MATH327: StatMech and Thermo

Wednesday, 26 March 2025

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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

Photon gas $\rightarrow$ Planck spectrum

$$\frac{\langle E\rangle_{ph}}{V} = \int_0^\infty P(\omega)\, d\omega = \int_0^\infty P(\lambda)\, d\lambda$$

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

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

Plan

Photon gas observations

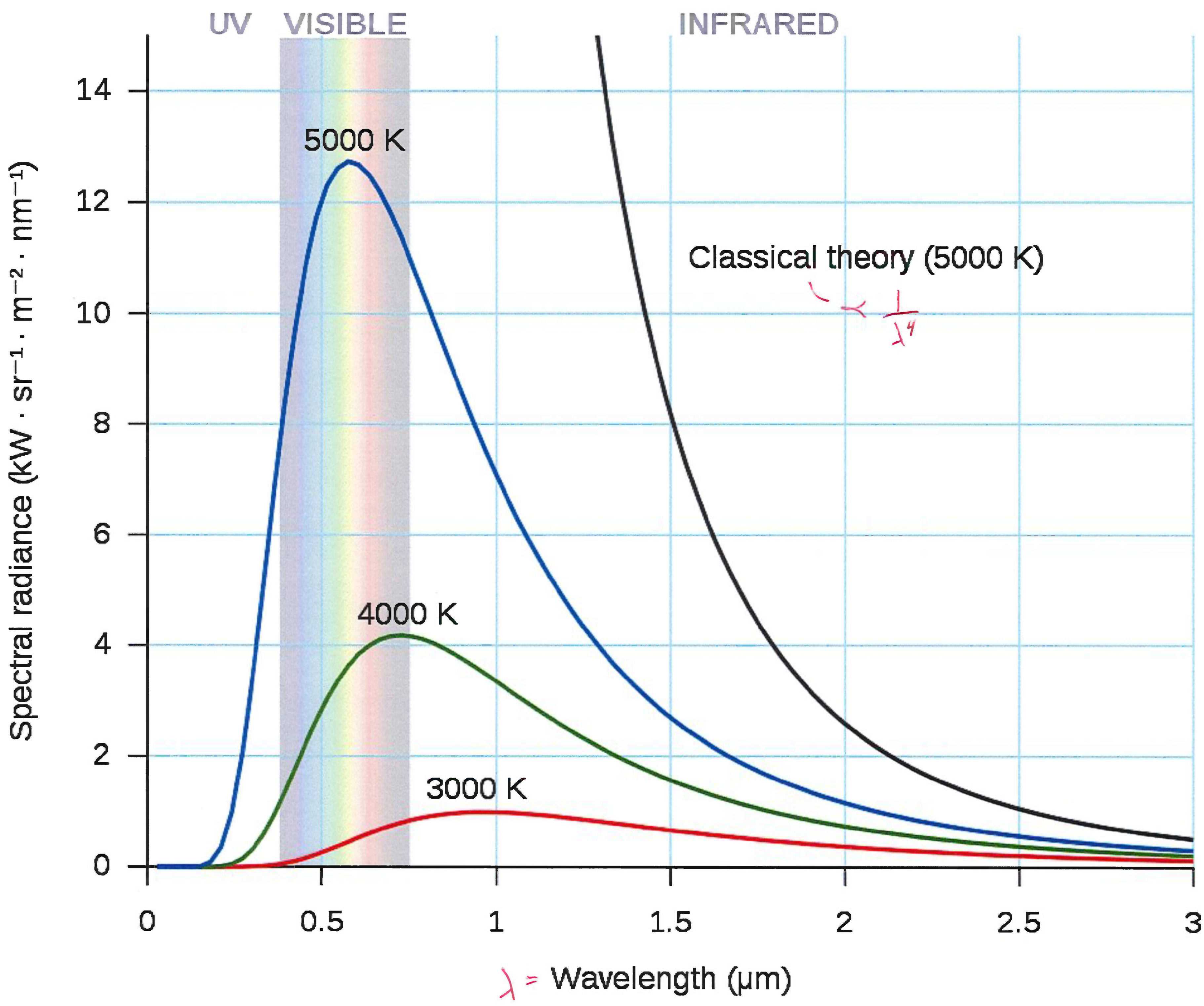
equation of gas

Fermion gas (non-rel.)

$$P(\lambda) \rightarrow \frac{8\pi T}{\lambda^4} \quad \text{for } \lambda \gg \beta\hbar c$$

classical Rayleigh – Jeans spectrum $\rightarrow \infty$ as $\lambda \rightarrow 0$

"ultraviolet catastrophe" $\rightarrow$ quantum



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)
$\propto \frac{1}{\lambda^4}$
0
0.5
1
1.5
2
2.5
3
λ = Wavelength (μm)

Full Planck spectrum has T-dependent peak

Around visible light for $T \sim 5000$ K

Because sunlight has $T \approx 5778$ K

Fit $P(\lambda) \rightarrow$ effective surface temperature

$T \lesssim 3500$ K for red stars

$T \gtrsim 10{,}000$ K for blue stars

$T_{CMB} \approx 2{,}725$ K for intergalactic space

cosmic microwave background

left over from Big Bang $\sim 13{,}7$ Gyr

Remove galaxies, compute T from remaining photons

Blue/red show small fluctuations around average T_{CMB}

$\Delta T \approx 0{,}0002$ K

Earlier average $T_{CMB} = 2{,}735 \pm 0{,}060$ from COBE (1990)

Here fit $P(f)$ $f = \frac{\omega}{2\pi}$

Peak around $f \sim 150$ GHz $= 1{,}5 \times 10^{-11}$ sec^{-1}

$\lambda = \frac{c}{\lambda} \sim 2$mm (microwave)

$\sim 1000\times$ longer than visible

Amazingly accurate description

given assumption of non-interacting ideal gas

Finish integrating Planck spectrum!

$$\langle E \rangle_{ph} = \frac{V\hbar}{\pi^2 c^3} \int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega}-1}\, d\omega$$

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

$d\omega = \frac{T}{\hbar}\, dx$

$$= \frac{V\hbar}{\pi^2 c^3}\left(\frac{T}{\hbar}\right)^4 \int_0^\infty \frac{x^3}{e^x - 1}\, dx$$

$\Gamma(4)\zeta(4) = 6\,\frac{\pi^4}{90} = \frac{\pi^4}{15}$

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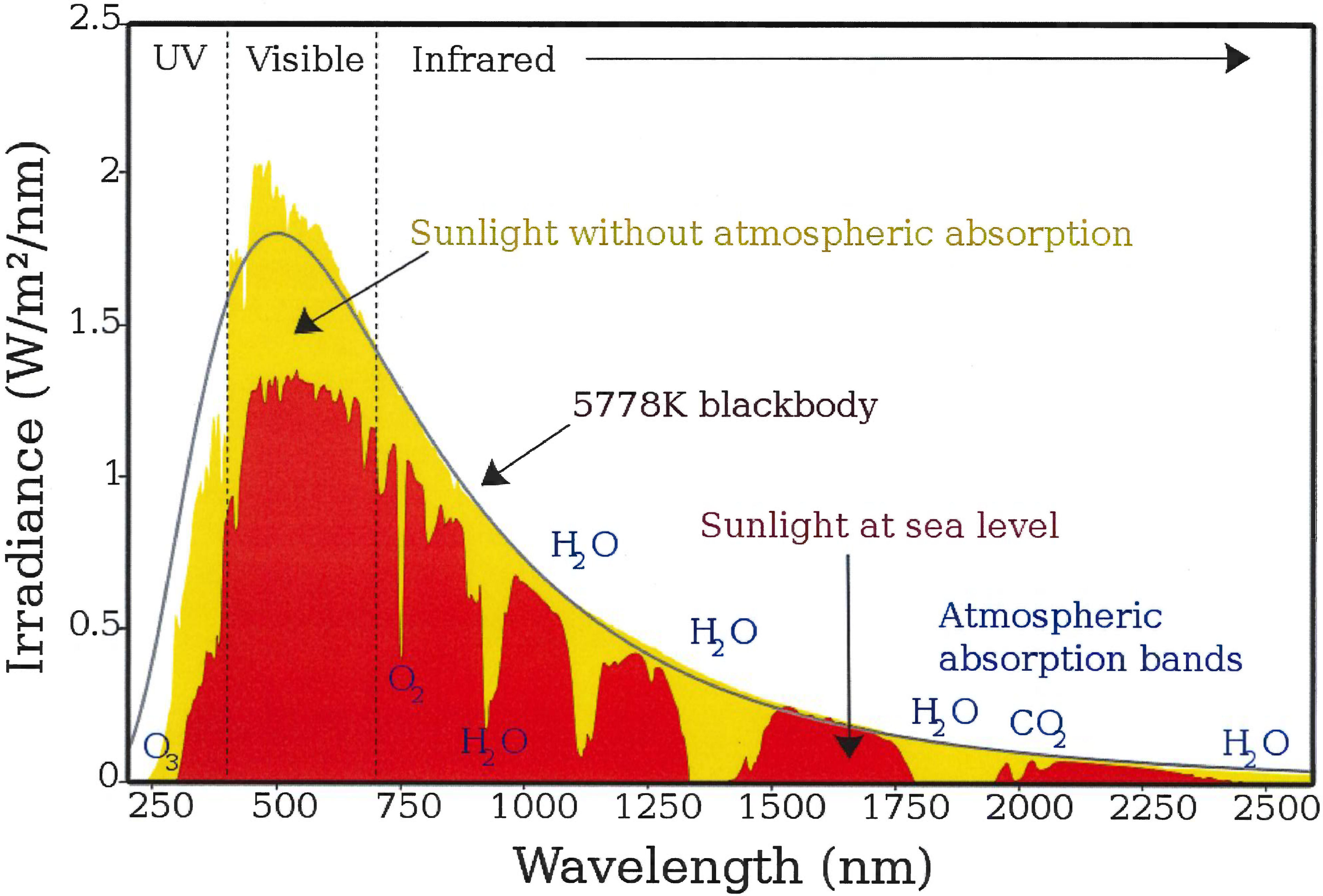
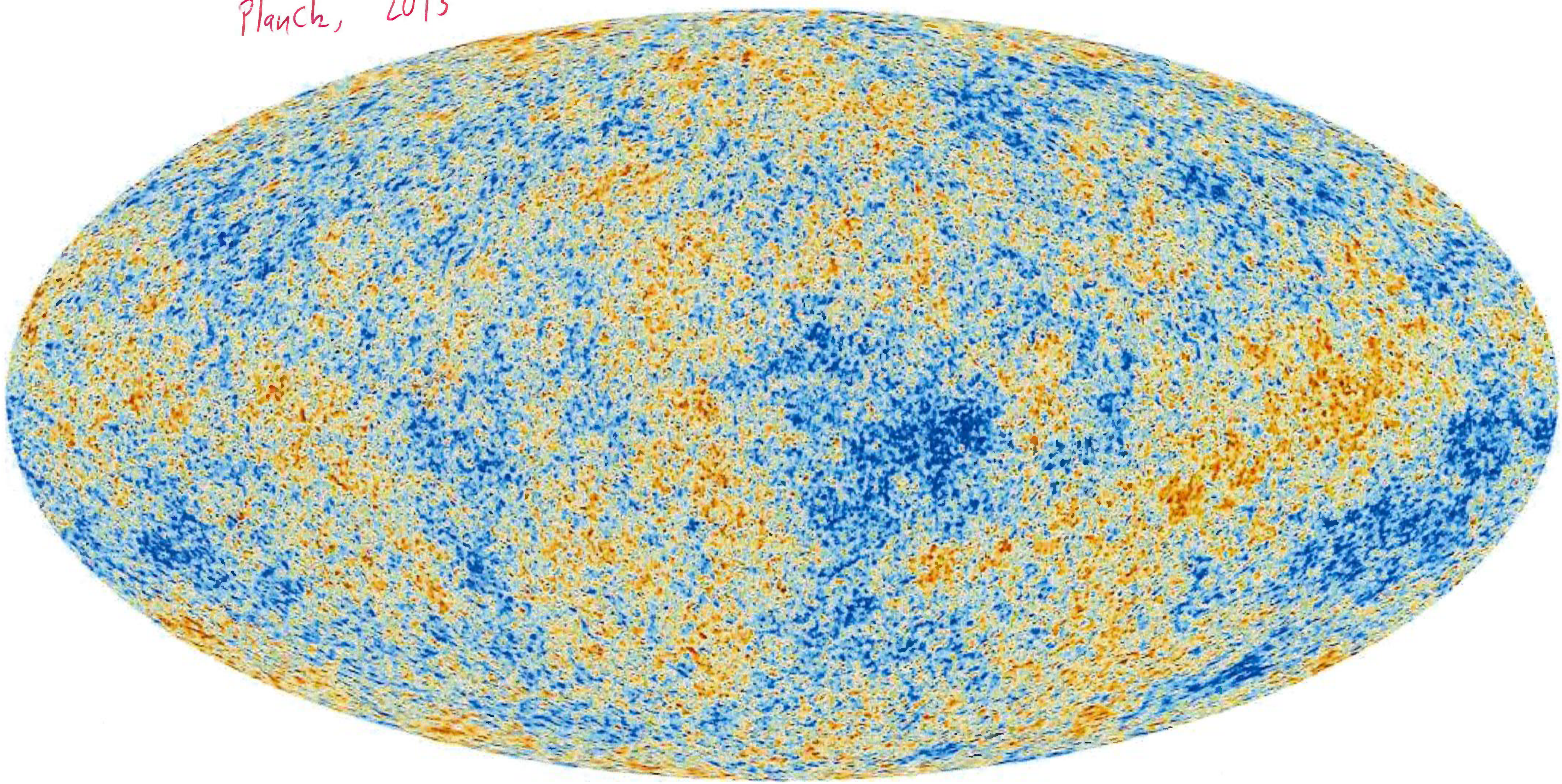
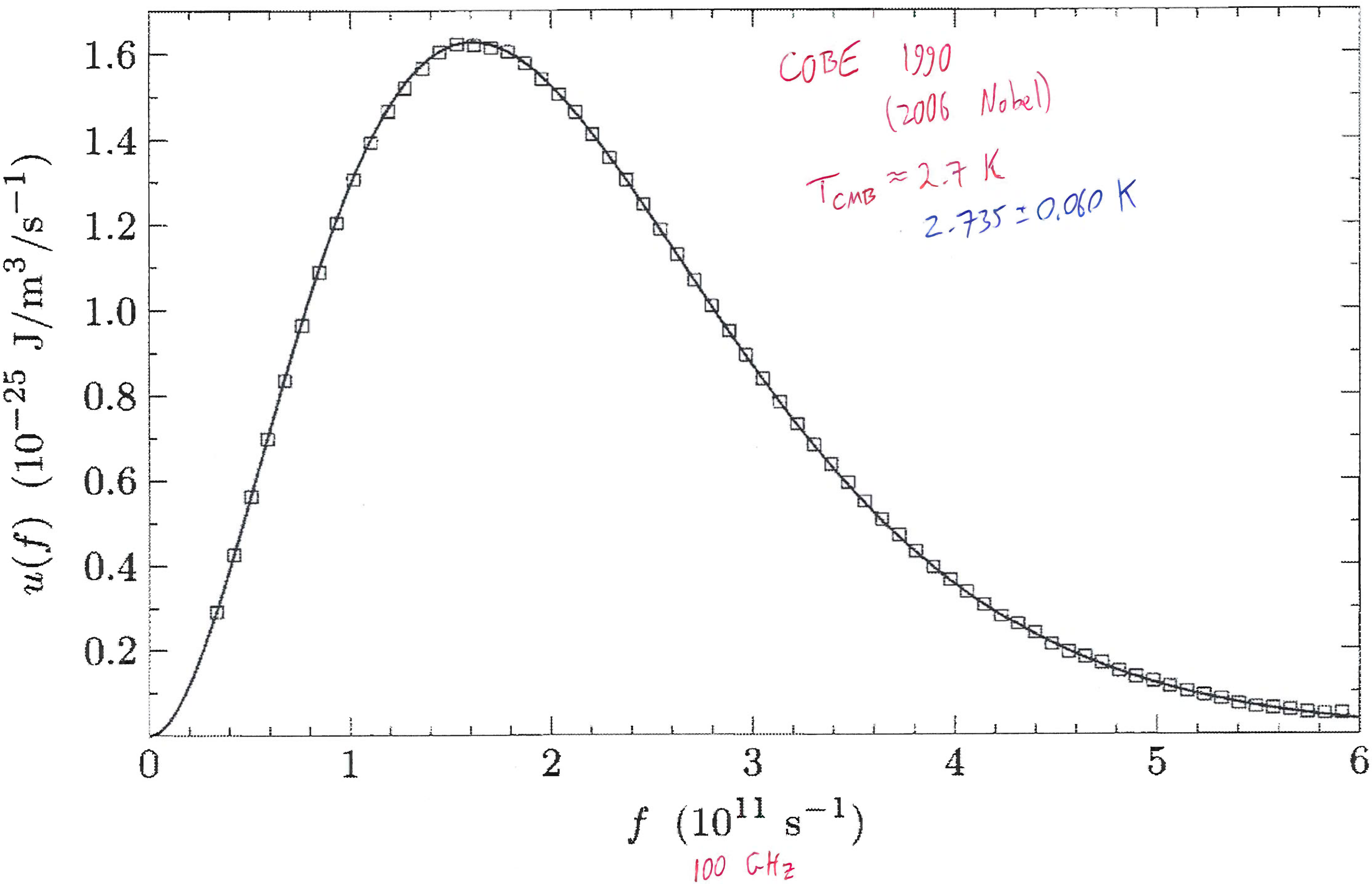
Spectrum of Solar Radiation (Earth)



Planck, 2013





COBE 1990
(2006 Nobel)
$T_{CMB} \approx 2.7$ K
2.735 ± 0.060 K
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
$u(f)$ $(10^{-25}$ J/m^3/s$^{-1})$
0
1
2
3
4
5
6
f $(10^{11}$ s$^{-1})$
100 GHz

$$\langle E\rangle_{ph} = \frac{\pi^2}{15\,\hbar^3 c^3} V T^4$$

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Compare with classical, canonical, non-rel. $\langle E\rangle = \frac{3}{2} N T$

$\to$ compute grand-canonical $\langle N\rangle_{ph} = \frac{-\partial}{\partial\mu}\Phi_{ph}\Big|_{\mu=0}$

$$\langle N\rangle_{ph} = -\frac{VT}{\pi^2 c^3}\int_0^\infty \omega^2 \frac{\partial}{\partial\mu}\log\left(1-e^{-\beta\hbar\omega}e^{\beta\mu}\right)d\omega\Big|_{\mu=0}$$

$$= \frac{\cancel{-}V\cancel{T}}{\pi^2 c^3}\int_0^\infty \frac{\omega^2\left(\cancel{-}e^{-\beta\hbar\omega}e^{\beta\mu}\cancel{\beta}\right)}{1-e^{-\beta\hbar\omega}e^{\beta\mu}}d\omega\Big|_{\mu=0}$$

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

$\hookrightarrow \Gamma(3)\zeta(3) = 2\zeta(3)$

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$$\langle N\rangle_{ph} = \frac{2\zeta(3)}{\pi^2\hbar^3 c^3} V T^3 \propto \frac{\langle E\rangle_{ph}}{T}$$

As before, $\langle E\rangle_{ph} \propto \langle N\rangle_{ph}\, T$

Constant factor $\left(\frac{\pi^2}{15\,\cancel{\hbar^3 c^3}}\right)\left(\frac{\pi^2\cancel{\hbar^3 c^3}}{2\zeta(3)}\right) = \frac{6\pi^4/90}{2\zeta(3)} = \frac{\Gamma(4)\zeta(4)}{\Gamma(3)\zeta(3)}$

≈ 2.7

<u>Radiation pressure</u> $P_{ph} = \frac{-\partial}{\partial V}\langle E\rangle_{ph}\Big|_{S_{ph}}$

Need constant entropy $S_{ph} = \frac{1}{T}\left(\langle E\rangle_{ph} - \Phi_{ph} - \cancel{\mu}_0\langle N\rangle\right)$

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

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

$\hookrightarrow -2\zeta(4) = \frac{-\pi^4}{45}$

$$S_{ph} = VT^3\left(\frac{\pi^2}{\hbar^3 c^3}\right)\left(\frac{1}{15}+\frac{1}{45}\right) = \underbrace{\frac{4\pi^2}{45\hbar^3 c^3} VT^3}_{\text{constant when } T = bV^{-1/3}}$$

$$\boxed{\begin{aligned} P_{ph} &= -\frac{\pi^2}{15\hbar^3 c^3}\frac{\partial}{\partial V}\left(b^4 V^{-1/3}\right) = \frac{1}{3V}\langle E\rangle_{ph} \\ P_{ph}V &= \frac{1}{3}\langle E\rangle_{ph} = \left(\frac{\cancel{\Gamma}(3)}{\Gamma(4)}\right)\left(\frac{\cancel{\Gamma}(4)\,\zeta(4)}{\Gamma(3)\,\zeta(3)}\right)\langle N\rangle_{ph}T \end{aligned}}$$

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E.S: $P_{ph}V = \underbrace{\frac{\pi^4}{90\,\zeta(3)}}_{0.9004}\langle N\rangle_{ph}T$

Photon gas E.S same form as ideal gas law
~10% different proportionality factor

Ideal gas of Fermions

$n_\ell = 0,1 \;\rightarrow\; \Phi_F = -T\sum_\ell \log\left(1+e^{-\beta(E_\ell-\mu)}\right)$

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

Non-relativistic regime has $p \ll mc$

$$\boxed{\begin{aligned} E = mc^2\sqrt{1+\frac{p^2}{m^2c^2}} &= mc^2\left[1+\frac{p^2}{2m^2c^2}+\mathcal{O}\left(\frac{p^4}{m^4c^4}\right)\right] \\ &\approx \underbrace{mc^2}_{\text{fixed}} + \frac{p^2}{2m} \end{aligned}}$$

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Constant mass energy irrelevant

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

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

Now ground-state $E_0 = 3\dfrac{\hbar^2\pi^2}{2mL^2} = 3\varepsilon$ for $\vec{k} = (1,1,1)$

Excited states:

$$\begin{array}{ll} 6\varepsilon & (2,1,1) \\ 9\varepsilon & (2,2,1) \\ 11\varepsilon & (3,1,1) \\ 12\varepsilon & (2,2,2) \end{array} \quad \left.\begin{array}{l} \\ \\ \\ \end{array}\right\} 3\times$$

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So $\Phi_F = \underbrace{-2}_{\text{two "spin" states per } \vec{k}} T \sum_{\vec{k}} \log\left[1 + \exp\left(\dfrac{-\hbar^2\pi^2 k^2}{2mL^2 T} + \dfrac{\mu}{T}\right)\right]$

two "spin" states per $\vec{k}$

As before, integrate over $\hat{k}_{x,y,z} > 0$ in spherical coords.

$$\Phi_F \approx -\pi T \int_0^\infty \hat{k}^2 \log\left[1 + \exp\left(-\frac{\hbar^2\pi^2\hat{k}^2}{2mL^2T} + \frac{\mu}{T}\right)\right] d\hat{k}$$

Change variable to energy $\hat{k} = \dfrac{L\sqrt{m}}{\pi\hbar}\sqrt{2E}$ $\quad d\hat{k} = \dfrac{L\sqrt{m}}{\pi\hbar}\dfrac{dE}{\sqrt{2E}}$

$$\boxed{\begin{aligned} \Phi_F &\approx -\pi T \cancel{8} \left(\frac{L\sqrt{m}}{\pi\hbar}\right)^3 \int_0^\infty (2E) \log\left(1 + e^{-\beta(E-\mu)}\right) \frac{dE}{\sqrt{2E}} \\ &= -VT\left(\frac{\sqrt{2m^3}}{\pi^2\hbar^3}\right) \int_0^\infty \log\left(1 + e^{-\beta(E-\mu)}\right) \sqrt{E}\, dE \end{aligned}}$$

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New simplification: Consider low T

Start with average particle density

$$\boxed{\begin{aligned} \frac{\langle N\rangle_F}{V} &= \frac{-\partial}{\partial\mu}\left(\frac{\Phi_F}{V}\right) = \cancel{T}\left(\frac{\sqrt{2m^3}}{\pi^2\hbar^3}\right) \int_0^\infty \frac{e^{-\beta(E-\mu)}\cancel{\beta}}{1 + e^{-\beta(E-\mu)}} \sqrt{E}\, dE \\ &= \frac{\sqrt{2m^3}}{\pi^2\hbar^3} \int_0^\infty \frac{1}{e^{\beta(E-\mu)} + 1} \sqrt{E}\, dE = \frac{\sqrt{2m^3}}{\pi^2\hbar^3} \int_0^\infty F(E)\sqrt{E}\, dE \end{aligned}}$$

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$F(E) = \dfrac{1}{e^{\beta(E-\mu)} + 1} \sim \langle n_e\rangle_{FD}$ is <u>Fermi Function</u>

Assume $\mu > 0$

Threshold at $F(E=\mu) = \frac{1}{2}$ for all T

$E > \mu \rightarrow$ exponentially suppressed $F(E) \rightarrow 0$

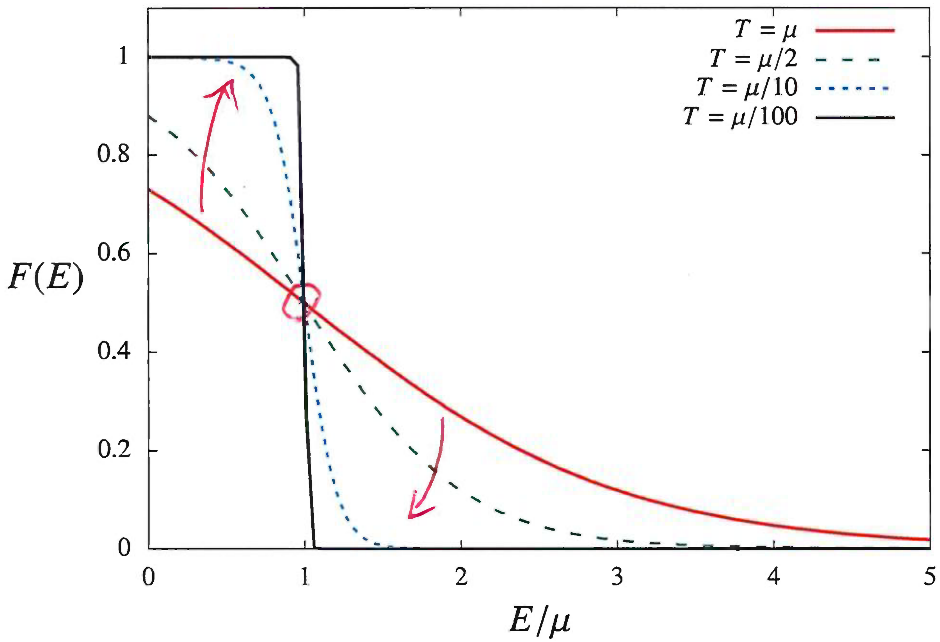
$E < \mu \rightarrow$ exponentially approach $F(E) \rightarrow 1$

Lower $T \rightarrow$ larger $\beta \rightarrow$ faster approach

Simplification: Approximate $F(E)$ as a step func.

$$F(E) = \begin{cases} 1 & 0 \leq E < \mu \\ 0 & \text{otherwise} \end{cases}$$

$$F(E) = \frac{1}{\exp\left[\frac{\mu}{T}\left(\frac{E}{\mu}-1\right)\right]+1} = \left(\left[\exp\left(\frac{E}{\mu}-1\right)\right]^{\mu/T}+1\right)^{-1}$$



μ/T
1
2
10
100