

Thermodynamics 4230

Aug. 20, 2011

Lecture Set 2

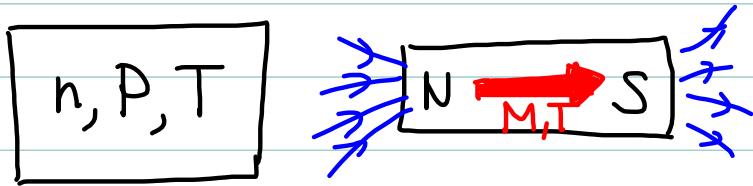
(Leo Radzhovsky)

Microcanonical Stat. Mech.: 2nd Law of Thermodynamics

States & their counting

Macrostates: gas (n, P, T), magnet (n, M, T), solid (u, σ, T)

- characterize bulk system
- very different probabilities

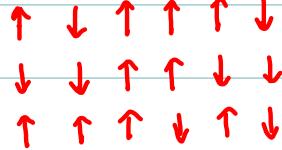
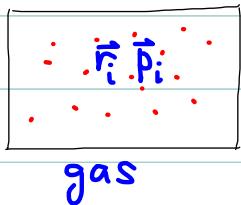


Microstates:

gas: (r_i, p_i) , $\vec{k}_n = \frac{2\pi\vec{n}}{L}$ (Q.M) $\Psi_{\vec{k}_n}, \dots$ (position/momentum)

magnet: \vec{S}_i (spin on every ion/site)

- microscopic, unique characterization of system
- equally probably at fixed E (postulate)



Huge # of microstates for each macrostate

→ bulk properties determined by multiplicity (#) $\Omega(E)$ of μ -states for each macrostate

⇒ need to count μ -states, $\Omega(E)$

Counting of μ -states

relation to bulk/thermodynamics:

$$\text{Prob. of macrostate } (A) = \frac{\#\Omega_A \text{ of } \mu\text{-states}}{\text{total } \#\text{ of } \mu\text{-states}}$$

isolated system w/ fixed E (" μ -canonical ensemble")

$$\underset{A}{\Omega}(E) = ???$$

counting depends on system type:

- binary systems:

e.g.: • "Ising" magnet w/ spin \uparrow, \downarrow

• coin up/down

• 1d random walk step R, step left

• binary #'s 0, 1

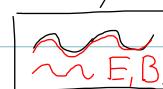
- quantum oscillators (bosons):

e.g.: • ion vibrations in a crystal (phonons)

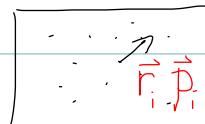


• EM modes e.g. BB radiation, μ -wave oven, etc

• bosonic atoms (\rightarrow BEC)



- Boltzmann (classical) gas:



Binary systems

Mathematics of counting: combinatorics

- permutations of N distinct objects $N! \approx \left(\frac{N}{e}\right)^N$
- " N choose m " - choose m identical objects out of N

$$\Omega(N, m) = \binom{N}{m} = \frac{N!}{m!(N-m)!} = C_m^N$$

e.g.:

→ binomial coeff. in:

$$(x+y)^N = \underbrace{(x+y)(x+y)\dots(x+y)}_{\text{choose } x \text{ or } y \text{ from each}} = \sum_{m=0}^N C_m^N x^m y^{N-m}$$

↑ Pascal triangle
of the N factors

→ flip N coins:

$$\# \text{ of ways to get } m \text{ heads} \quad \Omega(m, N) = C_m^N$$

$$\# \text{ of total combinations} \quad 2^N$$

$$\Rightarrow P(m, N) = \frac{C_m^N}{2^N} = C_m^N \left(\frac{1}{2}\right)^m \left(\frac{1}{2}\right)^{N-m}$$

note: $\sum_{m=0}^N P(m, N) = \left(\frac{1}{2} + \frac{1}{2}\right)^N = 1$

prob of m heads prob of $N-m$ tails

$$\bullet P(N, N) = P(0, N) = \frac{1}{2^N} \rightarrow 0 \quad \rightarrow \underline{\text{very unlikely!}}$$

$$\bullet P\left(\frac{N}{2}, N\right) = \frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!} \frac{1}{2^N} \approx 1 \quad \rightarrow \underline{\text{most likely}} \text{ (check)}$$

binary #'s: 4 bits $\Rightarrow 2^4 = 16$ total

0 0 0 0
0 0 0 1

$$\Omega(0, 4) = \Omega(4, 4) = 1 = \frac{4!}{0! 4!} = 1 \quad \checkmark$$

0 0 1 0

0 0 1 1

0 1 0 0

$$\Omega(1, 4) = \Omega(3, 4) = 4 = \frac{4!}{1! 3!} = 4 \quad \checkmark$$

0 1 0 1

0 1 1 0

0 1 1 1

$$\Omega(2, 4) = 6 = \frac{4!}{2! 2!} = 6 \quad \checkmark$$

1 0 0 0

note:

1 0 1 0

1 0 1 1

$$(x+y)^4 = 1x^4y^0 + 4x^3y^1 + 6x^2y^2 + 4xy^3 + 1x^0y^4$$

1 1 0 0

1 1 0 1

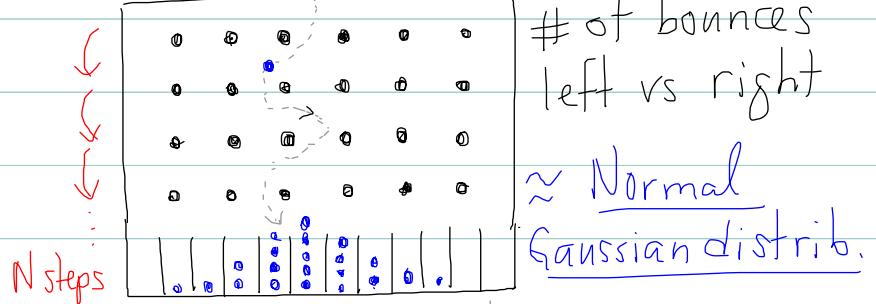
1 1 1 0

1 1 1 1

Binary systems

• Galton board

$$P(m, N) = \frac{N!}{m!(N-m)!} \frac{1}{2^N}$$



• 1d random walks (diffusion): (cf rubber)

ΔN → N steps left or right

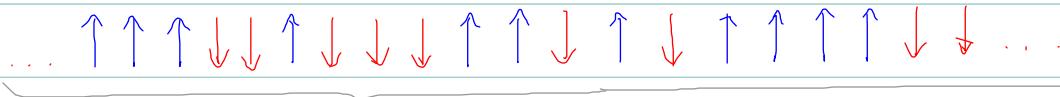
$N_L, N_R = N - N_R$

$$P(N_L, N) = \frac{N!}{N_L!(N-N_L)!} \frac{1}{2^N} \rightarrow P(\Delta N, N) = \frac{N!}{(\frac{N-\Delta N}{2})!(\frac{N+\Delta N}{2})!} 2^{-N}$$

$$\langle \Delta N \rangle = 0 \Leftrightarrow \langle N_L \rangle = \langle N_R = N - N_L \rangle = \frac{N}{2}$$

$$(N_R - N_L)_{rms} = \Delta N_{rms} = \sqrt{N_R}$$

• Ising (up/down) magnet:



$$N - \text{spins}, N_{up} - \text{up}, N_{down} = N - N_{up} - \text{down}$$

$$P(N_\uparrow, N_\downarrow, N) = \tilde{P}(M = \Delta N, N) = \frac{N!}{(\frac{N+M}{2})!(\frac{N-M}{2})!} \frac{1}{2^N}$$

$$M = N_\uparrow - N_\downarrow$$

$$\Rightarrow \langle M \rangle = 0 \Leftrightarrow \langle N_\uparrow \rangle = \langle N_\downarrow \rangle = \frac{N}{2}$$

Other fun problems

• Birthday problem/paradox

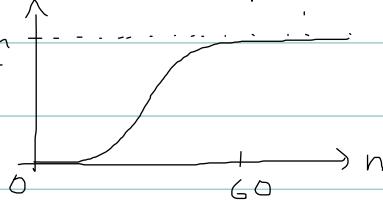
Prob_N of 2 people out of N having same b-date?

$$P_{366} = 1, P_{60} \approx 0.99, P_{23} \approx \frac{1}{2}, P_2 \approx \frac{1}{365}$$

$$\overline{P}_n = 1 \cdot \left(1 - \frac{1}{365}\right) \cdot \left(1 - \frac{2}{365}\right) \cdots \left(1 - \frac{n-1}{365}\right)$$

not having same b-day = $\frac{365!}{(365-n)!} \frac{1}{365^n} \rightarrow \text{no } \frac{1}{n!} \text{ b.c. } n \text{ are distinct}$

$$\Rightarrow \overline{P}_n = 1 - \overline{P}_n \approx 1 - e^{-\frac{n}{365}}$$



• Monty Hall problem/paradox (Let's make a deal)

- prize behind one of 3 doors

- choose a door $\rightarrow \frac{1}{3}$ prob of winning

- host opens door w/ no prize & asks if you would like to change between your choice & 2nd closed door

- always switch, since $P = \frac{1}{3} \rightarrow P_{\text{switch}} = \frac{2}{3}$!

mathematics

- $N! \approx \underbrace{N^N e^{-N} \sqrt{2\pi N}}_{(\text{Stirling approx})} \left(\approx \left(\frac{N}{2}\right)^N \right) = \underbrace{N \cdot (N-1) \cdot (N-2) \dots 3 \cdot 2 \cdot 1}_{N}$

- $P_{\text{Bin}}(m, N) = \frac{N!}{m!(N-m)!} p^m (1-p)^{N-m}$

$\left\{ \begin{array}{l} P_{\text{Poisson}}(m) \approx \frac{\bar{m}^m}{m!} e^{-\bar{m}}, \text{ for } p \rightarrow 0, N \rightarrow \infty \\ (\bar{m} = Np, \delta m^2 = \bar{m}) \end{array} \right.$

 \approx

 $\left\{ \begin{array}{l} P_{\text{Gauss (Normal)}} \approx \frac{1}{\sqrt{2\pi\bar{m}}} e^{-\frac{(m-\bar{m})^2}{2\bar{m}}}, \text{ for } p \text{ fixed, } N \rightarrow \infty \\ (\delta m^2 = (\bar{m} - \bar{m})^2 = \bar{m}) \\ \Rightarrow \delta m_{\text{rms}} \approx \sqrt{\bar{m}} \ll \bar{m} = \frac{N}{2} \end{array} \right.$

details:

$$P(m) = \frac{N(N-1)\dots(N-m+1)}{m!} p^m (1-p)^{N-m}$$

Poisson

limit: $N \gg m \gg 1, pN \rightarrow \text{fixed}$

$$\approx \frac{(pN)^m}{m!} e^{-pN} \Rightarrow P_{\text{Poisson}}(m) = \frac{\bar{m}^m}{m!} e^{-\bar{m}}, \text{ with } \boxed{\bar{m} = pN}$$

moments of $P_{\text{Poisson}}(m)$:

- $\sum_{m=0}^{\infty} P_p(m) = 1$

- $\langle m \rangle = \sum_{m=0}^{\infty} m P_p(m) = \sum_{m=1}^{\infty} \frac{\bar{m}^m}{m!} e^{-\bar{m}} m = \bar{m} \sum_{m=1}^{\infty} \frac{\bar{m}^{m-1}}{(m-1)!} e^{-\bar{m}}$

$$\boxed{\langle m \rangle = \bar{m} = pN}$$

- $\langle m^2 \rangle = \sum_{m=0}^{\infty} m^2 P_p(m) = \bar{m} + \bar{m}^2$

$$\langle m^2 \rangle = \sum_{m=0}^{\infty} m^2 \frac{\bar{m}^m}{m!} e^{-\bar{m}} = \bar{m} \sum_{m=1} (\bar{m}-1+1) \frac{\bar{m}^{m-1}}{(m-1)!} e^{-\bar{m}}$$

$$= \bar{m}^2 \sum_{m=2} \frac{\bar{m}^{m-2}}{(m-2)!} e^{-\bar{m}} + \bar{m} \sum_{m=1} \frac{\bar{m}^{m-1}}{(m-1)!} e^{-\bar{m}}$$

$$= (\bar{m})^2 + \bar{m} \Rightarrow \langle m^2 \rangle - \langle m \rangle^2 = \bar{m} = \langle (m-\langle m \rangle)^2 \rangle = m_{rms}^2$$

$$\Rightarrow m_{rms}^p = \sqrt{\bar{m}}$$

Binomial distribution moments:

$$\bullet \bar{m} = \sum_{m=1}^N P(m)m = \sum_{m=1}^N \frac{m N!}{m!(N-m)!} p^m (1-p)^{N-m}$$

$$= pN \underbrace{\sum_{m=1}^N \frac{(N-1)!}{(m-1)! (N-1-(m-1))!} p^{m-1} (1-p)^{N-1-(m-1)}}_1 = pN = \bar{m}$$

$$\bullet \bar{m}^2 = \sum_{m=1}^N \frac{m^2 N!}{m!(N-m)!} p^m (1-p)^{N-m} = p^2 N \sum_{m=1}^N \frac{(N-1)! (m-1+1)}{(m-1)! (N-m)!} p^{m-2} (1-p)^{N-m}$$

$$= p^2 N(N-1) \underbrace{\sum_{m=2}^N \frac{(N-2)!}{(m-2)! (N-2-(m-2))!} p^{m-2} (1-p)^{N-m}}_1 + pN \underbrace{\sum_{m=1}^N \frac{(N-1)!}{(m-1)! (N-m)!} p^{m-1} (1-p)^{N-m}}_1 = 1$$

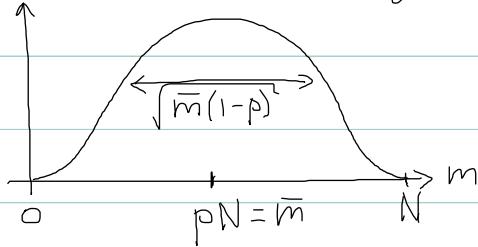
$\rightarrow 1$ in Poisson $p \rightarrow 0$ limit

$$\Rightarrow \bar{m}^2 = \bar{m}^2 + \bar{m} - p^2 N = \bar{m}^2 + \bar{m} (1-p)$$

$$\Rightarrow \bar{m}^2 - \bar{m}^2 = m_{rms}^2 = \bar{m}(1-p) \Rightarrow m_{rms} = \sqrt{\bar{m}(1-p)}$$

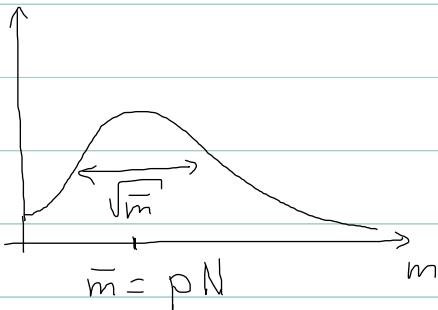
Binomial, Poisson, Gaussian Distributions

- Binomial: arbitrary, m, N, p



$$P_B(m) = \frac{N!}{m!(N-m)!} p^m (1-p)^{N-m}$$

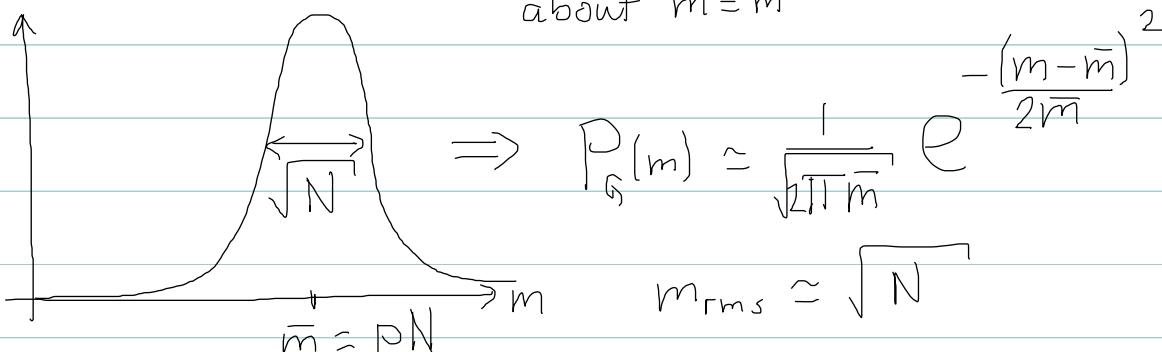
- Poisson: $N \gg m \gg 1, p \rightarrow 0$ w/ $pN = \text{fixed}$



$$P_p(m) = \frac{\bar{m}^m}{m!} e^{-\bar{m}}$$

- Gaussian (Normal): $N \gg 1, m \gg 1, p - \text{fixed}$

Taylor-expand $\ln P \approx -\frac{(m-\bar{m})^2}{\bar{m}}$
about $m = \bar{m}$



$$\Rightarrow P_G(m) \approx \frac{1}{\sqrt{2\pi\bar{m}}} e^{-\frac{(m-\bar{m})^2}{2\bar{m}}}$$

$$m_{rms} \approx \sqrt{N}$$

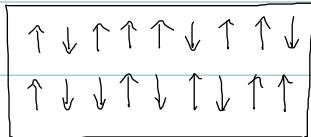
narrows (in relative terms) $\Rightarrow \frac{m_{rms}}{\bar{m}} \sim \frac{1}{\sqrt{N}} \rightarrow 0$

e.g. sum random $\pm 1 \Rightarrow S = \sum_N$ obeys Gaussian distribution.

"Ising" magnet

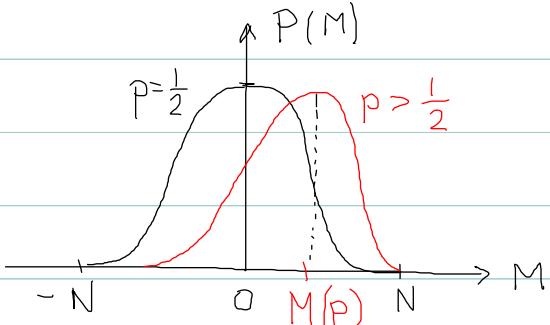
$$P(n_{\uparrow}, n_{\downarrow}) = \frac{N!}{n_{\uparrow}! n_{\downarrow}!} p^{n_{\uparrow}} (1-p)^{n_{\downarrow}}$$

M ↑



$$n_{\uparrow} + n_{\downarrow} = N, \quad n_{\uparrow} - n_{\downarrow} = M$$

$$P(M) = \frac{N!}{\underbrace{\left(\frac{N+M}{2}\right)! \left(\frac{N-M}{2}\right)!}_{\Omega(M)}} \frac{1}{2^N}, \quad (p = \frac{1}{2} \Rightarrow \uparrow, \downarrow \text{ are equivalent})$$



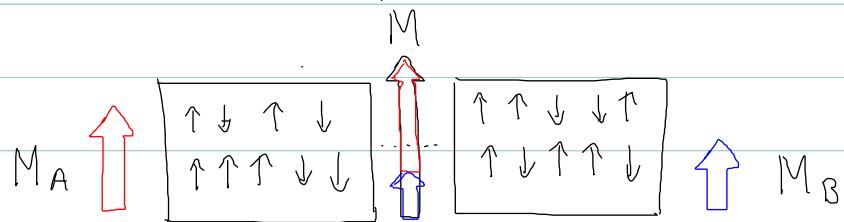
$p \geq \frac{1}{2}$ biases for $M \neq 0$

physically via magnetic field $E = -H \cdot M$

$$p = \frac{e^h}{e^h + e^{-h}}, \quad q = 1-p = \frac{e^{-h}}{e^{-h} + e^h}, \quad h \equiv \frac{H \cdot M}{k_B T}$$

Two "Ising" magnets in equilibrium

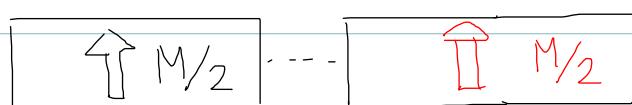
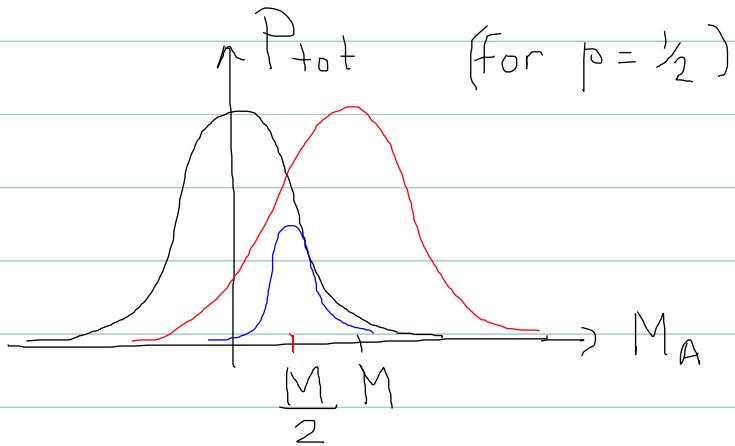
two magnets in thermal equilibrium: $M_A + M_B = M$



$$\Omega_{\text{tot}}(M_A) = \Omega(M_A) \Omega(M - M_A); \quad \Omega_{\text{grand}} = \sum_{M_A=-N}^N \Omega_{\text{tot}}(M_A)$$

$$P_{\text{tot}}(M_A, M_B) = \frac{\Omega(M_A) \Omega(M_B)}{\Omega_{\text{grand}}(M)}$$

[maximize P_{tot} by $M_A = M_B = \frac{M}{2}$]

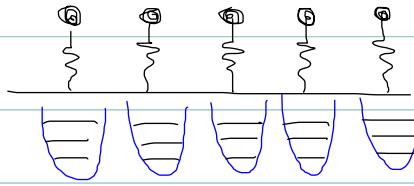


most probable
macrostate for
 $p = \frac{1}{2}$

Quantum oscillators (bosons)

e.g. phonons, EM modes, ...

- simple example: Einstein model of phonons (lattice vibrations)



$$E_i = \hbar \omega_0 n_i$$

$\uparrow D(\omega)$ \uparrow^N all same
 ω_0

$$E_{n_1, n_2, \dots, n_N}^{\text{tot}} \equiv E_{\{n_i\}} = \hbar \omega_0 \underbrace{(n_1 + n_2 + \dots + n_N)}_{N}$$

(in reality $3N$ coupled oscillators \rightarrow
 $\rightarrow 3N$ normal modes with ω_k freq.'s.)

$$\Omega(N, n) = ?$$

\hookleftarrow $\stackrel{n}{\vdots}$ \Rightarrow

$\rightarrow N=2 \rightarrow n :$ $\boxed{1} \quad \boxed{1}$

$$\begin{array}{c|c}
\frac{0}{1} & \frac{n}{n-1} \\
\hline
\frac{1}{2} & \frac{n-1}{n-2} \\
\hline
\frac{2}{3} & \frac{n-2}{n-3} \\
\hline
\vdots & \vdots \\
\hline
\frac{n}{n} & \frac{0}{0}
\end{array}$$

$\boxed{\Omega(2, n) = n+1} = \sum_{n_1=0}^n 1 = \sum_{n_1, n_2=0}^n \delta_{n_1+n_2, n}$

$$\rightarrow N = 3, n :$$

$$\begin{array}{r} 0 \\ \hline 0 & 0 & 4 \end{array}$$

$$\begin{array}{r} 0 \\ \hline 0 & 1 & 3 \end{array}$$

$$\begin{array}{r} 0 \\ \hline 0 & 2 & 2 \end{array}$$

$$\begin{array}{r} 0 \\ \hline 0 & 3 & 1 \end{array}$$

$$\begin{array}{r} 0 \\ \hline 0 & 4 & 0 \end{array}$$

$$\begin{array}{r} 1 \\ \hline 1 & 0 & 3 \end{array}$$

$$\begin{array}{r} 1 \\ \hline 1 & 1 & 2 \end{array}$$

$$\begin{array}{r} 1 \\ \hline 1 & 2 & 1 \end{array}$$

$$\begin{array}{r} 1 \\ \hline 1 & 3 & 0 \end{array}$$

$$\begin{array}{r} 2 \\ \hline 2 & 0 & 2 \end{array}$$

$$\begin{array}{r} 2 \\ \hline 2 & 1 & 1 \end{array}$$

$$\begin{array}{r} 2 \\ \hline 2 & 2 & 0 \end{array}$$

$$\begin{array}{r} 3 \\ \hline 3 & 0 & 1 \end{array}$$

$$\begin{array}{r} 3 \\ \hline 3 & 1 & 0 \end{array}$$

$$\begin{array}{r} 4 \\ \hline 4 & 0 & 0 \end{array}$$

$$\Omega(2,4) = 5$$

$$\Omega(2,3)$$

$$= 4$$

$$\Omega(2,2) = 3$$

$$\Omega(2,1) = 2$$

$$\Omega(2,0) = 1$$

$$N = \# \text{ atoms} \approx 10^{23}$$

\Rightarrow incomprehensibly huge

$$= \Omega(3,4) = 5+4+3+2+1 = 15$$

$$\Omega(3,n) = \sum_{\substack{n_1, n_2, n_3 = 0}}^N \Omega(n_1+n_2+n_3, n)$$

$$= \frac{1}{2} (n+2)(n+1)$$

$$(= \frac{1}{2} \cdot 6 \cdot 5 = 15)$$

in general: $\Omega(N, n) = \frac{(N+n-1)!}{n!(N-1)!} \rightarrow$ # of ways to distrib.
n balls among N boxes

= $\frac{\text{total perm. of } n \text{ balls} + N-1 \text{ partitions}}{(\text{identical balls})(\text{ident. partitions})}$



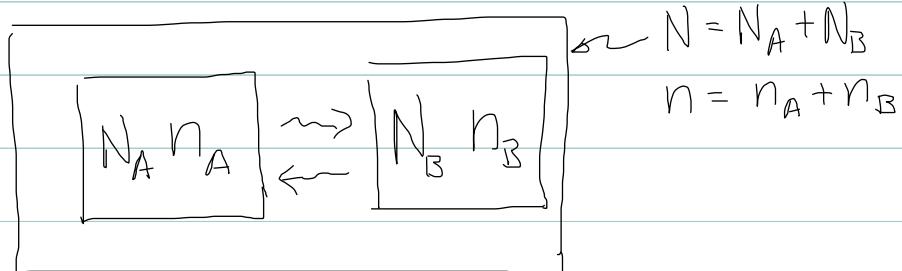
contrast: $C_n^N \times y^{N-n} \rightarrow 2 \text{ "boxes" } (x, y) \Rightarrow 2^N \text{ terms}$

here: " C_n^N " $\rightarrow 1 \Rightarrow \underline{N+1 \text{ terms}} \ll 2^N$

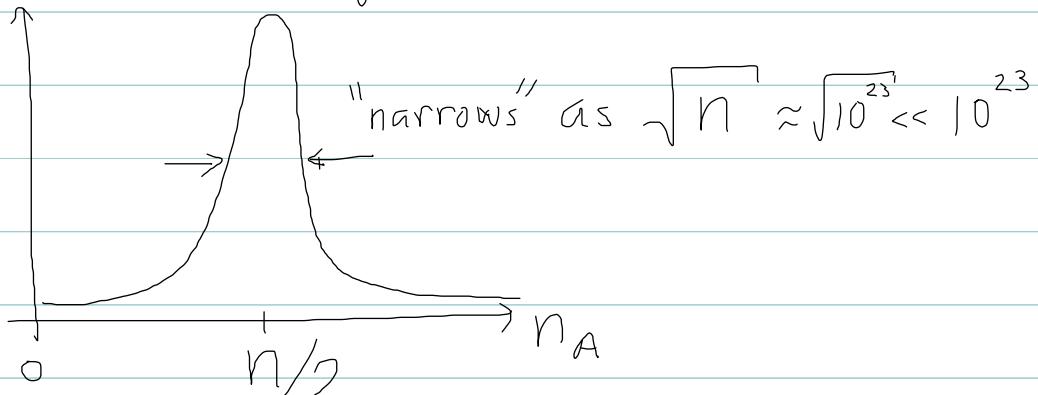
check: $\Omega(N, n) = \frac{(N+n-1)!}{n!(N-1)!}$

$$\Omega(2, n) = \frac{(n+1)!}{n! 1!} = n+1 \quad ; \quad \Omega(3, n) = \frac{(n+2)!}{n! 2!} = \frac{1}{2}(n+1)(n+2)$$

Two (Einstein) solids in contact \rightarrow thermal equilibrium:
 (A, B)



$$P(n_A) = \frac{\Omega_A(n_A) \Omega_B(n - n_A)}{\Omega_{\text{grand}}(n)}$$



(if $N_A = N_B$)

equilibrates s.t. $n_A \rightarrow n/2$

$$\Omega(N, n) = \frac{(n+N-1)!}{n!(N-1)!} \quad (\text{exact}) \quad \text{cf } 2^N$$

$$(\text{classical limit}) \approx \left(\frac{e n}{N}\right)^N \rightarrow \text{high occup.} \approx \left(\frac{\# \text{excitations}}{\text{oscill.}}\right)^N$$

2nd Law of thermodynamics

$n_{rms} \approx \sqrt{n} \ll n \Rightarrow$ essentially single macrostate in
"thermodynamic limit", i.e. $N \rightarrow \infty$; all others $P \rightarrow 0$!

$$\text{Entropy} = S = k_B \ln \Omega(E)$$

2nd Law: Large system in equilibrium will be in a macrostate with maximum entropy S .

S increases for bulk (large) system

S is additive:

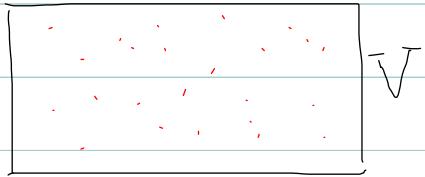
$$S_{tot} = S_A + S_B$$

$$k_B \ln \Omega = k \ln \Omega_A \Omega_B = k_B \ln \Omega_A + k_B \ln \Omega_B$$

$$\text{note: } \Omega_{tot} \approx \Omega_{grand} = \sum_{n_A} \Omega_{tot}(n_A)$$

Boltzmann gas

$$\Omega(E, V) = ?$$



determined by phase-space volume of shell w/ $R = \sqrt{E}$
 states determined by (\vec{r}_i, \vec{p}_i) ← 6N-dimension.

$$\Omega(E, V) = \sum_{\{\vec{r}_i, \vec{p}_i\}} 1, \text{ w/ energy } E \pm \Delta E$$

$$\begin{aligned} &= \frac{1}{N!} \int \frac{d^{3N}r d^{3N}p}{(2\pi\hbar)^{3N}} \delta(E - \sum_{i=1}^N \frac{p_i^2}{2m}) \Delta E \\ &\sim \frac{V^N}{N!} \frac{(2\pi)^{3N/2}}{\left(\frac{3N}{2}-1\right)!} \frac{(2mE)^{\frac{3N-1}{2}}}{h^{3N}} \frac{2m}{2\sqrt{2mE}} \Delta E \\ &\sim \frac{1}{N!} \frac{\pi^{3N/2}}{\left(\frac{3N}{2}\right)!} \frac{(2m)^{3N/2}}{h^{3N}} V^N E^{-3N/2} \end{aligned}$$

$$\Rightarrow S = k_B \ln \Omega(E) = k_B N \left[\frac{5}{2} + \ln \left(\frac{V}{N} \left(\frac{4\pi m E}{3N h^2} \right)^{3/2} \right) \right]$$

$$\left(A_d = \frac{2\pi^{d/2}}{\left(\frac{d}{2}-1\right)!} r^{d-1} \right) \quad (\text{Sackur-Tetrode eqn})$$

"quick & dirty":

$$\Omega(E) = \frac{1}{N!} \int \frac{d^{3N}r d^{3N}p}{(2\pi\hbar)^{3N}} = \underbrace{\frac{1}{N!}}_{\text{box}} \underbrace{(2\pi\hbar)^{3N}}_{\text{quantiz.}} \underbrace{\frac{2\pi}{(\frac{3N}{2}-1)!}}_{\frac{3N}{2}} \underbrace{\frac{P^{3N-1}}{\Delta P}}_{\text{Area}(P)} \approx P^{3N}$$

$$\Omega(E) \approx \underbrace{\frac{V^N}{N!}}_{(LK)^{3N}} \underbrace{\frac{1}{(2\pi)^{\frac{3N}{2}}} \cdot \frac{1}{\frac{3N}{2}!}}_{\text{dimensionless}} \left(\frac{2mE}{\hbar^2} \right)^{\frac{3N}{2}}$$

$$\ln \Omega = N \left[\frac{5}{2} + \ln \left(\frac{V}{N} \cdot \left(\frac{4\pi m E}{3\hbar^2 N} \right)^{3/2} \right) \right]$$

$$S(E) \approx N f(V E^{3/2})$$

↑
extensive!

$$\Rightarrow V T^{3/2} \sim V T^{f/2} \quad (f=3)$$

const for isentropic/adiabatic

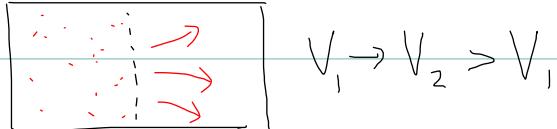
Gibbs' $\frac{1}{N!}$ factor

$$\text{Ideal gas: } \Omega(N, U, V) = f(N) V^N U^{3N/2}$$

V increasing processes:



- Free expansion: $Q=0, W=0 \Rightarrow \Delta U=0$



$$Q=0, \text{ but } \Delta S = S_f - S_i = Nk_B \ln \frac{V_f}{V_i} > 0$$

created (increased) entropy in irreversible process!

- Quasi-static, isothermal expansion: $T=\text{const} \Rightarrow \Delta U=0$

$$\Delta S = Nk_B \ln \frac{V_f}{V_i} = \frac{Q}{T} \quad \checkmark$$

transfer of S from environment:

$$\begin{aligned} S_{\text{universe}} &= S_{\text{system}} + S_{\text{environment}} = \text{const} \\ \Rightarrow \text{reversible: } TdS &= Q \end{aligned}$$

in general: $TdS \geq Q$

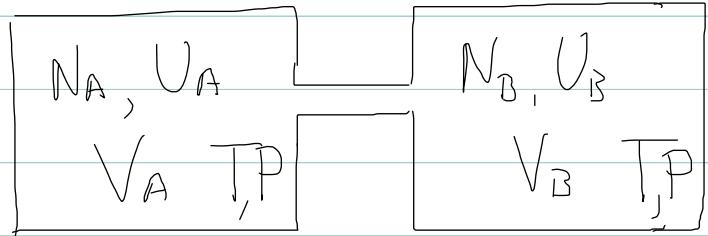
- quasi-static, adiabatic expansion: $\Delta U = W < 0$

$$\underline{Q=0}: \quad V U^{3/2} = \text{const}$$

$\Rightarrow S_{\text{system}} = \text{const} \Rightarrow \Delta S_{\text{universe}} = 0$, for reversible adiabatic process.

Entropy of mixing

A, B gases \rightarrow free expansions:



$$\Rightarrow V_f = V_A + V_B$$

$$S_{\text{tot}} = S_A + S_B, \quad \Delta S = \Delta S_A + \Delta S_B$$

$$\Delta S_{\text{tot}} = N_A k_B \ln \left(\frac{V_f}{V_A} \right) + N_B k_B \ln \frac{V_f}{V_B} = \text{entropy of mixing}$$

$$\Delta S_{\text{tot}} = -N k_B [x \ln x + (1-x) \ln (1-x)]$$

Ising magnet distribution

- binomial distribution of m up spins (probability p) out of N spins

```
In[88]:= P[m_, N_, p_] := N! / m! / (N - m)! p^m (1 - p)^(N - m)
```

```
In[89]:= P[m, N, p]
```

$$\text{Out}[89]= \frac{N! p^m (1-p)^{N-m}}{m! (N-m)!}$$

Normal (Gaussian) distribution limit:

```
In[91]:= Log[P[m, N, p]]
```

```
In[94]:= Series[Log\left(\frac{N! p^m (1-p)^{N-m}}{m! (N-m)!}\right) /. p \rightarrow 1/2, {m, N/2, 2}]
```

$$\text{Out}[94]= \log\left(\frac{2^{-N} N!}{\Gamma\left(\frac{N}{2} + 1\right)^2}\right) - \left(m - \frac{N}{2}\right)^2 \psi^{(1)}\left(\frac{N}{2} + 1\right) + O\left(\left(m - \frac{N}{2}\right)^3\right)$$

```
In[102]:= Series[
```

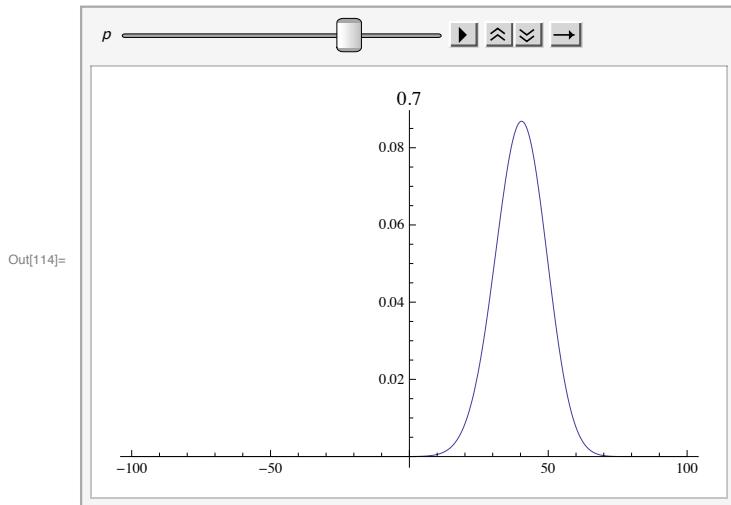
```
N Log[N] - N - m Log[m] + m - (N - m) Log[N - m] + N - m - N Log[2], {m, N/2, 2}]
```

$$\text{Out}[102]= -\frac{2 \left(m - \frac{N}{2}\right)^2}{N} + O\left(\left(m - \frac{N}{2}\right)^3\right)$$

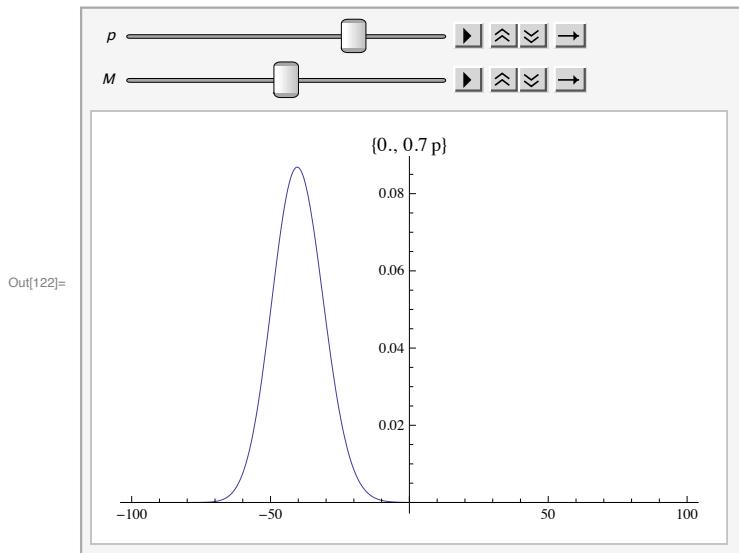
- Plots as function of magnetization ma for system A, B for different biases

$p = \frac{e^h}{e^h + e^{-h}}$ of up spin (corresponds to external field h) and magnetization M:

```
In[114]:= Animate[Plot[P[(100 + ma)/2, 100, p], {ma, -100, 100}, PlotLabel \rightarrow p,
PlotRange \rightarrow All], {p, 0.1, 0.9}, AnimationRunning \rightarrow False]
```



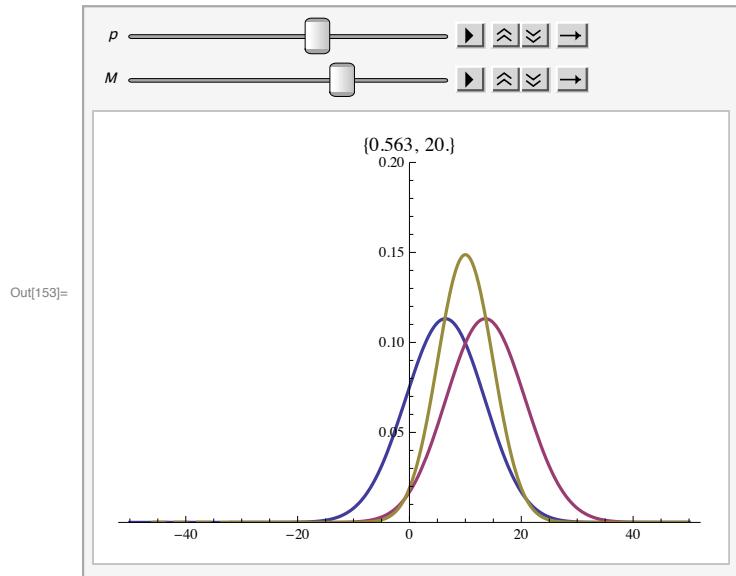
```
In[122]:= Animate[Plot[P[(100 + M - ma) / 2, 100, p],  
{ma, -100, 100}, PlotLabel -> {"M" M, "p" p}, PlotRange -> All],  
{p, 0.1, 0.9}, {M, -90, 90}, AnimationRunning -> False]
```



■ Plots of P for a combined A-B system (with $ma + mb = M$) as function of ma

for different biases $p = \frac{e^h}{e^h + e^{-h}}$ of up spin (corresponds to external field h) and magnetization M:

```
In[153]:= Animate[Plot[{P[(N+ma)/2, N, p] /. N -> 50, P[(N+M-ma)/2, N, p] /. N -> 50,
15 P[(N+ma)/2, N, p] P[(N+M-ma)/2, N, p] /. N -> 50}, {ma, -50, 50},
PlotStyle -> Thick, PlotLabel -> {p, M}, PlotRange -> {0, 0.20}],
{p, 0.2, 0.8}, {M, -50, 50}, AnimationRunning -> False]
```



```
In[149]:= Export["magnetAB.pdf", %147]
```

```
Out[149]= magnetAB.pdf
```

std = $\langle m^2 \rangle - \langle m \rangle^2 = \langle m \rangle(1-p)$ for binomial distribution:

```
In[15]:= Sum[P[m, N, p] (m^2 - N^2 p^2), {m, 0, N}]
```

```
Out[15]= -N(p^2 - p)
```