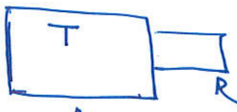
The canonical ensemble

We have been working in what is known as the <u>micro-canonical</u> ensemble:

$$E < H < E + \Delta E \qquad \boxed{H}$$

Energy specified precisely.
All states with the constraint equally probable

Now, we look at the <u>canonical ensemble</u>



Big Heat source at temperature T

our system with $\langle H \rangle = E$
Energy can fluctuate, all energies are possible, but average is E.

If μ-state i has energy E_i with probability p_i,
We maximize entropy with that constraint:

$$\text{Maximize} \quad -k\sum_i p_i \ln p_i + \Lambda_1\Big(\sum_i p_i - 1\Big) + \Lambda_2\Big(\underbrace{\sum_i p_i E_i}_{\langle E\rangle} - E\Big)$$

$$\frac{\partial}{\partial p_k} \rightarrow \; -k \ln p_k - k + \Lambda_1 + \Lambda_2 E_k = 0$$

$$p_k = e^{(-k + \Lambda_1 + \Lambda_2 E_k)/k} = \underset{\substack{\uparrow \\ \text{Normalization} \\ \text{constant}}}{C}\, e^{\Lambda_2 E_k}$$

Λ_2 must be negative for convergence

This max value is then the entropy of the system

$$S = -k_B \sum_i p_i \left(\ln C + \Lambda_2 E_i\right)$$

$$= -k_B \left[\ln C + \Lambda_2 U\right]$$

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$dU = dQ - PdV$

$dU = TdS - PdV$

$\left.\frac{\partial U}{\partial S}\right)_V = T$

$\left.\frac{\partial S}{\partial U}\right)_T = \frac{1}{T}$

$$\left.\frac{\partial S}{\partial U}\right)_V = -k_B \Lambda_2 = \frac{1}{T} \Rightarrow \Lambda_2 = -\frac{1}{k_B T}$$

$$p_k = C\, e^{-E_k / k_B T} \quad \text{: Maxwell-Boltzmann distribution}$$

"The Boltzmann factor"

In normalized form:

$$P_k = \frac{e^{-E_k/k_BT}}{Z}$$

"The partition function"

$$Z = \sum_k e^{-E_k/k_BT}$$

Average of any quantity A_k

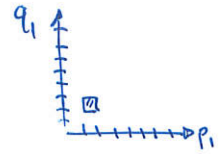
$$\langle A \rangle = \sum_k A_k p_k = \sum_k A_k e^{-E_k/k_BT}/Z$$

Some consequences

Equipartition theorem

For a classical system

Single particle 1-dim



$$\sum_k \longrightarrow \int \frac{dp_1\,dq_1}{h^2 N!}$$

sum over μ-states

$$\sum_k \longrightarrow \int \cdots \int \frac{dp_{1x} \cdots dq_{Nz}}{h^{3N} N!} = \int \frac{d^{3N}p\, d^{3N}q}{h^{3N} N!}$$

Average of any quadratic term in H is $\frac{k_BT}{2}$:

Suppose $H = \cancel{\tfrac{1}{2}}\frac{p_1^2}{2m} + \cancel{\tfrac{1}{2}}\frac{p_2^2}{2m} + \frac{1}{2}k_1x_1^2 + \frac{1}{2}k_2x_2^2 + a x_3^2 + \cdots$

for example

$$\langle a x_3^2 \rangle = \frac{\int \frac{d^{3N}p\, d^{3N}q}{N!\, h^{3N}}\; e^{-\frac{1}{k_BT}\left[\cancel{\frac{p_1^2}{2m}} + \cancel{\frac{p_2^2}{2m}} + \cdots + a x_3^2 + \cdots\right]}\; a x_3^3}{\int \frac{d^{3N}p\, d^{3N}q}{N!\, h^{3N}}\; e^{-\frac{1}{k_BT}\left[\cancel{p_1^2/2m} + \cancel{p_2^2/2m} + \cdots + a x_3^2 + \cdots\right]}}$$

$$= \frac{\int dx_3\, e^{-\frac{1}{k_BT} a x_3^2}\, a x_3^2}{\int dx_3\, e^{-\frac{a}{k_BT} x_3^2}}$$

$$\int_{-\infty}^{\infty} e^{-\alpha x^2}\, dx = \sqrt{\frac{\pi}{\alpha}}$$

$$-\frac{\partial}{\partial\alpha} \Rightarrow \int_{-\infty}^{\infty} e^{-\alpha x^2} x^2\, dx = \sqrt{\frac{\pi}{\alpha}}\,\frac{1}{2\alpha}$$

$$= \frac{\sqrt{\pi/\alpha}}{\sqrt{\pi/\alpha}} \cdot a\,\frac{1}{2\alpha} = a\,\frac{1}{2\left(\frac{a}{k_BT}\right)} = \frac{k_BT}{2}$$

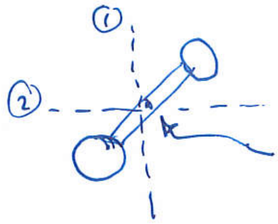
Many applications: Ideal gas: $H = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$ 3N quadratic terms

$$\Rightarrow \langle H \rangle = U = 3N\,\frac{k_BT}{2}$$

Diatomic molecule

1-D $\quad H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{1}{2}k(x_1 - x_2)^2 \leftarrow$ 3 quadratic terms

3-D $\quad \frac{p_{1x}^2}{2m} + \frac{p_{2x}^2}{2m} + \frac{p_{1y}^2}{2m} + \frac{p_{2y}^2}{2m} + \frac{p_{1z}^2}{2m} + \frac{p_{2z}^2}{2m} + \frac{k}{2}(\vec{r}_1 - \vec{r}_2)^2$



rotational modes

7 quadratic terms

$$\frac{p_{cmx}^2}{4m} + \frac{p_{cmy}^2}{4m} + \frac{p_{cmz}^2}{4m} + \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2} + \underbrace{\frac{1}{2\mu}p_{rel}^2 + \frac{1}{2}kx_{rel}^2}_{\text{vibrational mode}}$$

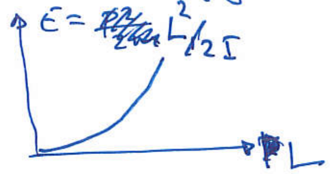
No L_3 because point particles ($I_3 \to 0$)

$$\langle H \rangle = N \cdot \frac{7}{2} k_B T$$

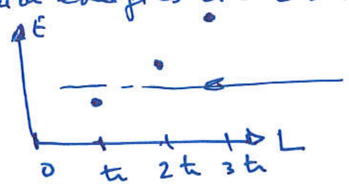
$$C_V = \frac{\partial U}{\partial t} = \frac{7}{2} N k_B$$

<u>Puzzle</u>: what about the contribution from the sub-particles? e^-, p, n, quarks, etc.

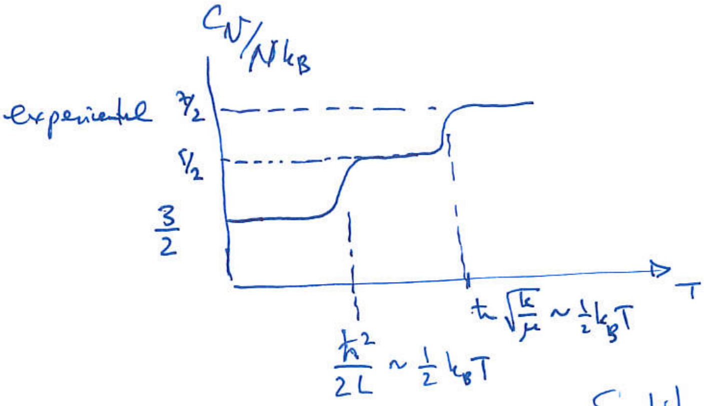
Classical energy spectrum is continious



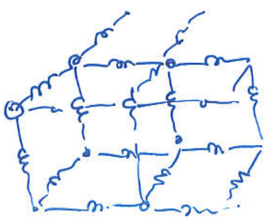
Quantum energies are discrete



If $\frac{kT}{2} \ll E_i$, that state will be unoccupied $p(E_i) \sim e^{-E_i/k_BT}$



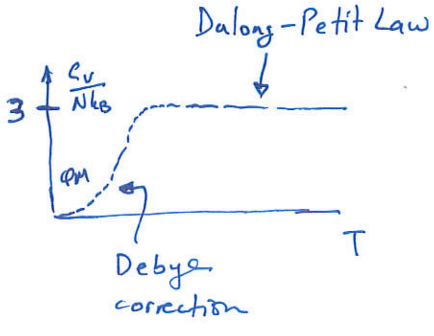
<u>Solids</u>



N atoms,
3 springs/atom

3 vibrational modes/atom) $3N$ altogether
each vib mode $\Rightarrow$ 2 quadratic terms) $\underline{6N}$

$$\langle H \rangle = 6N \frac{k_B T}{2}$$



$$S = -k_B \sum_i P_i \ln P_i$$

$$P_i = e^{-\beta E_i}/Z \qquad \beta = \frac{1}{k_B T} \qquad Z = \sum_i e^{-\beta E_i}$$

$$U = \langle E \rangle = \sum E_i e^{-\beta E_i}/Z$$

$$S = -k_B \sum P_i \left[-\beta E_i - \ln Z\right]$$

$$= \underbrace{k_B\beta}_{\frac{1}{T}} U + k_B \ln Z$$

$dU = dQ - PdV$

$A = U - TS$

$$ST = U + k_B T \ln Z \Rightarrow -k_B T \ln Z = -ST + U \equiv A$$ Helmholtz free energy

$-dA = TdS + SdT - dU$
$= dQ - dU + SdT$
$= PdV + SdT$

$-\frac{\partial A}{\partial V}\Big)_T = P \ ; \ \frac{\partial A}{\partial T}\Big)_V = -S$

Also, $U = \frac{\sum e^{-\beta E_i} E_i}{\sum_i e^{-\beta E_i}} = -\frac{\partial}{\partial \beta} \ln Z$

Example: Classical Ideal Gas

$$E = H = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$$

$$Z = \int \frac{dp^{3N} dq^{3N}}{h^{3N} N!} e^{-\beta \sum_{i=1}^{3N} \frac{p_i^2}{2m}}$$

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

$$\ln Z = N \ln\left[V (2\pi m k_B T)^{3/2}\right] - 3N \ln h - \overbrace{\ln N!}^{-N\ln N + N}$$

$$U = -\frac{\partial}{\partial \beta} \ln Z = N \frac{3}{2} \frac{1}{\beta} = \frac{3}{2} k_B T N$$

$$P = -\frac{\partial A}{\partial V}\Big)_V = \frac{\partial}{\partial V} k_B T \left[N \ln V\right] = N k_B T / V \qquad S = \ldots$$

The density matrix

$$\rho = \sum_n |\psi_n\rangle \, p_n \langle \psi_n|$$

p_n: prob that the system is in state n

Define ensemble average

$$[A] = \sum_n p_n \langle A \rangle_n = \sum_n p_n \langle \psi_n | A | \psi_n \rangle$$

p_n: ordinary probability; $\langle \psi_n | A | \psi_n \rangle$: quantum expectation value

$|\psi_n\rangle$'s are normalized, so $\langle \psi_n | \psi_n \rangle = 1$ e.g.

But not necessarily orthonormal, possibly incomplete

$$\mathrm{Tr}\,\rho = \sum_i \langle i | \rho | i \rangle \qquad |i\rangle\text{'s are complete}$$

$$= \sum_{in} \underbrace{\langle i | \psi_n \rangle \, p_n \langle \psi_n | i \rangle}_{\mathbb{1}} = \sum_n p_n \underbrace{\langle \psi_n | \psi_n \rangle}_{1} = 1$$

$$\mathrm{Tr}(\rho A) = \sum_i \langle i | \rho A | i \rangle = \sum_{in} \underbrace{\langle i | \psi_n \rangle \, p_n \langle \psi_n | A | i \rangle}_{\mathbb{1}}$$

$$= \sum_n p_n \langle \psi_n | A | \psi_n \rangle$$

$$= \sum_n p_n \langle A \rangle_n = [A]$$

$$\boxed{\mathrm{Tr}\,\rho = 1} \quad \boxed{\mathrm{Tr}(\rho A) = [A]}$$

ρ for μ-canonical quantum ensemble: $\rho = \sum p_n |\psi_n\rangle\langle\psi_n|$

with $p_n = p$ for $E < E_n < E + \Delta$ (p chosen so that it is normalized)

for canonical ensemble: $\rho = e^{-\beta H}/Z$; $Z = \mathrm{Tr}(e^{-\beta H}) = \sum_i \langle i | e^{-\beta H} | i \rangle = \sum_i e^{-\beta E_i}$

Consider the energy eigenstates $H|u_i\rangle = E_i |u_i\rangle$

$$\rho = \frac{1}{Z} \sum_{ij} |u_i\rangle \underbrace{\langle u_i | e^{-\beta H} | u_j \rangle}_{e^{-\beta E_i} \delta_{ij}} \langle u_j | = \sum_i |u_i\rangle \frac{e^{-\beta E_i}}{Z} \langle u_i |$$

$$[A]_{\text{canonical}} = \sum_i \frac{e^{-\beta E_i}}{Z} \langle u_i | A | u_i \rangle$$

If the system is composed of independent components.

$$H = H_1 + H_2 + \cdots + H_N$$

(classical ideal gas)

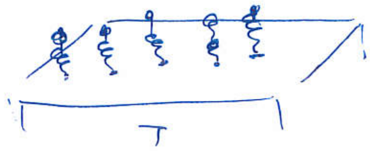
(a collection of harmonic oscillators)

(a collection of magnetic moments)

Then $Z = \sum_{\substack{\text{sum} \\ \text{over} \\ \text{states}}} e^{-\beta H} = \left(\sum e^{-\beta H_1}\right)\left(\sum e^{-\beta H_2}\right) \cdots \left(e^{-\beta H_N}\right)$

$$= \left(\sum e^{-\beta H_1}\right)^N$$

Example: Harmonic oscillators



Classical $\quad H = \sum_i \frac{p_i^2}{2m} + \frac{k}{2}\sum_i y_i^2$

Equipartition $\Rightarrow U = 2N \frac{1}{2} k_B T$

Quantum Mechanical

$$Z = \left(\sum_{n=0}^{\infty} e^{-\beta\hbar\omega_c(n+1/2)}\right)^N$$

$$= \left(\frac{e^{-\beta\hbar\omega_c/2}}{1 - e^{-\beta\hbar\omega_c}}\right)^N$$

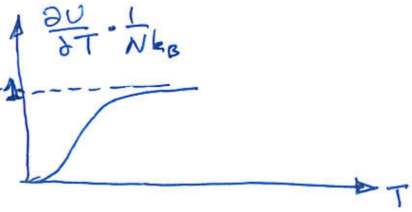
$$U = -\frac{\partial}{\partial\beta}\ln Z = N\left\{-\frac{\partial}{\partial\beta}\left[-\beta\hbar\omega_c/2\right] + \frac{\partial}{\partial\beta}\left[1 - e^{-\beta\hbar\omega_c}\right]\right\}$$

$$= \frac{N\hbar\omega_c}{2} + N\frac{\hbar\omega_c e^{-\beta\hbar\omega_c}}{1 - e^{-\beta\hbar\omega_c}} = \frac{N}{2}\hbar\omega_c + N\hbar\omega_c\frac{1}{e^{\beta\hbar\omega_c} - 1}$$

High T → small $\beta \Rightarrow U = \frac{N}{2}\hbar\omega_c + \frac{N}{\beta}$

equipartition limit

$$\frac{\partial}{\partial T} = \frac{d\beta}{dT}\frac{\partial}{\partial\beta} = -\frac{1}{k_B T^2}\frac{\partial}{\partial\beta}$$



$$\frac{\partial U}{\partial T} = -\frac{1}{k_B T^2}\frac{\partial U}{\partial\beta} = \frac{N\hbar\omega_c}{k_B T^2}\frac{\hbar\omega_c e^{\beta\hbar\omega_c}}{\left(e^{\beta\hbar\omega_c} - 1\right)^2}$$

High T → low β $\quad \frac{C_V}{Nk_B} \rightarrow \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{1}{(1 + \beta\hbar\omega_c - 1)^2} = 1$

Low T → High β $\quad \frac{C_V}{Nk_B} \rightarrow \left(\frac{\hbar\omega_c}{k_B T}\right)^2 e^{-\beta\hbar\omega_c}$

Two level system

magnetic moment

Example: $H = -\vec{\mu}\cdot\vec{B}$ $\qquad \vec{\mu} = -\gamma\vec{S}$ ← gyromagnetic ratio: $\frac{e}{m}$

(Actually, $H = -\vec{B}\cdot(\vec{\mu}_1+\vec{\mu}_2+\cdots\vec{\mu}_N)$
$Z = \sum e^{-\beta H}$
$= (\sum e^{-\beta H_1})^N$
$= (Z_1^N)$)

Choose $\vec{B} = B\hat{z}$

$$H = \gamma B S_z$$

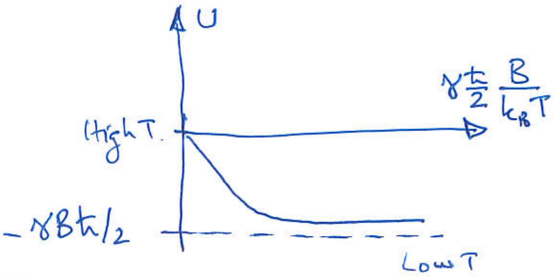
Two eigenstates $H|\uparrow\rangle = \gamma B\frac{\hbar}{2}|\uparrow\rangle \qquad \epsilon_1 = +\gamma B\frac{\hbar}{2}$

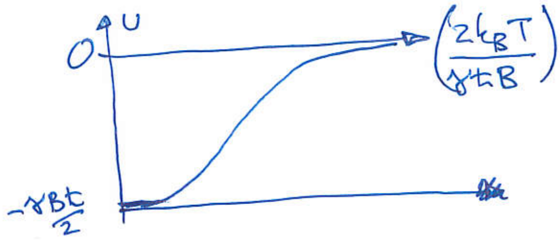
$H|\downarrow\rangle = -\gamma B\frac{\hbar}{2}|\downarrow\rangle \qquad \epsilon_2 = -\gamma B\hbar/2$

$$Z = e^{-\epsilon_1/k_BT} + e^{-\epsilon_2/k_BT} = e^{-\beta\gamma B\frac{\hbar}{2}} + e^{\beta\gamma B\frac{\hbar}{2}}$$

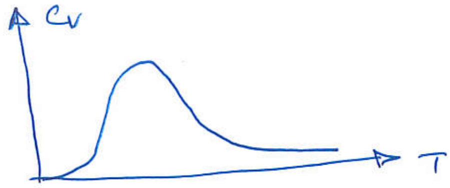
$$= 2\cosh\left[\beta\gamma B\tfrac{\hbar}{2}\right]$$

$$U = -\frac{\partial}{\partial\beta}\ln Z = -\gamma B\frac{\hbar}{2}\frac{\sinh[\beta\gamma B\frac{\hbar}{2}]}{\cosh[\beta\gamma B\frac{\hbar}{2}]} = -\gamma B\frac{\hbar}{2}\tanh\left[\beta\gamma B\tfrac{\hbar}{2}\right]$$





discuss "negative temperature"?



What is the expectation value of magnetisation?

$(\langle S_x\rangle_i = \langle S_y\rangle_i = 0)$

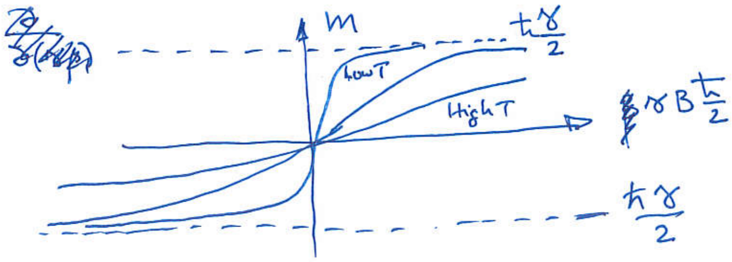
$$\vec{m} = [\vec{\mu}] = [-\gamma\vec{S}] = \hat{z}\sum_i \langle -\gamma S_z\rangle_i e^{-\beta\epsilon_i}/Z$$

$$= \left(-\gamma\frac{\hbar}{2}e^{-\beta\gamma B\hbar/2} + \gamma\frac{\hbar}{2}e^{\beta\gamma B\hbar/2}\right)/Z$$

$$= \hbar\gamma/2 \cdot 2\sinh[\beta\gamma B\hbar/2]/2\cosh\left[\beta\gamma B\tfrac{\hbar}{2}\right]$$

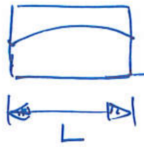
$$= \hbar\frac{\gamma}{2}\tanh\left[\beta\gamma B\tfrac{\hbar}{2}\right]$$

$$\frac{\partial}{\partial(B\beta)}\ln Z$$



"paramagnetism"

Photons – to be treated as harmonic oscillator modes in a box



$E = \sin k_n x \qquad k_n = \frac{n\pi}{L} x$

$$k = \frac{2\pi}{\lambda} \; ; \quad kc = \frac{2\pi c}{\lambda} = 2\pi\nu = \omega$$

Every ω a different oscillator

$$E_n = \hbar\omega(n + 1/2)$$

$n=0$ – no photons
$n=1$ – 1 photon
$n=2$ – 2 photons
etc

What is the average energy of a photon state?

$$Z = \sum_{n=0}^{\infty} e^{-\beta(n+1/2)\hbar\omega}$$

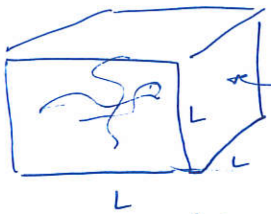
$$= e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega} = e^{-\beta\hbar\omega/2} \frac{1}{1-e^{-\beta\hbar\omega}}$$

$$\langle E \rangle = -\frac{\partial}{\partial\beta}\ln Z = -\frac{\partial}{\partial\beta}\left[-\beta\frac{\hbar\omega}{2} - \ln(1-e^{-\beta\hbar\omega})\right]$$

$$= \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$$

zero-point energy.

$\Rightarrow$ space has an infinite amount of this energy. Not possible to observe directly, but discuss "Casimir effect"

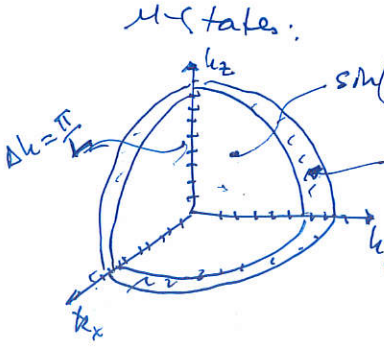


what is the ~~energy~~ frequency distribution like?

We will consider second term only.

Box with B.C.

μ-states:



$\sin(n_x \frac{\pi}{L} x)\sin(n_y \frac{\pi}{L} y)\sin(n_z \frac{\pi}{L} z)$

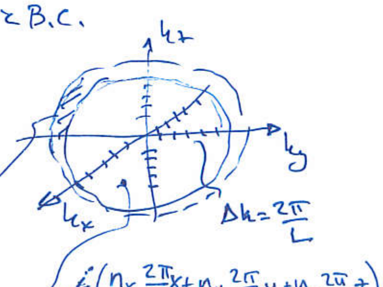
$$\frac{4\pi k^2 dk}{8(\pi/L)^3} \times 2 \; \mu\text{-states between } k \text{ and } k+dk$$

2 polarizations

$\frac{1}{8}$th of a sphere

Periodic B.C.

OR

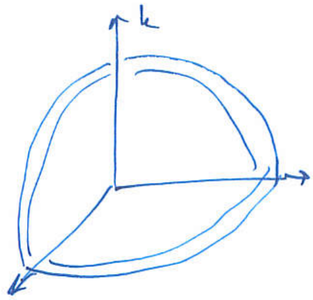


$e^{i(n_x \frac{2\pi}{L}x + n_y \frac{2\pi}{L}y + n_z \frac{2\pi}{L}z)}$

Same

$$\underbrace{\frac{4\pi k^2 dk}{(2\pi/L)^3}}_{\text{"density of states"} \times dk} \times 2 \quad \mu\text{-states}$$

15.5



$$\frac{4\pi k^2}{8}\,dk\,\frac{1}{(\frac{\pi}{L})^3}\times 2 = \frac{V k^2 dk}{\pi^2}$$

$$ck=\omega$$
$$c\,dk = d\omega$$

$$\frac{V\omega^2 d\omega}{c^3\pi^2}$$

Each oscillator has average energy

$$\langle E\rangle = \frac{\sum_i E_i e^{-\beta E_i}}{\sum e^{-\beta E_i}}$$

$$\sum_{n=0}^{\infty}(\cancel{n+\tfrac12)\hbar\omega}\; e^{-\beta(n+\frac12)\hbar\omega} \Big/ \sum_n e^{-\beta(n+\frac12)\hbar\omega}$$

$$= -\frac{\partial}{\partial\beta}\ln\sum_i e^{-\beta E_i} \qquad = e^{-\frac{\beta\hbar\omega}{2}}$$

$$= -\frac{\partial}{\partial\beta}\ln\frac{e^{-\hbar\omega\beta/2}}{1-e^{-\beta(n+\frac12)\hbar\omega}} =$$

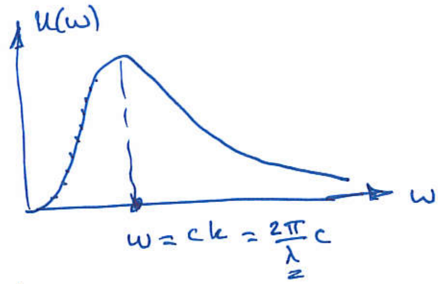
$$-\frac{\partial}{\partial\beta}\ln\sum_{n=0}^{\infty} e^{-\hbar\beta\frac{\omega}{2}}\, e^{-\beta n\hbar\omega} = -\frac{\partial}{\partial\beta}\ln\left[e^{-\hbar\beta\omega/2}\frac{1}{1-e^{-\beta\hbar\omega}}\right]$$

$$= \frac{\partial}{\partial\beta}\ln\left(1-e^{-\beta\hbar\omega}\right)+\hbar\omega/2$$

$$= \frac{\hbar\omega}{2}+\frac{\hbar\omega e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} = \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}+\frac{\hbar\omega}{2} \sim k_B T \text{ for small } \beta$$

$$u(\omega)\,d\omega = \frac{\omega^2 d\omega}{c^3\pi^2}\left(\frac{\hbar\omega}{2}+\frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right) = \frac{\hbar\omega^3}{c^3\pi^2}\,\frac{1}{e^{\beta\hbar\omega}-1}$$

zero point energy



$\lambda_{max} T = \text{const} \sim 5.1\ \text{mm}\cdot\text{K}$

Sun 5000K → ~1 μm

$$\beta\hbar\omega = x \qquad \omega = \frac{x}{\beta\hbar}$$

$$U = \int \frac{\hbar\omega^3 d\omega}{c^3\pi^2}\,\frac{1}{e^{\beta\hbar\omega}-1} =$$

$$= \int \frac{\hbar\, x^3 dx}{(\beta\hbar)^4 c^3\pi^2}\,\frac{1}{e^x-1} = \frac{1}{c^3\pi^2\hbar^3\beta^4}\underbrace{\int\frac{x^3dx}{e^x-1}}_{\pi^4/15} = \frac{\pi^2}{15c^3\hbar^3}(k_BT)^4$$

$$= \frac{4}{c}\sigma T^4$$

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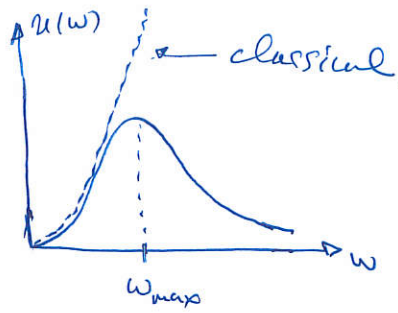
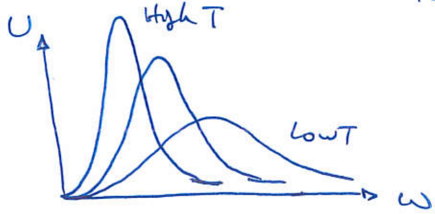
Density of frequency-states $\quad k = \frac{\omega}{c} \Rightarrow dk = \frac{1}{c} d\omega$

$$V \frac{k^2 dk}{\pi^2} = V \frac{\omega^2}{\pi^2 c^3} d\omega$$

Energy density $u(\omega) = \frac{U(\omega)}{V} = \frac{\omega^2}{\pi^2 c^3} \cdot \underbrace{\frac{\hbar\omega}{e^{\beta\hbar\omega}-1}}_{\sim k_B T \text{ classically}}$



leads to "ultraviolet catastrophe"



Some properties:

$$u = \frac{(\hbar\beta\omega)^3}{\pi^2 \hbar^2 \beta^3} \frac{1}{e^{\beta\hbar\omega}-1}$$

For constant T ⇒ constant β, This is a function of $\beta\hbar\omega$. Maximum is wrt $\beta\hbar\omega = x_{max}$

$ck = \frac{2\pi}{\lambda} c = 2\pi\nu = \omega$

At maximum, $\frac{1}{k_B T} \hbar \cdot \frac{2\pi c}{\lambda} = x_{max} \Rightarrow \lambda T = \left(\frac{2\pi\hbar c}{x_{max} k_B}\right) = \underline{5.1 \text{ mm K}}$

Sun $(1\mu m)(5000 K)$

Cosmic background $(2mm)(2.7K) \sim$ Wien's Law

$\pm 10^{-5} \times 2.7 K$

Total energy in the box:

$x = \beta\hbar\omega$

$$u = \int u(\omega) d\omega = \frac{\hbar}{(\beta\hbar)^4 \pi^2 c^3} \underbrace{\int \frac{x^3}{e^x - 1} dx}_{\pi^4/15} = \frac{\pi^2 k_B^4}{15 c^3 \hbar^3} T^4 = \frac{4\sigma}{c} T^4$$

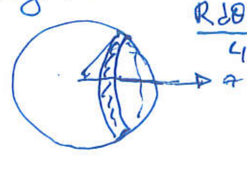
Relation to black body radiation

All black objects have the same spectrum = cavity spectrum

Stefan-Boltzmann const: $\sigma = 5.67 \times 10^{-8} W m^{-2} K^{-4}$

Amount of energy leaving the box through a hole of area A in time Δt

Ratio of photons moving in direction θ



$$\frac{R d\theta \cdot 2\pi R \sin\theta}{4\pi R^2} = \frac{1}{2}\sin\theta\, d\theta$$

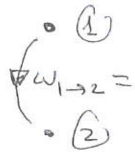
$u \cdot c\Delta t \cos\theta \cdot \frac{1}{2}\sin\theta\, d\theta$

$= \frac{u \Delta t c}{4}$

Power $= \frac{uc}{4} = \sigma T^4$

The Poisson process

16.5



$P_1(\cancel{t+\Delta t}) = 1$

Probability that the system is in state 1 for time Δt, then a transition occurs

$(1-\omega\Delta t)\,\omega\Delta t$

For $2\Delta t$: $(1-\omega\Delta t)(1-\omega\Delta t)\,\omega\Delta t$

For $3\Delta t$: $(1-\omega\Delta t)^3\,\omega\Delta t$

$\Delta t = \frac{T}{N}$

Prob nothing happens for time T, then it ~~happens~~ happens

$$\underbrace{\left(1-\omega\frac{T}{N}\right)^N}\omega\Delta t$$

$$e^{N\ln\left(1-\frac{\omega T}{N}\right)}\omega\Delta t = e^{N\left[-\frac{\omega T}{N}-\frac{\omega^2T^2}{N^2}\right]}\omega\Delta t$$

$\ln(1+x) \sim x$ ...

$$\sim e^{-\omega T}\omega\Delta t$$

$$\ln(1+\epsilon) \sim \epsilon - \frac{\epsilon^2}{2} + \frac{\epsilon^3}{3} \ldots$$

$$\int_0^\infty e^{-\alpha t}dt = \frac{1}{\alpha}$$

$$-\frac{\partial}{\partial\alpha} \Rightarrow \int t e^{-\alpha t}dx = \frac{1}{\alpha^2}$$

prob that event happens sometime

$$\int_0^\infty e^{-\omega t}\omega\, dt = 1 \checkmark$$

$$\langle t\rangle = \int_0^\infty t e^{-\omega t}\omega\, dt = \frac{1}{\omega}\int_0^\infty(\omega t)e^{-\omega t}\omega\, dt$$

$$= -\frac{1}{\omega}\underbrace{\int_0^\infty x e^{-x}dx}_{1} = \frac{1}{\omega}$$

For general $\omega(t)$

$$e^{-\omega t} \longrightarrow e^{-\omega_1\Delta t}e^{-\omega_2\Delta t}\cdots e^{-\omega_N t} = e^{-\int_0^t\omega(t)dt}\,\omega(t)\,dt$$

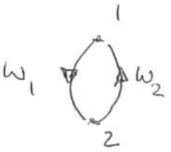
$P(t+\Delta t) = P(t)(1-\Delta t\,\omega)$

$P(t+\Delta t) - P(t) = -\omega\cdot\Delta t$

$$\frac{d}{dt}P_1 = -\omega P_1 \quad\Rightarrow\quad P_1(t) = P_1(0)\,e^{-\omega t}$$

---

discuss n-state problem here



$$\frac{dP_1}{dt} = -\omega_1 P_1 + \omega_2 P_2$$

$$\frac{dP_2}{dt} = -\omega_2 P_2 + \omega_1 P_1$$

$$\frac{d}{dt}\begin{pmatrix}P_1\\P_2\end{pmatrix} = \begin{pmatrix}-\omega_1 & \omega_2\\ \omega_1 & -\omega_2\end{pmatrix}\begin{pmatrix}P_1\\P_2\end{pmatrix}$$

$$\frac{d}{dt}\mathbb{P} = \mathcal{L}\,\mathbb{P}$$

$$\mathcal{L}\psi = \lambda\psi$$

$$\begin{vmatrix}-\omega_1-\lambda & \omega_2\\ \omega_1 & -\omega_2-\lambda\end{vmatrix} = (\lambda+\omega_1)(\lambda+\omega_2) - \omega_1\omega_2$$

$$= \lambda^2 + \lambda(\omega_1+\omega_2) = 0$$

$$\lambda = 0,\quad \lambda = -(\omega_1+\omega_2)$$

$$(1\ a)\begin{pmatrix}-\omega_1 & \omega_2\\ \omega_1 & -\omega_2\end{pmatrix} = -(\omega_1+\omega_2)\,(1\ a)$$

$-\omega_1 + a\omega_1 = -\omega_1-\omega_2 \qquad a = -1$

$\lambda = 0$

Right eigenvectors $\begin{pmatrix}-\omega_1 & \omega_2\\ \omega_1 & -\omega_2\end{pmatrix}\begin{pmatrix}1\\a\end{pmatrix} = \begin{pmatrix}0\\0\end{pmatrix} \Rightarrow -\omega_1 + a\omega_2 = 0$

$\lambda = -(\omega_1+\omega_2) \Rightarrow \psi_1 = \begin{pmatrix}1\\-1\end{pmatrix}$

$a = \frac{\omega_1}{\omega_2} \Rightarrow \psi_0 = \begin{pmatrix}\omega_2\\\omega_1\end{pmatrix}\frac{1}{\omega_1+\omega_2}$

$\phi_1 = (\omega_1\ -\omega_2)\,/(\omega_1+\omega_2)$

$\phi_0 = (1\ 1)$

$$\boxed{\begin{pmatrix}1\\0\end{pmatrix} = \begin{pmatrix}\omega_2\\\omega_1\end{pmatrix}\frac{1}{\omega_1+\omega_2} + \begin{pmatrix}1\\-1\end{pmatrix}\frac{\omega_1}{\omega_1+\omega_2}}$$

The master eqn.

Markov process (State of system depends only on the present state. No memory)

$$\frac{d}{dt} P_i = -\sum_{j\neq i} P_i (w_{i\to j}) + \sum_{j \neq i} P_j w_{j\to i} \qquad \boxed{16.6}$$

$$\frac{d}{dt} \mathbb{P} = \mathcal{L} \mathbb{P}$$

$$\mathbb{P} = \begin{pmatrix} P_1 \\ P_2 \\ P_3 \end{pmatrix} \qquad \mathcal{L} = \begin{pmatrix} -w_{1\to 2} - w_{1\to 3} & w_{2\to 1} & w_{3\to 1} \\ w_{1\to 2} & -w_{2\to 1} - w_{2\to 3} & w_{3\to 2} \\ w_{1\to 3} & w_{2\to 3} & -w_{3\to 1} - w_{3\to 2} \end{pmatrix}$$

conservation of probability
columns add up to zero
$\Rightarrow$ dependent equations
$\Rightarrow$ a zero-eigenvalue

Solution:

$$\mathbb{P}(t) = e^{t\mathcal{L}} \mathbb{P}(0)$$

Expand $\mathbb{P}(0)$ in terms of eigenvalues of $\mathcal{L}$: $\mathcal{L} \psi_i = \lambda_i \psi_i$

So, for $\mathbb{P}(0) = \sum_i c_i \psi_i$

$$e^{t\mathcal{L}} \mathbb{P}(0) = \sum_i c_i e^{t\lambda_i} \psi_i \to \psi_0 \text{ as } t \to \infty$$

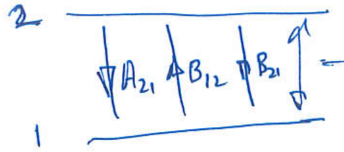
So, $c_0 = 1$, $\lambda_0 = 0$
all other $\lambda_i < 0$

To form the expansion, construct the left-eigenvectors as well

$\phi_i \mathcal{L} = \lambda_i \phi_i$. Note that $\phi_i \neq \psi_i^T$ as $\mathcal{L}$ is not Hermitian

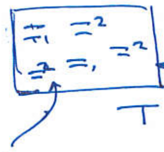
But still, $\phi_i \psi_j = \delta_{ij}$ (properly normalized.)

Einstein A & B coefficients.



$\leftarrow \hbar\omega$. Two energy states $\hbar\omega$ apart

A_{21}: spontaneous emission
B_{21}, B_{12}: stimulated emission, absorption

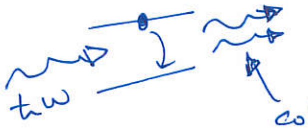


$\leftarrow$ cavity

atoms

$$\frac{d}{dt} N_2 = -A_{21} N_2 - B_{21} N_2 u + B_{12} u N_1$$

$$\frac{d}{dt} N_1 = A_{21} N_2 + B_{21} N_2 u - B_{12} u N_1$$



Master eqn. $\frac{d}{dt} N = \mathcal{L} N$ $\quad N = \begin{pmatrix} N_1 \\ N_2 \end{pmatrix}$ $\quad \mathcal{L} = \begin{pmatrix} B_{12}u & -A_{21}-B_{21}u \\ -B_{12}u & A_{21}+B_{21}u \end{pmatrix}$

columns add up to 0
$\Rightarrow$ zero eigenvalue
Eigenvector: steady state

$$\frac{d}{dt} N_{eq} = \mathcal{L} N_{eq} = 0$$

Expand $N(0) = N_{eq} + \psi_1$

$$N(t) = e^{t\mathcal{L}} N(0) = e^{t\mathcal{L}}(N_{eq} + \psi_1) = e^0 N_{eq} + e^{\lambda_1 t}\psi_1$$

Simple case $N_1 = 0$.

$$\frac{d}{dt} N_2 = -A_{21} N_2 \Rightarrow \quad N_2(t) = N_2(0)\, e^{-A_{21}t}$$

Equilibrium: $\frac{dN_1}{dt} = 0$, $\frac{dN_2}{dt} = 0$

$$\frac{d}{dt} N_2 = 0 = -A_{21} N_{2eq} - B_{21} N_{2eq} u + B_{12} u N_{1eq}$$

$$A_{21} N_{2eq} = u\left(-B_{21} N_{2eq} + B_{12} N_{1eq}\right)$$

$$u = \frac{A_{21} N_2}{B_{12} N_1 - B_{21} N_2} = \frac{A_{21}/B_{21}}{\frac{B_{12}}{B_{21}} N_1/N_2 - 1}$$

$$= \frac{A_{21}/B_{12}}{\frac{B_{12}}{B_{21}} e^{\beta\hbar\omega} - 1} \Rightarrow \underbrace{B_{12} = B_{21}}_{\text{Emission, absorption rates equal}} \qquad A_{21}/B_{12} = \frac{\hbar\omega^3}{\pi c^3}$$

$$= \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\beta\hbar\omega} - 1}$$

$$A_{21} = \underbrace{\frac{\hbar\omega^3}{\pi c^3}}_{\substack{\text{zero point energy photon density} \\ \text{(indep of T)}}} \underset{\text{rate per photon}}{B}$$

(factor 2 correction with proper QED calculation)

The sun and the Earth.

(18)

Power output from the sun

$$(\sigma T_{sun}^4)\, 4\pi R_{sun}^2$$

The amount of power that hits the Earth

$$\cancel{\sigma}(\cancel{\sigma} T_{sun}^4)\, \cancel{4\pi} R_{sun}^2 \cdot \frac{\cancel{\pi R_{earth}^2}}{4\pi D^2} = \sigma T_{earth}^4 \cdot 4\pi \cancel{R_{earth}^2}$$

$$T_{sun}^4 \cdot \frac{R_{sun}^2}{4D^2} = T_{earth}^4$$

$$T_{eath} = T_{sun} \sqrt{\frac{R_{sun}}{2D}}$$

$$= 280 K$$

$R_{sun} = 10^8 \times 7$ m

$D = 1.5 \times 10^{11}$ m

$T_{sun} = 5800 K$

If Earth has albedo A : Absorbs a ratio of $1-A$ of the incident radiation

Then

$$T_{sun}^4 \cdot \frac{R_{sun}^2}{4D^2}(1-A) = T_{eath}^4$$

$$T_{earth} = T_{sun}(1-A)^{1/4}\sqrt{\frac{R_{sun}}{2D}}$$

or $(1-A) = \left(\frac{T_{earth}}{T_{sun}}\right)^4 \frac{4D^2}{R_{sun}^2}$

e.g. $1 - A = \left(\frac{270}{5800}\right)^4 \cdot \frac{4 \times (1.5 \times 10^{11})^2}{(7 \times 10^8)^2} = 0.86$

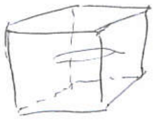
Power from Sun at Earth

$$\sigma (T_{sun})^4\, 4\pi R_{sun}^2 / 4\pi D^2 = \sigma T_{sun}^4 \frac{R_{sun}^2}{D^2} = 5.67 \cdot 10^{-8} \cdot (5800)^4 \left(\frac{7 \cdot 10^8}{1.5 \cdot 10^{11}}\right)^2 \quad \mathrm{W/m^2}$$

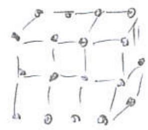
$$= 1400\ \mathrm{W/m^2}$$

Phonons

19



Vibrations $\leftrightarrow$ oscillation modes



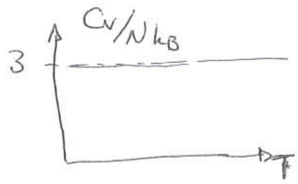
N atoms

$3N-6$ vibrational modes

$\uparrow$ motion and rotation of whole crystal

$\sim 3N$

Classical: Equipartition



$$U = 3Nk_BT$$

$$C_V = \frac{\partial U}{\partial T} = 3Nk_B$$

The Einstein model

Assume all oscillators have same frequency

$$Z = \prod_{i=1}^{3N} z_i \qquad z_i = \sum_{n_i=0}^{\infty} e^{-\beta(n_i+1/2)\hbar\omega_E}$$

$$= e^{-\beta\hbar\omega_E/2}\frac{1}{e^{\beta\hbar\omega_E}-1}$$

$$\ln Z = 3N\left[-\beta\hbar\omega_E/2 - \ln(e^{\hbar\omega_E\beta}+1)\right]$$

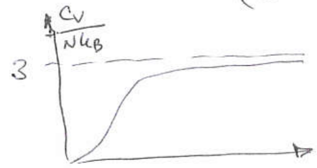
$$\frac{\partial}{\partial T} = \frac{d\beta}{dT}\frac{\partial}{\partial\beta} = -\frac{1}{k_BT^2}\frac{\partial}{\partial\beta}$$

$$\frac{U}{N} = -\frac{\partial}{\partial\beta}\ln Z = 3\left[\frac{\hbar\omega_E}{2} + \hbar\omega_E\frac{1}{e^{\hbar\beta\omega_E}-1}\right]$$

$$\frac{C_V}{N} = \frac{1}{N}\frac{\partial U}{\partial T} = 3\hbar\omega_E\frac{1}{k_BT^2}\frac{\hbar\omega_E}{(e^{\hbar\beta\omega_E}-1)^2}$$

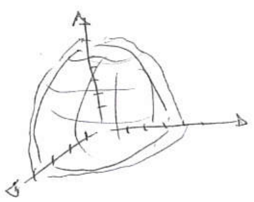
$$\frac{C_V}{Nk_B} = 3\frac{(\beta\hbar\omega_E)^2}{(e^{\hbar\beta\omega_E}-1)^2} \longrightarrow \begin{cases} 3 & \text{for } T\to\infty \\ 0 & \text{for } T\to 0\end{cases}$$

$$\frac{e^{-\alpha/T}}{T^2} \to \frac{+\frac{\alpha}{T^2}e^{-\alpha/T}}{2T} \sim \frac{e^{-\alpha/T}}{T^3}$$



Debye model

Orthogonal modes of oscillation



$$\frac{1}{8}\frac{4\pi k^2 dk}{(\frac{\pi}{L})^3}\times 3 \text{ modes between } k \text{ and } k+dk$$

$\uparrow$ 2 transverse + 1 longitudinal

$$\frac{3}{2}V\frac{1}{\pi^2}\int_0^{k_D}k^2dk = 3N$$

use $\omega = k v_s$

$$\frac{3}{2}V\frac{v_s^3}{\pi^2}\underbrace{\int_0^{\omega_D}\omega^2 d\omega}_{\omega_D^3/3} = 3N \implies \omega_D^3 = \frac{6N\pi^2}{V v_s^3}$$

$$\frac{3}{2}\frac{Vv_s^3}{\pi^2} = \frac{9N}{\omega_D^3}$$

$$U = \int_0^{\omega_D}\frac{3}{2}V\frac{v_s^3}{\pi^2}\omega^2 d\omega\left[\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right] = \text{zero pt} + \underbrace{\frac{3Vv_s^3}{2\pi^2}}_{9N/\omega_D^3}\int_0^{\omega_D}\frac{\hbar\omega^3 d\omega}{e^{\beta\hbar\omega}-1}$$

$\hbar\omega = x \quad \hbar\omega_D = x_D$

$$C_V = \frac{\partial U}{\partial T} = -\frac{1}{k_BT^2}\frac{\partial}{\partial\beta}U = \frac{1}{k_BT^2}\underbrace{\frac{Vv_s^3}{2\pi^2}}_{9N/\omega_D^3}\int_0^{\omega_D}\frac{1}{\hbar^2}\frac{(\hbar\omega)^4 d\omega}{(e^{\beta\hbar\omega}-1)^2}e^{\beta\hbar\omega} = \frac{9Nk_B}{x_D^3}\int_0^{x_D}\frac{x^4 dx\, e^x}{(e^x-1)^2}$$

$$\frac{C_V}{Nk_B} = \begin{cases}\frac{9}{x_D^3}\int_0^{x_D}x^2dx = 3 & \text{high } T \\ \frac{9}{x_D^3}\int_0^{\infty}\cdots dx \sim T^3 & \text{low } T\end{cases}$$