N particles in a 3D box

<u>trick</u>: count microstates assuming particles are distinguishable (easier) and then correct for our overcounting by dividing by N!

⇒ one particle in 3D box

microstates energy $\leq E$ = volume positive part of 3D sphere $R = \left(\frac{2L}{h}\right)(2mE)^{1/2}$

⇒ N particles in 3D box

microstates energy $\leq E$ = volume positive part of 3N - dimensional hypersphere $R = \left(\frac{2L}{h}\right)(2mE)^{1/2}$

will derive in discussion

$$V_n(R) = \frac{2\pi^{n/2}}{n\,\Gamma(n/2)} R^n$$

volume of n-dimensional hypersphere

gamma function

$\Gamma(n) = (n-1)!$ for integer n (generalization of factorial) volume of positive part of hypersphere

$$V_n^*(R) = \left(\frac{1}{2}\right)^n V_n(R)$$

we are considering 3N-dimensional hypersphere so

$$V_n^*(R) = \left(\frac{1}{2}\right)^{3N} \frac{2\pi^{3N/2}}{3N\left(\frac{3N}{2}-1\right)!} R^{3N}$$

$$= \left(\frac{1}{2}\right)^{3N} \frac{\frac{1}{2}}{\frac{1}{2}} \frac{2\pi^{3N/2}}{3N\left(\frac{3N}{2}-1\right)!} R^{3N}$$

$$= \left(\frac{1}{2}\right)^{3N} \frac{\pi^{3N/2}}{\frac{3N}{2}\left(\frac{3N}{2}-1\right)!} R^{3N}$$

$$= \left(\frac{1}{2}\right)^{3N} \frac{\pi^{3N/2}}{\left(\frac{3N}{2}\right)!} R^{3N}$$

plugging in for R, $R = \frac{2L}{h}(2mE)^{1/2}$

$$= \cancel{\left(\frac{1}{2}\right)^{3N}} \frac{\pi^{3N/2} \cancel{2^{3N}} L^{3N}}{h^{3N}\left(\frac{3N}{2}\right)!} (2mE)^{3N/2}$$

$$= \left(\frac{L}{h}\right)^{3N} \frac{(2\pi mE)^{3N/2}}{\left(\frac{3N}{2}\right)!}$$

$$= \left(\frac{V}{h^3}\right)^{N} \frac{(2\pi mE)^{3N/2}}{\left(\frac{3N}{2}\right)!}$$

To get the correct # microstates, we need to divide by $1/N!$, e.g. $\Gamma(E,V,N) = \frac{1}{N!} V_N^*(E,V)$

$$\boxed{\Gamma(E,V,N) = \frac{1}{N!}\left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{3N/2}}{(3N/2)!}}$$

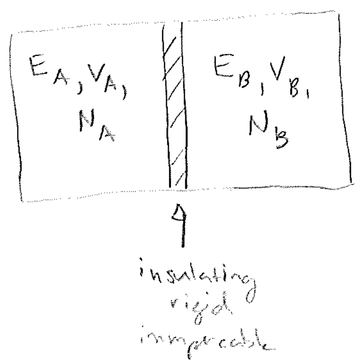
We will now discuss selecting the correct ensemble, which is done by considering the constraints on the system. The choice of ensemble (the constraints) determine how the thermodynamic variables are related the number of microstates.

We will go over each of these in detail, but to summarize:

ensemble	macrostate	prob. distribution	thermodynamics
microcanonical	E, V, N	$P = 1/\Omega$	$S(E,V,N) = k \log \Omega$
canonical	T, V, N	$P_s = e^{-\beta E_s}/Z$	$F(T,V,N) = -kT \log Z$
grand canonical	T, V, μ	$P_s = e^{-\beta(E_s - \mu N_s)}/Z_G$	$\Omega_G(T,V,\mu) = -kT \log Z_G$

We will begin by discussing the microcanonical ensemble, appropriate for a system at fixed $\underline{E, V, N}$.

Consider two isolated systems:



- microstates in each system

$$\Omega_A(E_A, V_A, N_A) \quad , \quad \Omega_B(E_B, V_B, N_B)$$

- microstates in composite system A+B:

$$\Omega = \Omega_A \Omega_B$$

- we would like to define entropy such that
  - it measures microstates of composite system
  - it is additive for independent systems ($S_{A+B} = S_A + S_B$)

Boltzman $\longrightarrow$ $S = k \log \Omega$

$$S_{A+B} = k \log(\Omega_A \Omega_B) = k \log \Omega_A + k \log \Omega_B = S_A + S_B$$

Now, relax constraint: insulating $\rightarrow$ conducting

- <u>thermal contact</u>, now A & B <u>exchange energy</u>

total energy fixed: $E = E_A + E_B$

(V_A, V_B, N_A, N_B remain the same)

What happens to # accessible microstates?

pick energy of left subsystem, call it E_A:

system A: $\Omega = \Omega_A(E_A)$

system B: $\Omega = \Omega_B(E - E_A)$

accessible microstates: $\Omega = \Omega_A(E_A)\,\Omega_B(E - E_A)$

total # accessible microstates $\Rightarrow$ sum over all possible E_A

$$\Omega(E) = \sum_{E_A}{}' \Omega_A(E_A)\,\Omega_B(E - E_A)$$

??? $\log(\Omega(E)) \neq f(E_A) + f(E - E_A)$

$\Rightarrow$ For $N \gg 1$, dominent term in sum is $E_A = \tilde{E}_A$ $\leftarrow$ most probable value

$$\Omega(E) \approx \Omega_A(\tilde{E}_A)\,\Omega_B(E - \tilde{E}_A)$$

and thus $S = k \log \Omega = S_A + S_B$ as before contact

$\Rightarrow$ entropy increases or remains unchanged after internal constrain related

$\Rightarrow$ this is our bridge between macro & micro

$$S = k \log \Omega$$

thermodynamics

microscopic physics

What about systems where E is a continous variable?

$$S = k \log \Gamma(E)$$

could also use $S = k \log[g(E)\,\Delta E]$

$g(E)$, $\Gamma(E)$ rapidly increasing functions, doesn't matter if we count $\leq E$ or $(E, E+\Delta E)$ (in limit of large N)

Now that we have defined S, we can compute whatever thermodynamic variables we need:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}$$

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

Ex: equations of state of ideal gas confined to box

(fixed E, V, N)

recall: $\Gamma(E,V,N) = \frac{1}{N!}\left(\frac{V}{h^3}\right)^N \frac{(2\pi m E)^{3N/2}}{(3N/2)!}$

$$S = k\log\Gamma(E,V,N)$$
$$= k\log\left[\tfrac{1}{N!}\right] + k\log\left(\tfrac{V}{h^3}\right)^N + k\log(2\pi mE)^{3N/2} - k\log(3N/2)!$$
$$= -k\log N! + kN\log(V/h^3) + \tfrac{3N}{2}k\log(2\pi mE) - k\log(3N/2)!$$

$(\log N! \approx N\log N - N)$

$$= k\left[-N\log N + N + N\log(V/h^3) + \tfrac{3N}{2}\log(2\pi mE) - \tfrac{3N}{2}\log\tfrac{3N}{2} + \tfrac{3N}{2}\right]$$
$$= k\left[-N\log N + \tfrac{5}{2}N + N\log V - \tfrac{3N}{2}\log h^2 + \tfrac{3N}{2}\log 2\pi mE - \tfrac{3N}{2}\log\tfrac{3N}{2}\right]$$
$$= k\left[N\log(V/N) + \tfrac{3N}{2}\log\left[\tfrac{1}{h^2}(2\pi mE)\tfrac{2}{3N}\right] + \tfrac{5}{2}N\right]$$

$$\boxed{S = kN\log(V/N) + \frac{3Nk}{2}\log\left(\frac{4\pi mE}{3Nh^2}\right) + \frac{5Nk}{2}}$$

Then, $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{3Nk}{2}\frac{1}{E}$

$$\boxed{E = \tfrac{3}{2}NkT}$$ as expected!

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{kN}{V}$$

$$\boxed{PV = NkT}$$

We have now derived these equations of state from first principles!

Ex: Find the temperature dependence of the energy in a system N noninteracting spins in a magnetic field

recall: if we say n of N spins are up,

(*) $E = n(-\mu B) + (N-n)\mu B = -(2n-N)\mu B$

$\Rightarrow$ we need to connect n with T

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,B} \qquad S = k \log \Omega \qquad \Omega(n) = \frac{N!}{n!(N-n)!}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,B} = \frac{dS(n)}{dn}\frac{dn}{dE} = \frac{dS(n)}{dn}\frac{d}{dE}\left(\frac{1}{2}\left(N - \frac{E}{\mu B}\right)\right)$$

$$= \frac{dS(n)}{dn}\left(-\frac{1}{2\mu B}\right)$$

$$S = k\left[\log N! - \log n! - \log(N-n)!\right]$$

recall: $\frac{d}{dx}\log x! = \log x \quad (x \gg 1)$

$$\frac{dS(n)}{dn} \approx -k\left(\log n - \log(N-n)\right) = k\,\frac{\log(N-n)}{\log n}$$

$$\frac{1}{T} = \frac{-k}{2\mu B}\log\frac{N-n}{n}$$

Now, solve for n to plug into (*)

$$-\frac{2\mu B}{kT} = \log \frac{N-n}{n}$$

$$e^{-2\mu B/kT} = \frac{N-n}{n}$$

$$N-n = n e^{-2\mu B/kT}$$

$$N = n\left(1+e^{-2\mu B/kT}\right)$$

$$n = \frac{N}{1+e^{-2\mu B/kT}}$$

$$E = -\mu B\left[\frac{2N}{1+e^{-2\mu B/kT}} - N\right]$$

$$= -\mu B N\left[\frac{2-(1+e^{-2\mu B/kT})}{1+e^{-2\mu B/kT}}\right]$$

$$= -\mu B N\left[\frac{1-e^{-2\mu B/kT}}{1+e^{-2\mu B/kT}}\right] \qquad \tanh x = \frac{e^{2x}-1}{e^{2x}+1}$$

$$= -\mu B N\left[\frac{e^{2\mu B/kT}-1}{e^{2\mu B/kT}+1}\right]$$

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

Note: we had to consider all N spins, even though they don't interact

$\Rightarrow$ E fixed for N spins, so can't consider orientation individually