MATH327: StatMech and Thermo

Monday, 24 March 2025

24 36 73

Something to consider

We have derived quantum statistics for ‘ideal’ non-interacting particles.

How good an approximation do you expect this to provide
for real physical systems?

Recap

Quantum approach to grand-canonical ens.

Define micro-states by occupation number n_ℓ of energy level ε_ℓ

Plan

Photon gas – specify ε_ℓ and energies

general $E^2 = (mc^2)^2 + (pc)^2$

Bosons with $m=0 \rightarrow E_{ph} = pc$

Quanta of electromagnetic waves (light)

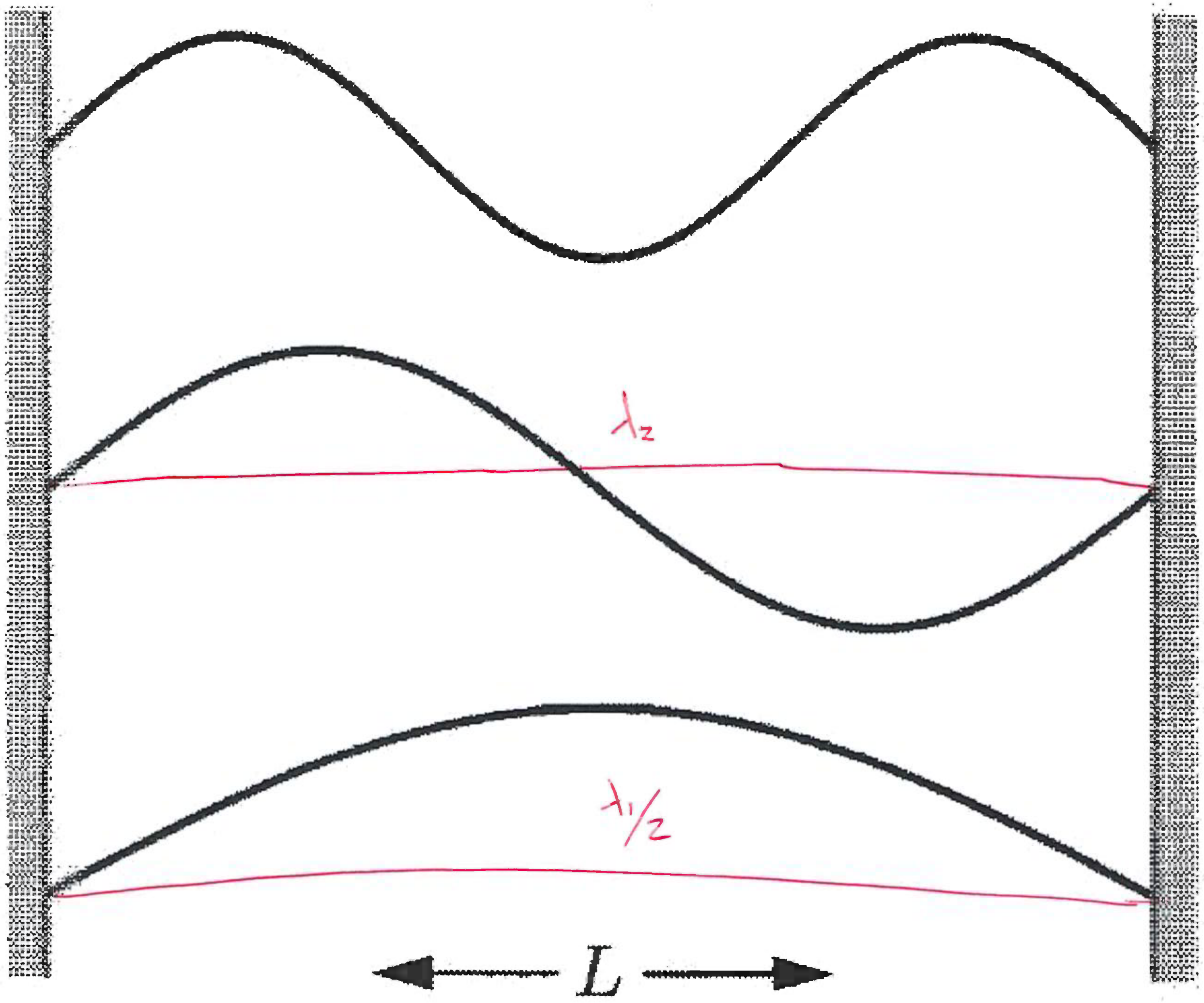
Constant speed of light $c = \frac{\lambda \omega}{2\pi}$

relates wavelength λ

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

Volume $V = L^3$ quantizes frequencies and energies

$L = k_i \left(\frac{\lambda}{2}\right) \rightarrow \lambda = \frac{2L}{k_i}$ "wavenumber" $k_{x,y,z} = 1, 2, \ldots$



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

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

$$\lambda_1 = 2L$$

$$w = \frac{2\pi c}{\lambda} = c\frac{\pi}{L}\underbrace{k}_{\sqrt{k_x^2+k_y^2+k_z^2}} = c\left(\frac{p}{\hbar}\right) \qquad p = \hbar\frac{\pi}{L}k$$

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

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

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

Photon gas grand-canonical potential

$$\Phi_{ph} = T\sum_{\ell}\log\left(1-e^{-\beta(E_\ell-\mu)}\right) = \underbrace{2}_{\text{two polarizations per } \vec{k}}T\sum_{\vec{k}}\log\left(1-e^{-\beta(\hbar w-\mu)}\right)$$

Simplification: $\mu = 0$

Photons easy to create and absorb with const. S

very little energy $\quad \mu = -T\left.\frac{\partial E}{\partial N}\right|_S = 0$

Simplification: $L \gg \lambda$ → integrate over closely spaced energies

$$\Phi_{ph} \approx 2T\int \log\left(1-e^{-\beta\hbar w}\right)\, d^3\hat{k}$$

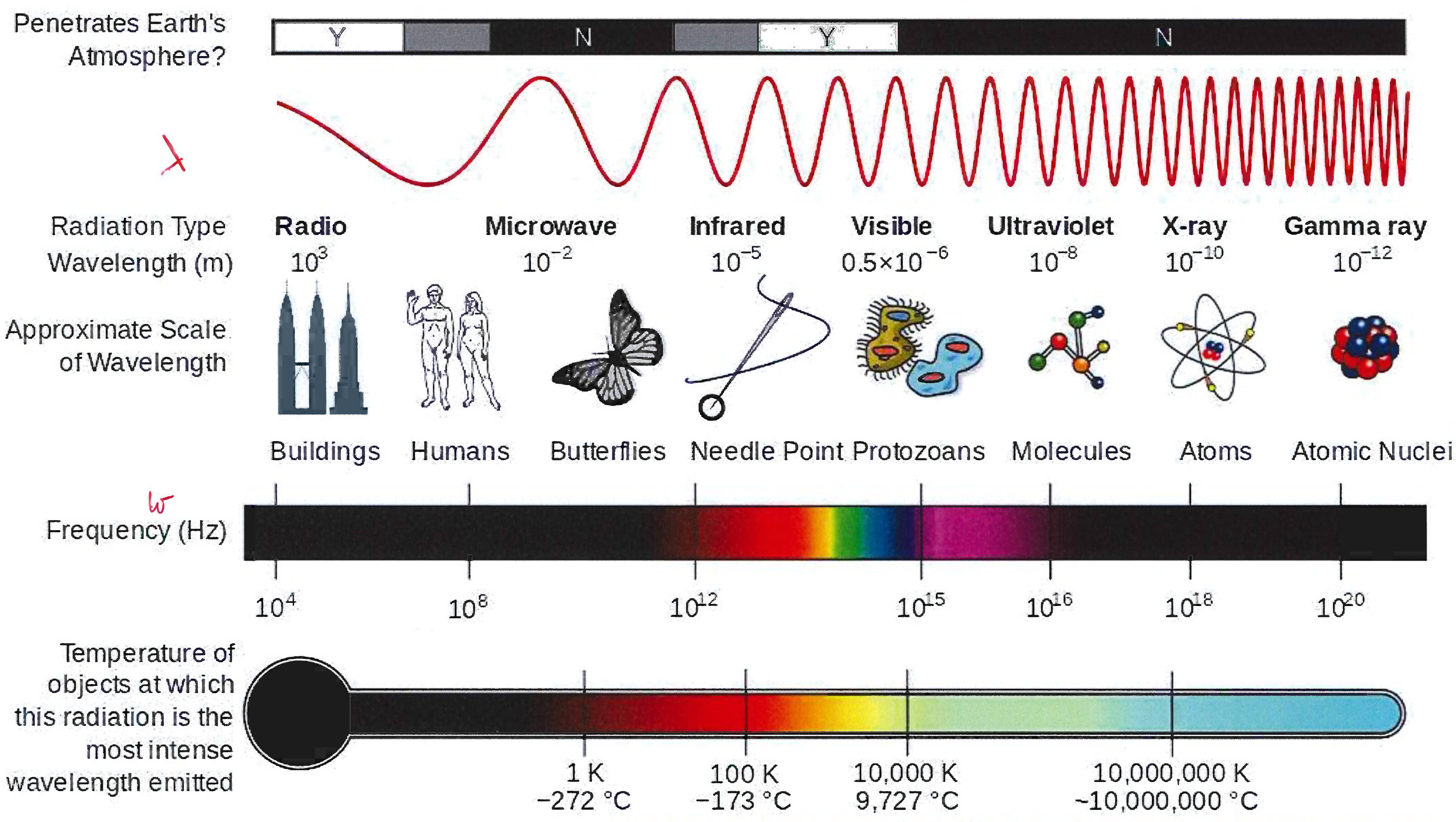
$w \propto \sqrt{k_x^2+k_y^2+k_z^2}$ → spherical coords

$k_{x,y,z} \geq 1$ → single octant

$$\int d^3\hat{k} = \int_0^\infty \hat{k}^2\, d\hat{k}\, \underbrace{\int_0^{\pi/2}\sin\theta\, d\theta}_{1}\, \underbrace{\int_0^{\pi/2} d\phi}_{\pi/2}$$

$$\Phi_{ph} \approx \pi T\int_0^\infty \hat{k}^2 \log\left(1-e^{-\beta\hbar w}\right) d\hat{k} \qquad \hat{k} = w\left(\frac{L}{c\pi}\right)$$

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



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

$$\langle E\rangle_{ph} = -T^2\frac{\partial}{\partial T}\left(\frac{\Phi_{ph}}{T}\right) + \underset{0}{\cancel{\mu}}\langle N\rangle_{ph} = \frac{\partial}{\partial\beta}\left(\beta\Phi_{ph}\right)$$

Density

$$\boxed{\begin{aligned}\frac{\langle E\rangle_{ph}}{V} &= \frac{1}{c^3\pi^2}\int_0^\infty \frac{\omega^2(+e^{-\beta\hbar\omega})(+\hbar\omega)}{1-e^{-\beta\hbar\omega}}\,d\omega \\ &= \frac{\hbar}{c^3\pi^2}\int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega}-1}\,d\omega = \int_0^\infty P(\omega)\,d\omega\end{aligned}}$$

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spectral density

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

Change variables to $\lambda = \frac{2\pi c}{\omega}$

$$\omega = \frac{2\pi c}{\lambda} \qquad d\omega = -\frac{2\pi c}{\lambda^2}\,d\lambda$$

$$\boxed{\begin{aligned}\frac{\langle E\rangle_{ph}}{V} &= \frac{\hbar}{c^3\pi^2}\int_\infty^{0} \frac{(2\pi c/\lambda)^3}{e^{2\pi\beta\hbar c/\lambda}-1}\left(-\frac{2\pi c}{\lambda^2}\right)d\lambda \\ &= 16\pi^2\hbar c\int_0^\infty \frac{d\lambda}{\lambda^5\left(e^{2\pi\beta\hbar c/\lambda}-1\right)} = \int_0^\infty P(\lambda)\,d\lambda\end{aligned}}$$

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

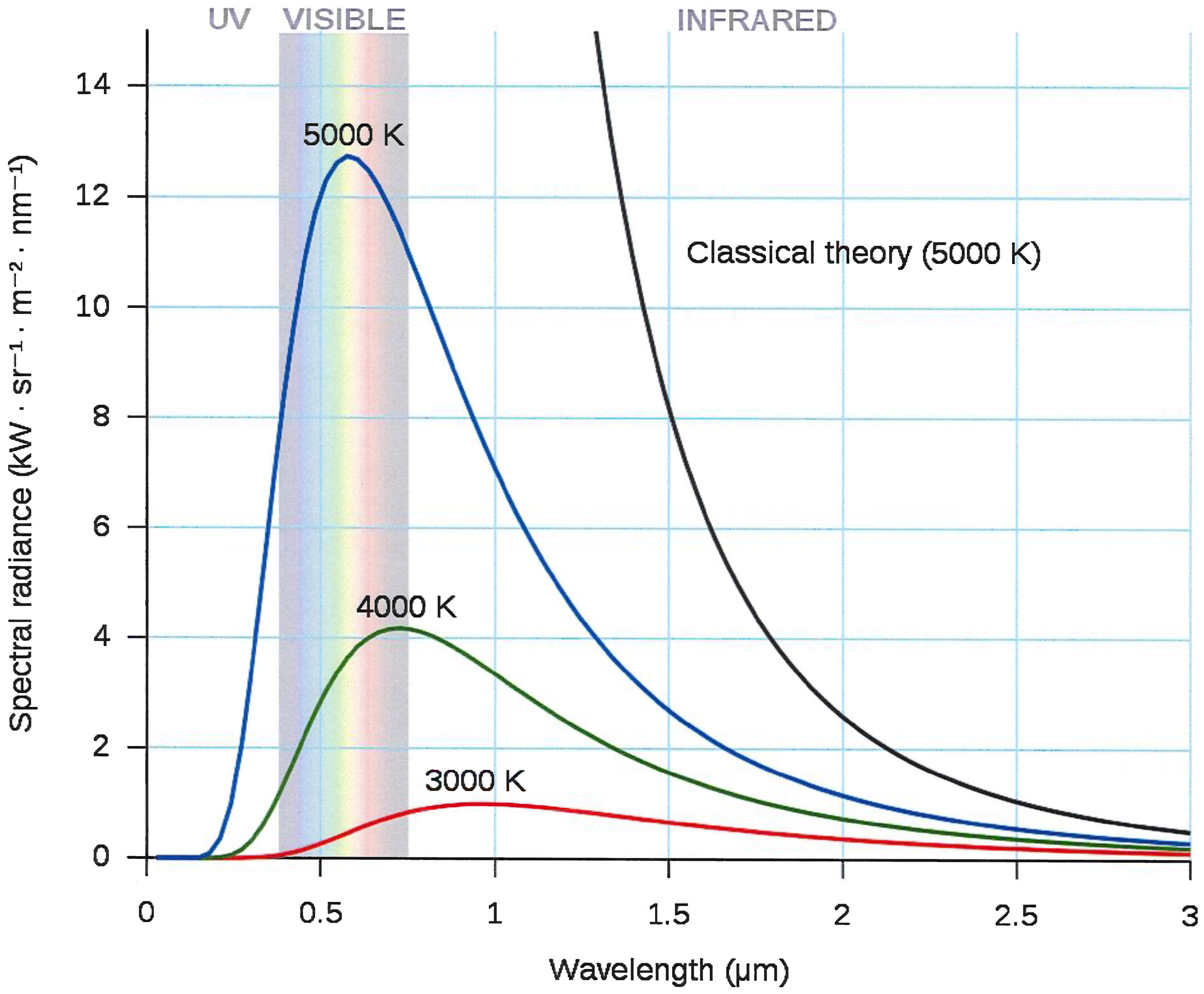
As always, consider limiting behaviour

UV: $\lambda \to 0$

Exponential factor dominates, $P(\lambda) \to 0$

IR: $\lambda \gg \beta\hbar c$ $\qquad e^{2\pi\beta\hbar c/\lambda} - 1 \approx \frac{2\pi\beta\hbar c}{\lambda}$

$$P(\lambda) \approx \left(\frac{16\pi^2\cancel{\hbar c}}{\lambda^5}\right)\left(\frac{\cancel{\lambda}}{2\pi\beta\cancel{\hbar c}}\right) = \frac{8\pi T}{\lambda^4}$$ Rayleigh-Jeans spectrum


UV
VISIBLE
INFRARED
Spectral radiance (kW · sr⁻¹ · m⁻² · nm⁻¹)
14
12
10
8
6
4
2
0
5000 K
4000 K
3000 K
Classical theory (5000 K)
0
0.5
1
1.5
2
2.5
3
Wavelength (µm)