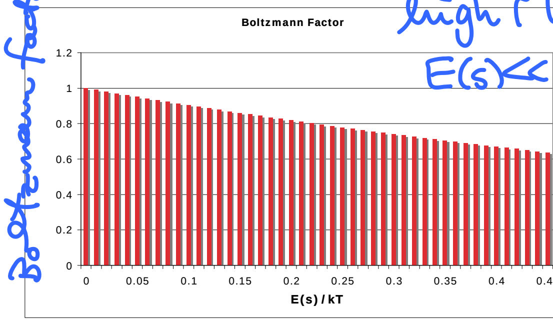
Review

- Comparing size of energy steps with kT
  - Different limits with temperature

$$P(s) = \frac{1}{Z} e^{-E(s)/kT} = \frac{1}{Z} e^{-\beta E(s)}$$

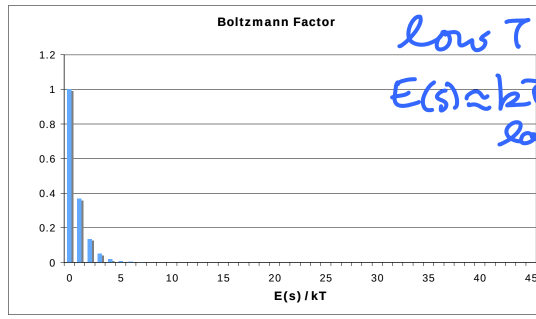
$$P(s) = \frac{\Omega(s)}{\Omega_{all}}$$

Boltzmann factor



high T limit

$E(s) \ll kT$



low T limit

$E(s) \approx kT$ or larger

Comparing systems

- In an isolated system (fixed energy U)
  - $\Omega(U)$, number of available microstates, is fundamental quantity
  - $S = k\ln\Omega$ tends to increase

- In a system in thermal equilibrium with a reservoir (fixed temperature T)
  - $Z(T)$ is property most analgous to Ω
  - Z essentially gives number of microstates available

  - So for this system, what tends to increase?

Partition Function and Free Energy

- Under these conditions, Helmholtz Free Energy tends to decrease
  - Intuitively, a function of this form describes system

$$F = -kT\ln Z$$

  - Gives appropriate units of energy
  - Also, can derive it from:

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S \qquad\qquad F = U - TS$$

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S = \frac{F-U}{T}$$

can show this is plausible form

look at temperature dependence

$T \to 0$ $\quad T=0 \quad f(0) = U(0)$

if $\tilde{f} = -kT\ln Z$

$\tilde{f}(0) = -kT\ln Z(0)$

at $T=0 \rightarrow Z(0) = e^{-E(0)/kT}$

$\tilde{f}(0) = -kT\ln\left(e^{-E(0)/kT}\right)$

$= U(0) = f(0)$

$E(0) = U(0)$ lowest energy

have right behavior

For the two-state paramagnet

- Recall that $\ln\Omega = N\ln N - N_\uparrow \ln N_\uparrow - N_\downarrow \ln N_\downarrow$

$$N_\uparrow = \frac{N}{2} - \frac{U}{2\mu B} \qquad N_\downarrow = \frac{N}{2} + \frac{U}{2\mu B}$$

$$\frac{U}{\mu B} = -N\tanh\left(\frac{\mu B}{kT}\right) \qquad x = \frac{\mu B}{kT}$$

can get

$$N_\uparrow = \frac{Ne^{x}}{2\cosh(x)} \qquad N_\downarrow = \frac{Ne^{-x}}{2\cosh(x)}$$

$$\frac{S}{k} = N\ln N - \frac{Ne^{x}}{2\cosh(x)}\ln\left(\frac{Ne^{x}}{2\cosh(x)}\right) - \frac{Ne^{-x}}{2\cosh(x)}\ln\left(\frac{Ne^{-x}}{2\cosh(x)}\right)$$

$\vdots$

$$S = Nk\left[\ln\left(2\cosh\left(\frac{\mu B}{kT}\right)\right) - \frac{\mu B}{kT}\tanh\left(\frac{\mu B}{kT}\right)\right]$$

using $f = U - TS$

$$f = \cancel{-N\mu B\tanh\left(\frac{\mu B}{kT}\right)}$$

$$-NkT\left[\ln\left(2\cosh\left(\frac{\mu B}{kT}\right)\right) \cancel{- \frac{\mu B}{kT}\tanh\left(\frac{\mu B}{kT}\right)}\right]$$

$$= -NkT\ln\left(2\cosh\left(\frac{\mu B}{kT}\right)\right)$$

if use $f = -kT\ln Z$

$$z = 2\cosh\left(\frac{\mu B}{kT}\right) \rightarrow Z = z^N$$

sub in $f = -kTN\ln\left(2\cosh\left(\frac{\mu B}{kT}\right)\right)$

get same answer!

Equipartition Theorem Revisited

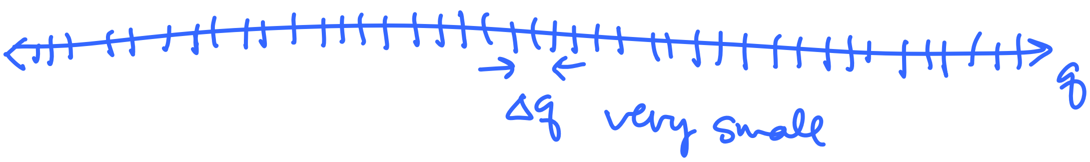
Initially, this was stated. Now, we will derive it.

- Applies to energies in form of quadratic degrees of freedom

$$E(q) = cq^2$$

- System is one degree of freedom in thermal equilibrium with reservoir at temperature T

- States of system, q, are independent and spaced by Δq



classical approach

$$Z = \sum_q e^{-\beta E(q)} = \sum_q e^{-\beta c q^2}$$

$$= \frac{1}{\Delta q} \sum_q e^{-\beta c q^2} \Delta q$$

$$= \frac{1}{\Delta q} \int_{-\infty}^{\infty} e^{-\beta c q^2} dq$$

Boltzmann factors versus q.

$$= \frac{1}{\Delta q} \frac{1}{\sqrt{\beta c}} \int_{-\infty}^{\infty} e^{-x^2} dx \qquad x \equiv \sqrt{\beta c}\, q \qquad dq = \frac{dx}{\sqrt{\beta c}}$$

$$Z = \frac{1}{\Delta q} \cdot \frac{1}{\sqrt{\beta c}} \sqrt{\pi} = C \beta^{-\frac{1}{2}} \qquad C \equiv \sqrt{\frac{\pi}{c}} \frac{1}{\Delta q}$$

$$\bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

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

$$= \frac{1}{2}\beta^{-1} = \frac{1}{2}kT$$

Composite Systems

- Moving from partition function for single particle to system of several particles

$$Z_{\text{total}} = \sum_s e^{-\beta[E_1(s)+E_2(s)]} = \sum_s e^{-\beta E_1(s)} e^{-\beta E_2(s)}$$

s – state of particles

$s(a, b)$ – a: particle 1, b: particle 2

$$Z_{total} = \sum_{a,b} e^{-E_1(a)\beta} e^{-E_2(b)\beta}$$

$$= \sum_a e^{-E_1(a)\beta} \sum_b e^{-E_2(b)\beta}$$

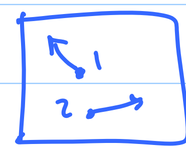
$$= Z_1 Z_2 \leftarrow \text{for non-interacting distinguishable particles}$$

$$Z_{total} = \left[e^{-E_1(\alpha)\beta} + e^{-E_1(\gamma)\beta} \ldots\right]\left[e^{-E_2(\alpha)\beta} + e^{-E_2(\gamma)\beta} \ldots\right]$$

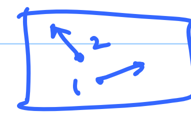
$$= e^{-[E_1(\alpha)+E_2(\alpha)]\beta} + e^{-[E_1(\gamma)+E_2(\alpha)]\beta} + e^{-[E_1(\alpha)+E_2(\gamma)]\beta} + e^{-[E_1(\gamma)+E_2(\gamma)]\beta} + \dots$$

if particles are indistinguishable

$$Z_{total} \approx \frac{Z_1 Z_2}{2}$$



$$\approx \frac{(Z_1)^2}{2}$$



$$Z_{total} = Z_1 Z_2 Z_3 \dots Z_N$$ distinguishable

Composite Systems

- In general, for non-interacting indistinguishable particles

$$Z_{\text{total}} \approx \frac{Z_1 Z_2 \cdots Z_N}{N!} = \frac{(Z_1)^N}{N!}$$

- We will apply this to an ideal gas
  - Rotational, vibrational, translational energies
- We will use semi-classical approach
  - Quantum mechanics to calculate energy levels (states)
  - Classical Boltzmann distribution to calculate thermodynamic properties (high temperature limit)