

Outline of lecture 2/15/2011

2/15
(1)

- (1) Finish discussion of Einstein solid, why is multiplicity $\Omega_{\text{total}}(q_A) \cong \Omega_A(q_A) \Omega_B(q_B)$ such a fantastically narrow peak for $N_A, N_B \sim 10^{23}$?
- sub theme: Functions raised to high powers look like Gaussian near global maximum

- (2) Heuristic derivation of multiplicity of ideal gas, $\Omega(N, U, V)$, for atoms

- discuss Gamma Γ^n $V^n(x)$
- surface area of d-dimensional hypersphere

- (3) Implications of $\Omega(N, U, V)$:

- Sackur-Tetrode equation for entropy $S(N, U, V) = k \ln \Omega$
- Ω very sharply peaked Γ^n of V_A, U_A, N_A for two subsystems of gases A, B
- entropy of mixing

2/15
(2)

Why Are Some Dimensionless Physical Ratios So Big or So Small?
Fine Tuning By Deity, Lottery Ticket?

Some basic constants of nature look big or small but this is misleading, result of choice of unit like m, s, kg

$$h \sim 10^{-33} \text{ J.s}$$

$$G \sim 10^{-10} \frac{\text{N.m}^2}{\text{kg}^2}$$

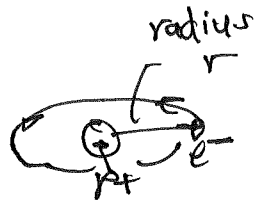
$$c \sim 10^8 \frac{\text{m}}{\text{s}}$$

$$e \sim 10^{-19} \text{ C}$$

$$m_e \sim 10^{-30} \text{ kg}$$

But what about dimensionless ratios of similar quantities, this gives pure number that has same value no matter what units are used.

Example: consider hydrogen atom from classical view point, what is ratio of electrical force to gravitational force?



$$F_{\text{electrical}} = \frac{k e^2}{r^2} \quad k \sim 10^{10} \frac{\text{N.m}^2}{\text{C}^2}$$

$$F_{\text{gravitational}} = \frac{G m_e m_p}{r^2} \quad G \sim 10^{-10}$$

$$\frac{F_{\text{elec}}}{F_{\text{grav}}} = \frac{k e^2}{G m_e m_p} \sim 10^{37}$$

a large # no matter what units are used

why would any dimensionless ratio be so large
(or its reciprocal so small)? Why not of order 1
or 10 or 100?

Dirac had insight when observed

$$\frac{\text{diameter of universe}}{\text{diameter of proton}} \sim \frac{10^{10} \text{ ly} \times 10^{16} \frac{\text{m}}{\text{ly}}}{10^{-15} \text{ m}} \sim 10^{41}$$

maybe two such large numbers must be related, one
explains the other.

But universe is expanding (Hubble 1922), so if related
conclude that

$$\frac{k e^2}{G m_e m_p}$$

must vary with time, i.e. some Fundamental constants are
not constant!

Can test by using big telescopes to look far out in
space and so look back in time, 10^{10} years in past,
no evidence for time dependence. So why the big #s?

Fine Tuning

One reason why Dirac was wrong is that he didn't consider smallest possible physical length, the Planck length

$$l_p = \left[\frac{\hbar G}{c^3} \right]^{1/2} \approx 10^{-35} \text{ m}$$

$$t_p = \frac{l_p}{c} = 10^{-43} \text{ s}$$

$$m_p \approx \sqrt{\frac{\hbar c}{G}} \approx 10^{-8} \text{ kg}$$

ratio $\frac{\text{size of universe}}{\text{planck length}} \sim \frac{10^{10} \text{ ly} \times 10^{16} \frac{\text{m}}{\text{ly}}}{10^{-35}} \sim 10^{61}$

of Planck volumes in universe $\sim (10^{61})^3 \approx 10^{180}$, much much smaller than Graham's # so physically impossible to write out that number

Strange fact: as big as $F_{\text{elec}}/F_{\text{grav}}$ is, small change in magnitude, say 10^{34} or 10^{39} , would lead to different kind of universe

stars would have lifetime $< 10^6 \text{ y} \Rightarrow$ no evolution, no life

stars fail to undergo fusion $\Rightarrow$ no periodic table, no life

Fine tuning of dimensionless quantities a mystery + nuisance
read "Just Six Minutes" by Martin Rees

Voyager II plaque

show on projector

~1972

how to identify length scales, time scales,
 energy scales with alien civilization?

Lincos mathematical language: • possible to
 communicate across worlds?

lingua
cosmica

Back To Einstein Solids And Multiplicity

(6)

Key insights from previous lecture

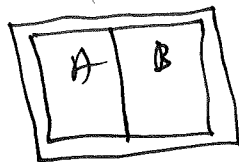
$$\Omega(N, q) = \binom{N+q-1}{q}$$

N quantum oscillators
with energy q

$$\Omega_{\text{total}}(q_A) \cong \Omega_A(q_A) \Omega_B(q_B)$$

$$q = q_A + q_B$$

two interacting subsystem



some macrostates much more likely than others if all accessible microstates are equally likely

$$\Omega(N, q) \cong \left(\frac{eq}{N}\right)^N \quad \text{for } q \gg N \gg 1$$

high temperature limit

make sure you can carry out this derivation using

Stirling's formula $\ln(n!) \approx n \ln n - n$ and Taylor

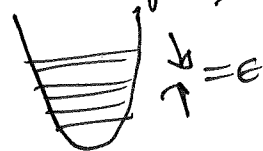
series approx $\ln(a+\epsilon) \approx \ln(a) + \frac{\epsilon}{a}$ if $|\frac{\epsilon}{a}| \ll 1$

(7)

Application of High-Temp Einstein
 Multiplicity: Show C_V satisfies
 Equipartition: $C_V \approx NkT$ $F=2$

$$\Omega(N, q) \approx \left(\frac{eq}{N}\right)^N \Rightarrow S = k \ln \Omega = Nk \ln \left[\frac{eq}{N}\right]$$

But $U = (\hbar\omega)q = \epsilon q$ if we define $\epsilon = \hbar\omega =$ energy level spacing



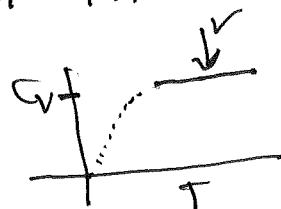
So

$$S = S(N, U) = Nk \ln \left[\frac{e}{N\epsilon} U \right]$$

$$= \underbrace{Nk \ln \left[\frac{e}{N\epsilon} \right]}_{\text{constant}} + Nk \ln U$$

$$= a + b \ln U$$

This is the recent quiz problem, we can calculate C_V by first deducing $T = T(U)$, then solving for $U = U(T)$ then differentiating to give $C_V = \frac{dU}{dT}$



$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_N = \frac{Nk}{U} \Rightarrow U = NkT$$

$$\Rightarrow C_V = Nk = N \cdot F \cdot \left(\frac{k}{2} \right) \text{ with } F=2$$

so high-temperature regime of Einstein solid agrees with equipartition.

In homework, you work out entire form $Q(T)$, study low and high- T approximations

(8)

Multiplicity of two coupled macroscopic Einstein solids has extremely narrow peak!

$$\text{width} \propto \frac{1}{\sqrt{N}} \approx 10^{-12} \text{ for } N \sim 10^{23}$$

To make discussion easier, assume equal number of identical non-interacting quantum harmonic oscillators in each subsystem

$$N_A = N_B = N \gg 1$$



$$q = q_A + q_B = \text{const}$$

Also assume high-temperature regime: $q \gg N \gg 1$,
a lot of energy in not so many oscillators

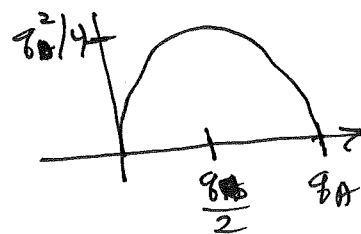
What is probability of observing macrostate with energy q_A in A, energy $q_B = q - q_A$ in B?

$$\Omega_{\text{total}}(q_A) \approx \Omega_A(q_A) \Omega_B(q_B)$$

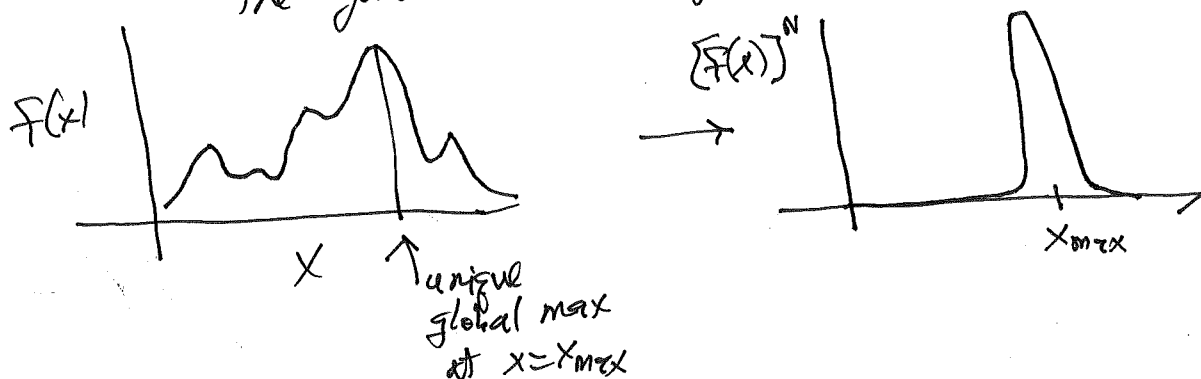
$$\approx \left(\frac{e^{q_A}}{N} \right)^N \left(\frac{e^{q_B}}{N} \right)^N$$

$$\Omega_{\text{total}} = \left(\frac{e}{N} \right)^{2N} [q_A (q - q_A)]^N$$

function $q_A (q - q_A)$ raised to high power
has single maximum of $\frac{q^2}{4}$ at $q_{\text{max}} = \frac{q}{2}$



Theorem: $F^N [F(x)]^N$ raised to high power
 N looks like Gaussian centered on
 the global maximum of $F(x)$



not too hard to see that peak shrinks in width as N increases

$$F(x)^N = F_{max}^N \left[\frac{F(x)}{F_{max}} \right]^N$$

but high powers of #'s less than one become quite small, only
 numbers near peak for which $F(x)/F_{max} \sim 1$ survive since
 $1^N = 1$ for all N

Use two standard tricks to analyze this situation

- take logarithm of $[F(x)]^N$ so we deal with large numbers rather than very large numbers
- use Taylor series to low order to get useful approximation about location of maximum

2/15
(10)

Let's see how it goes

$$g(x) = [F(x)]^N$$

define g for convenience
assume $f(x) > 0$ everywhere

$$\ln g(x) = N \ln f(x)$$

$$\approx N \ln \left[f(x_{\max}) + f'(x_{\max})(x - x_{\max}) + \frac{1}{2} f''(x_{\max})(x - x_{\max})^2 + \text{higher order terms} \right]$$

$= 0$ since expanding around maximum

$$\approx N \ln \left[f(x_{\max}) + \frac{1}{2} f''(x_{\max})(x - x_{\max})^2 \right]$$

? if x close enough to $x_{\max}$ so $|x - x_{\max}|$ small

$$\boxed{\ln g(x) \approx N \ln f(x_{\max}) + \frac{N}{2} \frac{f''(x_{\max})}{f(x_{\max})} (x - x_{\max})^2} \quad (*)$$

where I used our favorite trick with logs:

$$\log(a + \epsilon) \approx \log a + \frac{\epsilon}{a} \quad \text{if } \left| \frac{\epsilon}{a} \right| \ll 1$$

Now exponentiate both sides of (*) to undo logarithm. Get

$$g(x) = [F(x)]^N \approx f_{\max}^N \exp \left[\frac{N}{2} \frac{f''(x_{\max})}{f(x_{\max})} (x - x_{\max})^2 \right]$$

remember that $f''(x_{\max}) < 0$ near a maximum since $f'(x)$ is changing from positive to negative about peak

$$f'' \approx \frac{f'(x_{\max} + \epsilon) - f'(x_{\max} - \epsilon)}{2\epsilon} < 0$$

negative positive



Apply "theorem" to coupled Einstein solid 11

$$F(q_A) = q_A(q - q_A) = -q_A^2 + q q_A \quad q \text{ constant}$$

$$F'(q_A) = -2q_A + q = 0 \quad \text{at} \quad q_A = q/2 = q_{\max}$$

$$F(q_{\max}) = q^2/4$$

$$F''(q_A) = -2 \quad \text{independent of } q_A$$

$$\begin{aligned} \text{So: } [q_A(q - q_A)]^N &\simeq \left(\frac{q^2}{4}\right)^N \exp\left[-\frac{N}{2} \cdot \frac{2}{(q^2/4)} \left(q_A - \frac{q}{2}\right)^2\right] \\ &\simeq \left(\frac{q^2}{4}\right)^N \exp\left[-N \left(\frac{q_A - q/2}{q/2}\right)^2\right] \end{aligned}$$

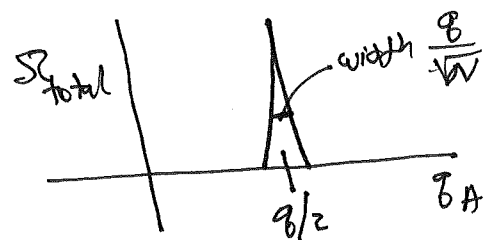
$$\text{so: } \boxed{\Sigma_{\text{total}} = \Sigma_A(q_A) \Sigma_B(q_B) = \left(\frac{eq}{2N}\right)^{2N} \exp\left[-N \left(\frac{q_A - q/2}{q/2}\right)^2\right]}$$

Deductions: $\left(\frac{eq}{2N}\right)^{2N}$ is very big # if $q \gg N \gg 1$, multiplicity has an enormous peak

width of peak defined by when $q_A - q/2$ causes $1/e \simeq 1/3$ drop from maximum

$$N \left(\frac{\Delta q}{q/2}\right)^2 \simeq 1 \Rightarrow \boxed{\Delta q \simeq \frac{q/2}{\sqrt{N}}}$$

$$\text{Full width half max} \simeq 2\Delta q \simeq \frac{q}{\sqrt{N}}$$



Preparation For Calculating Multiplicity of Atomic Ideal Gas: Gamma f^n (12)

Read Appendix B.2 on Gamma f^n

Start with observation: for real $a > 0$,

$$\int_0^{\infty} e^{-ax} dx = \frac{e^{-ax}}{-a} \Big|_0^{\infty} = \frac{1}{a} = a^{-1}$$

Can differentiate both sides w.r.t. "a" (theorem says this is ok)

so get:

$$\begin{aligned} \frac{d}{da} \int_0^{\infty} e^{-ax} dx &= \int_0^{\infty} \frac{d}{da} (e^{-ax}) dx = \frac{d}{da} (a^{-1}) \\ &= \int_0^{\infty} (-x) e^{-ax} dx = -a^{-2} \end{aligned}$$

conclude: $\int_0^{\infty} x e^{-ax} dx = a^{-2}$

repeat $n-1$ more times

$$\int_0^{\infty} x^2 e^{-ax} dx = 2a^{-3}$$

$$\int_0^{\infty} x^3 e^{-ax} dx = 6a^{-4}$$

:

$$\int_0^{\infty} x^n e^{-ax} dx = n! a^{-(n+1)}$$

set $a=1$ on both sides

note: differentiation of definite integral w.r.t a parameter extremely powerful trick, faster and easier than integration by parts. Keep it in mind

Euler's Gamma Function

Define $\Gamma(x+1) = \int_0^{\infty} x^x e^{-x} dx$ x a real # > 0

This was Euler's insight of how to extend the idea of factorial to the real (even complex) numbers:

$$\boxed{x! = \Gamma(x+1)}$$

definition of factorial
for arbitrary x

For example: $0! = \Gamma(1) = \int_0^{\infty} e^{-x} dx = 1$

$n! = \Gamma(n+1)$ we proved this on previous page for integer n

In homework, you relate $\Gamma(\frac{1}{2})$ to Gaussian integral $\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$ and conclude

$$\left(-\frac{1}{2}\right)! = \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$$

you also show recursion relation similar to $n! = (n-1)! \cdot n$

$$\boxed{\Gamma(x+1) = x \Gamma(x)} \text{ for real } x > 0$$

This lets us get other values

~~$$\left(-\frac{3}{2}\right)! = \Gamma\left(-\frac{1}{2}\right) = \Gamma\left(-\frac{3}{2} + 1\right) = -$$~~

$$\left(\frac{1}{2}\right)! = \Gamma\left(\frac{3}{2}\right) = \Gamma\left(\frac{1}{2} + 1\right) = \frac{1}{2} \Gamma\left(\frac{1}{2}\right) = \frac{\sqrt{\pi}}{2}$$

etc

Gamma Γ^x is unique way to extend $n!$ to real #'s if one assumes $\Gamma(1)=1$ and $\ln \Gamma(x)$ is convex
Bohr-Mollerup theorem

Stirling's Formula Applies To

(148)
2/15

$$\Gamma(x): \Gamma(x+1) \approx \sqrt{2\pi x} \left(\frac{x}{e}\right)^x$$

We derived Stirling's formula $n! \approx \sqrt{2\pi n} \left(\frac{n}{e}\right)^n$ for integer n by writing $\ln(n!) = \ln 1 + \ln 2 + \dots + \ln n$ and approximating sum by integral

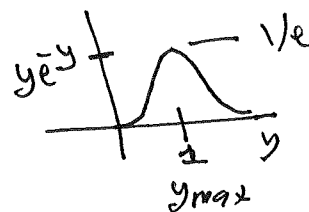
But one can prove result directly for Gamma f^n nsa applications of theorem that high powers of f^n look like Gaussian. Here is outline of proof (close to Schroeder p. 320):

$$\Gamma(\alpha+1) = \int_0^\infty x^\alpha e^{-x} dx = \int_0^\infty (x e^{-x/\alpha})^\alpha dx$$

$$y = \frac{x}{\alpha}$$

$$dx = \alpha dy$$

$$\Gamma(\alpha+1) = \alpha^{\alpha+1} \int_0^\infty (y e^{-y})^\alpha dy$$



We have function $f(y) = y e^{-y}$ has single global maximum at $y=1$ (please verify) with value $f_{\max} = \frac{1}{e}$

$$f''(y_{\max}) = -\frac{1}{e}$$

$$\text{so: } (y e^{-y})^\alpha \approx \left(\frac{1}{e}\right)^\alpha \exp[-\alpha(y-1)^2]$$

$$\Rightarrow \Gamma(\alpha+1) \approx \alpha \left(\frac{\alpha}{e}\right)^\alpha \int_0^\infty e^{-\alpha(y-1)^2} dy$$

$$\text{let } z = y-1$$

$$\approx \alpha \left(\frac{\alpha}{e}\right)^\alpha \int_{-1}^\infty e^{-\alpha z^2} dz$$

small error to extend -1 to $-\infty$ since peak is narrow and centered at 0

$$\approx \alpha \left(\frac{\alpha}{e}\right)^\alpha \int_{-\infty}^\infty e^{-\alpha z^2} dz = \sqrt{2\pi\alpha} \left(\frac{\alpha}{e}\right)^\alpha \text{ qed.}$$

Multiplicity and Entropy of Monoatomic Ideal Gas

(15)

Am going to show that for N atoms of ideal gas in volume V

$$\Omega(u, V, N) = f(N) V^N u^{3N/2} \quad N \gg 1 \quad (*)$$

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

This will let us calculate the entropy $S = k \ln \Omega$ of atomic gas, giving valuable formula, Sackur-Tetrode equation

Two observations:

- (*) contains Planck's constant h , so need quantum mechanics to get answer
- (*) contains mass of atom m , $\Rightarrow$ entropy varies with m , getting larger with bigger m

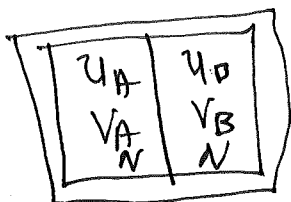
Will follow Schroeder's argument pages 68-72

This is heuristic simplified argument that avoids more difficult and lengthy quantum derivation. Qualitative ideas are correct so useful.

(16)

$$S(U, V, N) \propto U^{3N/2} V^N$$

implies multiplicity sharply peaked for macroscopic system of two interacting ideal gases of same N



partition allows U_A, V_A to vary

$$U_A + U_B = U$$

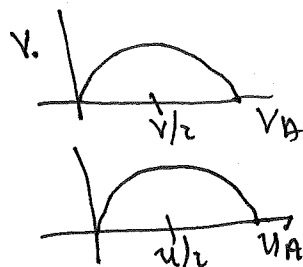
$$V_A + V_B = V$$

$$S_{\text{total}}(U_A, V_A) \approx S_A(U_A, V_A) S_B(U_B, V_B)$$

$$= [F(N)]^2 [V_A(V - V_A)]^N [U_A(U - U_A)]^{3N/2}$$

$$\Delta V_A \sim \frac{V}{\sqrt{N}}$$

$$\Delta U_A \sim \frac{U}{\sqrt{\frac{3N}{2}}}$$



expect same argument as Einstein solid

get enormous, extremely narrow peaks centered on equilibrium values

$$V_A = \frac{V}{2} \quad U_A = \frac{U}{2}$$

extremely unlikely to observe anything but equilibrium values,

Challenge: can you work out details if # of atoms can vary between A and B?

$$S_{\text{total}}(N_A) = F(N_A) F(N - N_A) = \dots$$

more complicated (too much so for this course)

(18)

Derivation of $\Omega(U, V, N)$

For N atoms of Ideal Gas in Volume V

1st question: what are microstates of system? need to count

atom described by six numbers (x, y, z, p_x, p_y, p_z)

location of center of mass (x, y, z)

momentum $\vec{p} = (p_x, p_y, p_z)$

momentum but not velocity enters quantum mechanics so avoid using velocity $\vec{v}$

Consider single atom $N=1$

guess $\Omega(U, V, 1) \propto V$

since $0 \leq x \leq L_x, 0 \leq y \leq L_y, 0 \leq z \leq L_z$
 $V = L_x L_y L_z$

energy conserved means

$$U = \frac{(\vec{p}_1)^2}{2m} = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2)$$

$$\text{or } p_x^2 + p_y^2 + p_z^2 = (\sqrt{2mU})^2$$

defines surface of sphere of radius $r = \sqrt{2mU}$

guess that multiplicity proportional to surface area of sphere

$$\Omega(U, V, 1) \propto V \underbrace{A_3(\sqrt{2mU})}_{\text{area of sphere in three dimensions}}$$

~~define~~