{\frac{dN}{2}} e^{N(1+d/2)}$$

$$\sim \left[\frac{V}{N \lambda^d}\right]^N \sim \left[\frac{1}{\rho \lambda^d}\right]^N \qquad \text{where } \rho = \frac{N}{V} = \text{particle density}$$

$$\Rightarrow S = \log(\Omega(E)) \sim N \log\left[\frac{1}{\rho \lambda^d}\right]$$

Quantum effects become important when

$$\rho \lambda^d \gtrsim 1$$ (small energies / large density)

Since classically, S becomes negative (!).

Again, $$P = T \left.\frac{\partial S}{\partial V}\right|_E = \frac{T N}{V} \Rightarrow \boxed{PV = NT}$$

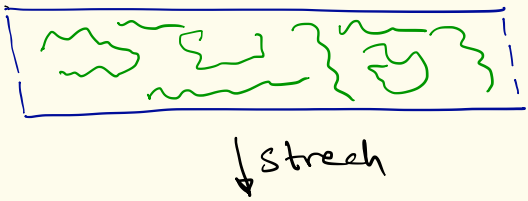
i.e. equation of state is unchanged compared to the case $m \to \infty$.

We will later see that when $\rho \lambda^d \gtrsim 1$, a system of bosons enter a new state of matter called Bose-einstein condensate (or a superfluid if the bosons are weakly interacting), while a system of fermions start to develop a well defined 'fermi surface'. Both of these are purely quantum effects which cannot be explained by classical stat. mech.

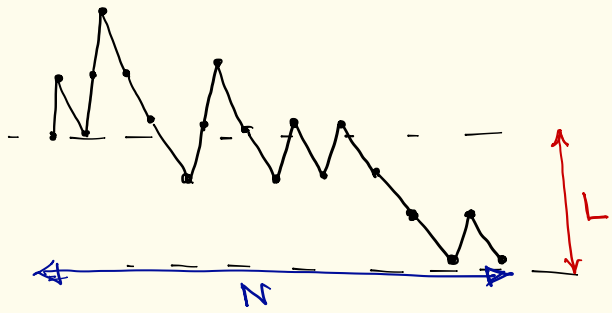
'Entropic Force' in a Rubber band

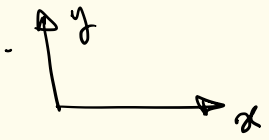
(see problem 5.12 in Sethna)

Consider a simple model of a rubber-band where it is composed of polymer molecules which undergo random walk.



Streching increases the length of the polymers making it entropically less favorable since a polymer of smaller length can explore a larger phase-space and consequently has a higher entropy. A simple model of a polymer consists of N links of unit length which can either point parallel or anti-parallel to the previous link, without any energy cost.





Let's calculate the entropy $S(L)$.

Denoting number of links pointing up/down as $N_\uparrow / N_\downarrow$

$$N_\uparrow + N_\downarrow = N$$

$$N_\uparrow - N_\downarrow = L$$

$$\Rightarrow \quad N_\uparrow = \frac{N+L}{2} \qquad N_\downarrow = \frac{N-L}{2}$$

$$\text{Entropy } S = \log \frac{(N_\uparrow + N_\downarrow)!}{N_\uparrow!\, N_\downarrow!}$$

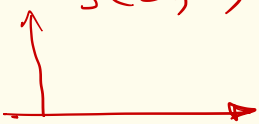
$$= \log \frac{N!}{\left(\frac{N+L}{2}\right)!\left(\frac{N-L}{2}\right)!}$$

$$= N \log N - N - \left(\frac{N+L}{2}\right)\log\left(\frac{N+L}{2}\right) + \left(\frac{N+L}{2}\right)$$

$$- \left(\frac{N-L}{2}\right)\log\left(\frac{N-L}{2}\right) + \left(\frac{N-L}{2}\right)$$

Since the energy cost for any configuration is zero $\Rightarrow \quad dE = 0 = T\,dS + F\,dx$

$$\Rightarrow \quad F = -T\, dS/dL$$



$\Rightarrow$ The polymer exerts a force $F = -T\frac{dS}{dL}$ at ends in resistance to being stretched.

Using the above expression for S:

$$F = -T\left[-\frac{1}{2}\log\left(\frac{N+L}{2}\right) + \frac{1}{2}\log\left(\frac{N-L}{2}\right)\right]$$

$$\boxed{F = \frac{T}{2}\log\left[\frac{N+L}{N-L}\right]}$$

The force $\to \infty$ as $L \to N$.

For $L \ll N$, $F = \frac{T}{2}\log\left[\frac{1+\frac{L}{N}}{1-\frac{L}{N}}\right]$

$$\simeq \frac{T}{2} \times \frac{2L}{N}$$

$$= \frac{TL}{N}$$

$\Rightarrow$ The polymer behaves like a spring with stiffness $\sim \frac{T}{N}$. As T increases, it becomes more stiff, since the entropy dominates more and more.

for a fixed force F, $L \sim \frac{NF}{T}$

$\Rightarrow$ Thermal expansion coefficient

$$\alpha = \frac{dL}{L\,dT} = -\frac{1}{T} < 0$$

as expected.