MATH327: Statistical Physics

Friday, 19 April 2024

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Something to consider

Quantum statistics should reproduce classical results when there would be a low probability of multiple particles occupying the same energy level.

What temperatures and chemical potentials correspond to this?

Recap

Bose - Einstein & Fermi-Dirac grand-canonical Z_g and $\Phi = -T \log Z_g$

Should reproduce classical Maxwell-Boltzmann statistics when E_ℓ multiple occupancy unlikely

$\rightarrow$ Many accessible energy levels compared to $\langle N \rangle$

$P_i \propto e^{-E_i/T} \rightarrow$ high temperature

Collect results	Z_g	Φ
MB	$\prod_\ell \exp\left[e^{-\beta(E_\ell - \mu)}\right]$	$-T \sum_\ell e^{-\beta(E_\ell - \mu)}$
BE $(E_\ell > \mu)$	$\prod_\ell \frac{1}{1 - e^{-\beta(E_\ell - \mu)}}$	$T \sum_\ell \log\left(1 - e^{-\beta(E_\ell - \mu)}\right)$
FD	$\prod_\ell \left(1 + e^{-\beta(E_\ell - \mu)}\right)$	$-T \sum_\ell \log\left(1 + e^{-\beta(E_\ell - \mu)}\right)$

Let's compute $\langle N \rangle = -\frac{\partial}{\partial \mu} \Phi$ for all three and check high-T

$$\boxed{\begin{aligned}\langle N \rangle_{MB} &= T \sum_l \frac{\partial}{\partial \mu} e^{-\beta(E_l - \mu)} = \sum_l \frac{1}{e^{\beta(E_l-\mu)}} = \sum_l \langle n_l \rangle_{MB} \\ \langle N \rangle_{BE} &= -T \sum_l \frac{-e^{-\beta(E_l-\mu)}\beta}{1 - e^{-\beta(E_l-\mu)}} = \sum_l \frac{1}{e^{\beta(E_l-\mu)} - 1} = \sum_l \langle n_l \rangle_{BE} \\ \langle N \rangle_{FD} &= T \sum_l \frac{e^{-\beta(E_l-\mu)}\beta}{1 + e^{-\beta(E_l-\mu)}} = \sum_l \frac{1}{e^{\beta(E_l-\mu)} + 1} = \sum_l \langle n_l \rangle_{FD}\end{aligned}}$$

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All occupation #s > 0 ✓

$$\langle n_l \rangle_{MB} = \frac{1}{e^{\beta(E_l-\mu)}}$$

$$\langle n_l \rangle_{BE} = \frac{1}{e^{\beta(E_l-\mu)} - 1} \qquad \langle n_l \rangle = \frac{1}{e^{\beta(E_l-\mu)} + 1}$$

All agree when $e^{\beta(E_l-\mu)} \gg 1 \rightarrow \langle n_l \rangle \ll 1$ ✓

(looks like large β = low T ???

Naive high-T limit $\beta \to 0$ with fixed $(E_l - \mu)$ gives

$\langle n_l \rangle_{MB} \to 1$ vs. $\langle n_l \rangle_{FD} \to \frac{1}{2}$ vs. $\langle n_l \rangle_{BE} \to \infty$

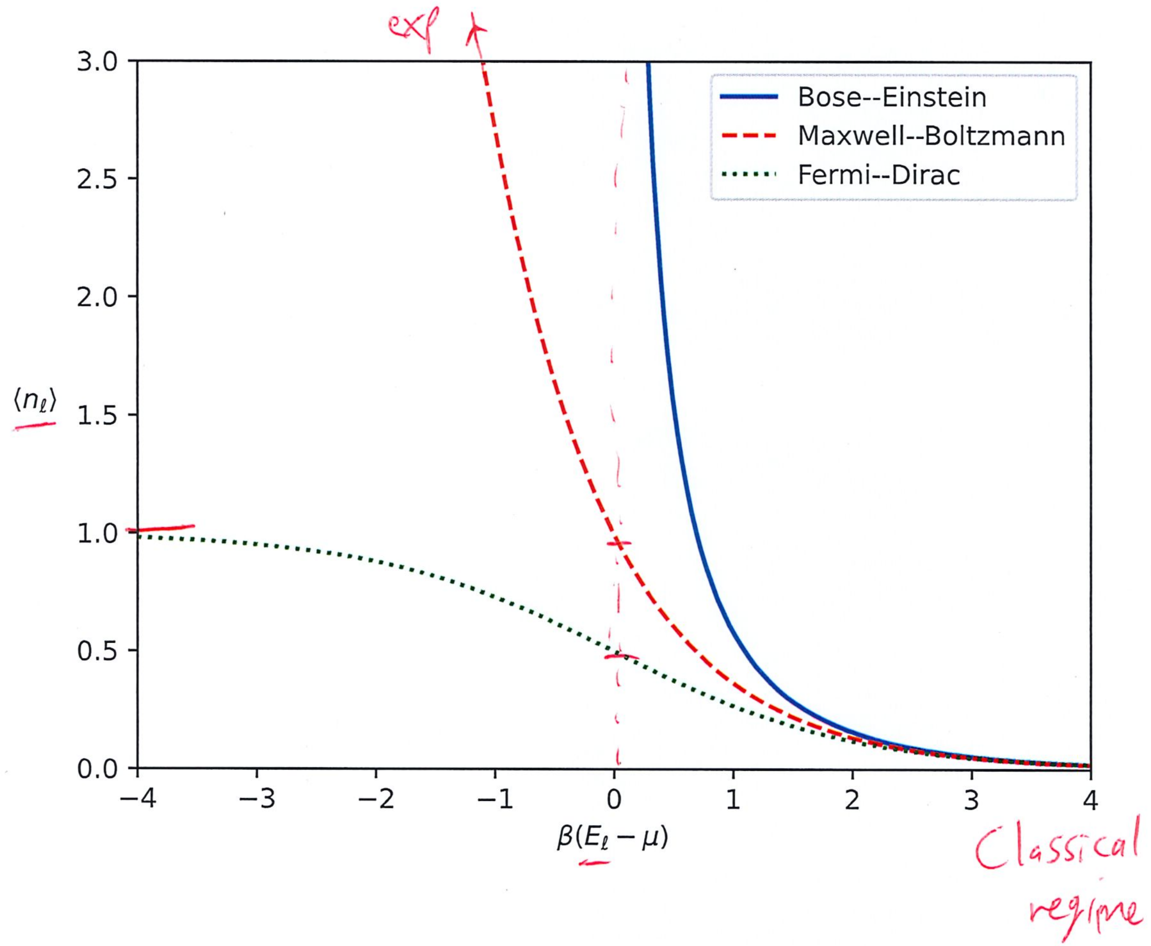
Quantum effects remain important!

True classical limit needs <u>both</u>

$T \to \infty$ (more accessible energy levels)

$-\mu \to \infty$ (fewer particles)

with $-\mu \gg T \gg E_l$


exp
3.0
2.5
2.0
1.5
1.0
0.5
0.0
$\langle n_\ell \rangle$
−4
−3
−2
−1
0
1
2
3
4
$\beta(E_\ell - \mu)$
Bose--Einstein
Maxwell--Boltzmann
Fermi--Dirac
Classical regime

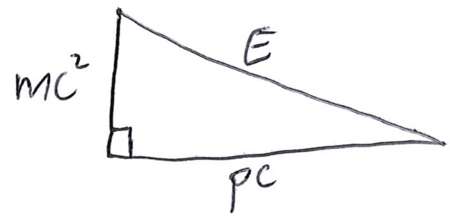
Quantum gases

Need to specify energy levels ε_ℓ

and corresponding energies E_ℓ

In general $E^2 = \underbrace{(mc^2)^2}_{\substack{\text{mass energy} \\ \text{(fixed)}}} + \underbrace{(pc)^2}_{\text{kinetic energy}}$ $\qquad p^2 = p_x^2 + p_y^2 + p_z^2$

(speed of light c just unit conversion)



("Einstein's triangle")

We will consider two simplified cases

1) "Ultra-relativistic" $p \gg mc$ (includes $m=0$)

$$E = pc$$

2) "Non-relativistic" $p \ll mc$

$$\boxed{E = mc^2\sqrt{1 + \frac{(pc)^2}{(mc^2)^2}} \approx mc^2\left(1 + \frac{p^2}{2m^2c^2} + \mathcal{O}\left(\frac{p^4}{m^4c^4}\right)\right) \approx mc^2 + \frac{p^2}{2m} + \mathcal{O}\left(\frac{p^4}{2m^3c^2}\right)}$$

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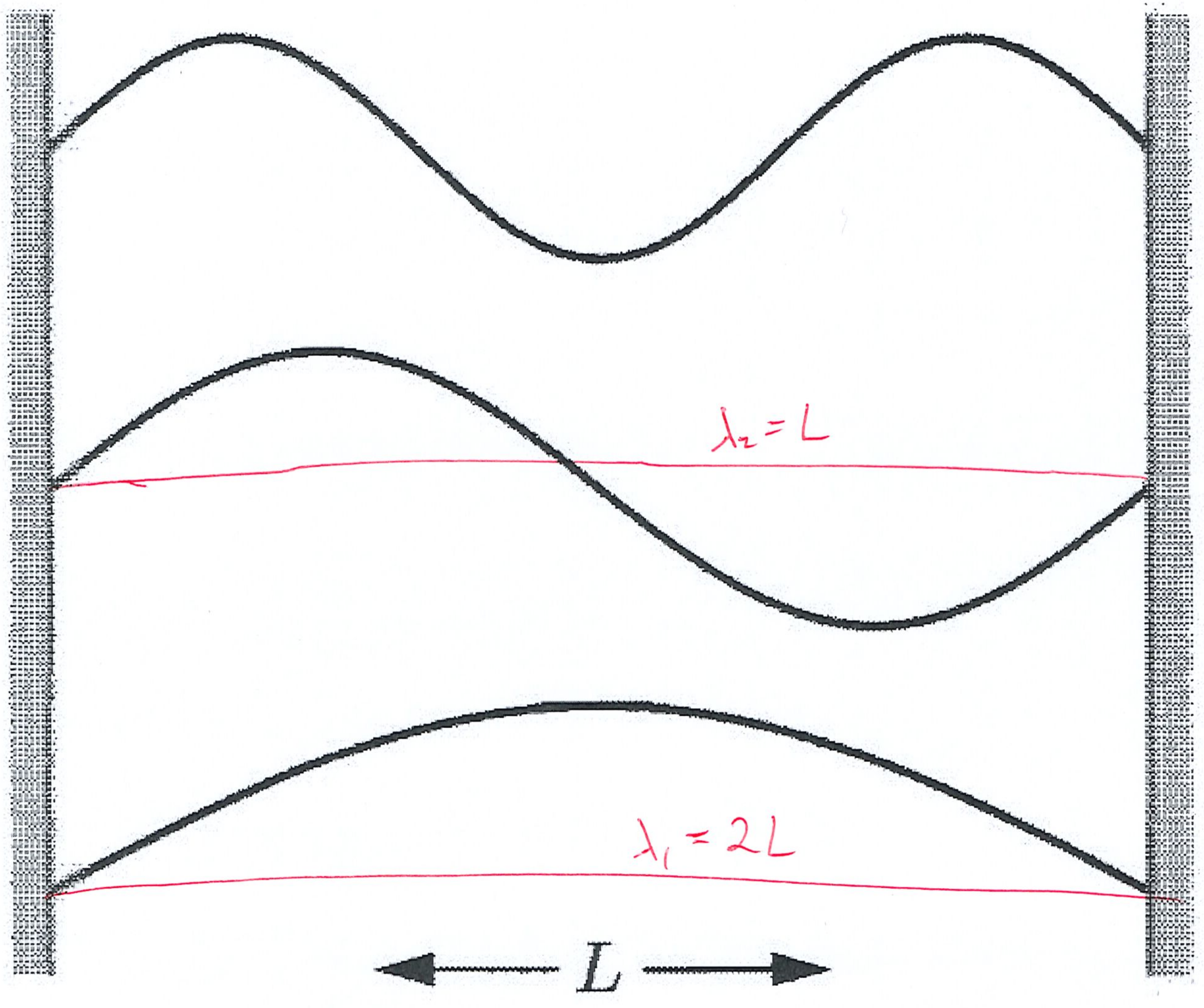
Fixed mass-energy irrelevant

$\rightarrow$ Usual $E = \frac{p^2}{2m} = \frac{\hbar^2\pi^2}{2mL^2}(k_x^2 + k_y^2 + k_z^2)$ in L^3 volume

One change: $k_{x,y,z} = 1, 2, 3, \ldots > 0$

(Due to Heisenberg uncertainty principle

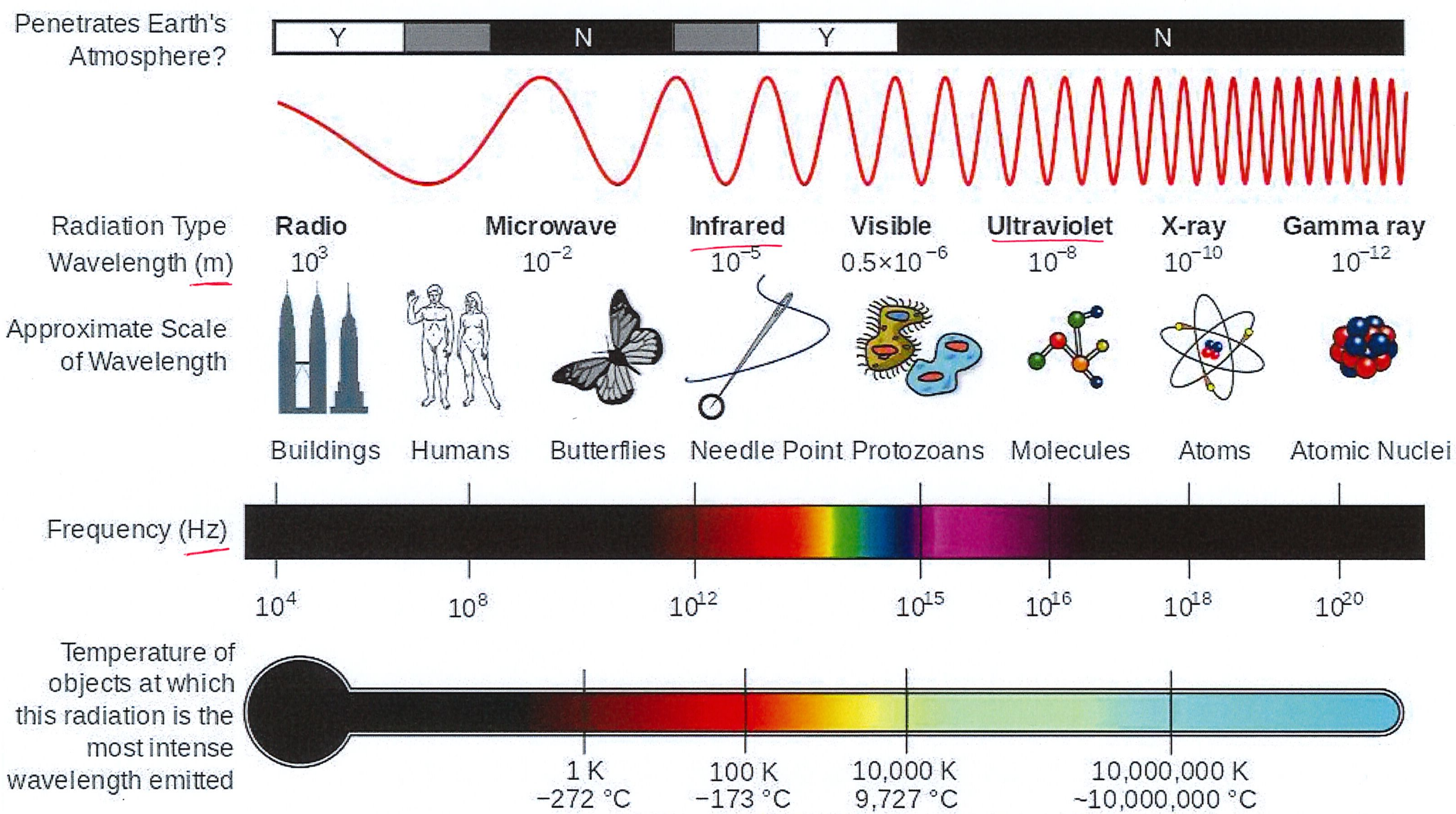
$\underbrace{(\Delta x)}_{\text{at most } L}(\Delta p) \gtrsim \hbar \quad \rightarrow \quad \Delta p \gtrsim \frac{\hbar}{L} > 0$)



$$\lambda_3 = \frac{2L}{3}$$

$$\lambda_2 = \frac{2L}{2}$$

$$\lambda_1 = 2L$$



commons.wikimedia.org/wiki/File:EM_Spectrum_Properties_edit.svg

Changes | ground state $E_0 = 3\varepsilon$ for $\vec{k} = (1,1,1)$ $\quad \varepsilon = \frac{\hbar^2 \pi^2}{2mL^2}$

Excited states:

$$\left.\begin{array}{ll} 6\varepsilon & (2,1,1) \\ 9\varepsilon & (2,2,1) \\ 11\varepsilon & (3,1,1) \end{array}\right\} \text{each } 3\times \text{ degeneracy}$$

$$12\varepsilon \quad (2,2,2)$$

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Consider a gas of photons

└ bosons with $m=0 \rightarrow E_{ph} = pc = \hbar c \frac{\pi}{L} k$

quanta of electromagnetic waves (light)

Constant speed of light $c = \frac{\lambda \omega}{2\pi}$

relates wavelength λ

and angular frequency $\omega = 2\pi f$

Volume $V = L^3$ quantizes frequencies like momenta

$$L = k_z \left(\frac{\lambda}{2}\right) \rightarrow \lambda = \frac{2L}{k_z} \qquad \text{"wavenumber" } k_z = 1,2,3,\ldots$$

$$\omega = \frac{2\pi c}{\lambda} = c\frac{\pi}{L} k_z = \left(\frac{c}{\hbar}\right) p_z$$

$$pc = E_{ph} = \hbar\omega$$

Large E ~ high freq. ~ short λ ("ultraviolet")

Small E ~ low freq. ~ long λ ("infrared")

Photon gas grand-canonical potential

$$\Phi_{ph} = T \sum_\ell \log\left(1 - e^{-\beta(E_\ell - \mu)}\right) = 2T \sum_{\vec{k}} \log\left(1 - e^{-\beta(\hbar\omega - \mu)}\right)$$

two polarization per $\vec{k}$

Simplification: $\mu = 0 < E_\ell$

Photons easy to create & absorb (in therm. equil)

$$\mu = \frac{\partial E}{\partial N}\Big|_S \to 0 \qquad \text{(energy unchanged)}$$

Simplification: Integrate over closely spaced momenta (large L)

$$\Phi \approx 2T \int \log\left(1 - e^{-\beta\hbar\omega}\right) d\hat{k}_x\, d\hat{k}_y\, d\hat{k}_z$$

$\omega \propto \sqrt{k_x^2 + k_y^2 + k_z^2} \to$ spherical coord.

$k_{x,y,z} \geq 1 \to$ single octant

$$\int_0^\infty d\hat{k}_x \int_0^\infty d\hat{k}_y \int_0^\infty d\hat{k}_z = \int_0^\infty \hat{k}^2\, d\hat{k} \underbrace{\int_0^{\pi/2} \sin\theta\, d\theta}_{1} \underbrace{\int_0^{\pi/2} d\phi}_{\pi/2}$$

$$= \frac{\pi}{2} \int_0^\infty \hat{k}^2\, d\hat{k}$$

Plug in $k = \omega\left(\frac{L}{c\pi}\right)$

$$\Phi_{ph} = \pi T \int_0^\infty \hat{k}^2 \log\left(1 - e^{-\beta\hbar\omega}\right) d\hat{k}$$

$$= \frac{VT}{c^3\pi^2} \int_0^\infty \omega^2 \log\left(1 - e^{-\beta\hbar\omega}\right) d\omega$$

Internal energy (density) $\langle E \rangle = -T^2 \frac{\partial}{\partial T}\left(\frac{\Phi}{T}\right) + \underbrace{\mu}_{0}\langle N \rangle$

$$= \frac{\partial}{\partial \beta}(\beta\Phi)$$

$$\frac{\langle E\rangle_{ph}}{V} = \frac{1}{c^3\pi^2}\int_0^\infty w^2 \frac{\partial}{\partial\beta}\log\left(1-e^{-\beta\hbar w}\right)dw$$

$$= \frac{1}{c^3\pi^2}\int_0^\infty \frac{w^2\left(-e^{-\beta\hbar w}\right)\left(-\hbar w\right)}{1-e^{-\beta\hbar w}}\,dw$$

spectral density

$$= \frac{\hbar}{c^3\pi^2}\int_0^\infty \frac{w^3}{e^{\beta\hbar w}-1}\,dw = \int_0^\infty P(w)\,dw$$

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$$P(w) = \left(\frac{\hbar}{c^3\pi^2}\right)\frac{w^3}{e^{\beta\hbar w}-1}$$ is <u>Planck</u> spectrum

Change variables to $\lambda = \frac{2\pi c}{w}$ $\qquad w = \frac{2\pi c}{\lambda}$ $\qquad dw = \frac{-2\pi c}{\lambda^2}d\lambda$

$$\frac{\langle E\rangle_{ph}}{V} = \frac{\hbar}{c^3\pi^2}\int_\infty^0 \frac{\left(2\pi c/\lambda\right)^3}{e^{2\pi\beta\hbar c/\lambda}-1}\left(-\frac{2\pi c}{\lambda^2}\right)d\lambda$$

$$= 16\pi^2\hbar c\int_0^\infty \frac{d\lambda}{\lambda^5\left(e^{2\pi\beta\hbar c/\lambda}-1\right)} = \int_0^\infty P(\lambda)\,d\lambda$$

$$P(\lambda) = \left(\frac{16\pi^2\hbar c}{\lambda^5}\right)\frac{1}{e^{2\pi\beta\hbar c/\lambda}-1}$$

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