MATH327: StatMech and Thermo

Thursday, 16 April 2026

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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

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

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

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

Plan

Photon gas observations
equation of state

Fermion gas (non-rel.)

As always, consider limiting behaviour

UV: $\lambda \to 0$

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

IR: $\lambda \gg \beta \hbar c$

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

$$P(\lambda) = \left(\frac{16\pi^2 \hbar c}{\lambda^5}\right)\left(\frac{\lambda}{2\pi \beta \hbar c}\right) = \frac{8\pi T}{\lambda^4}$$

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

"ultraviolet catastrophe" $\to$ quantum

Full Planck spectrum has T-dependent peak

For $T \sim 5000$ K, peak around visible light because sunlight has $T \approx 5778$ K

Fit $P(\lambda) \to$ 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 ~13.7 Gyr

Remove galaxies, compute T from remaining photons

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

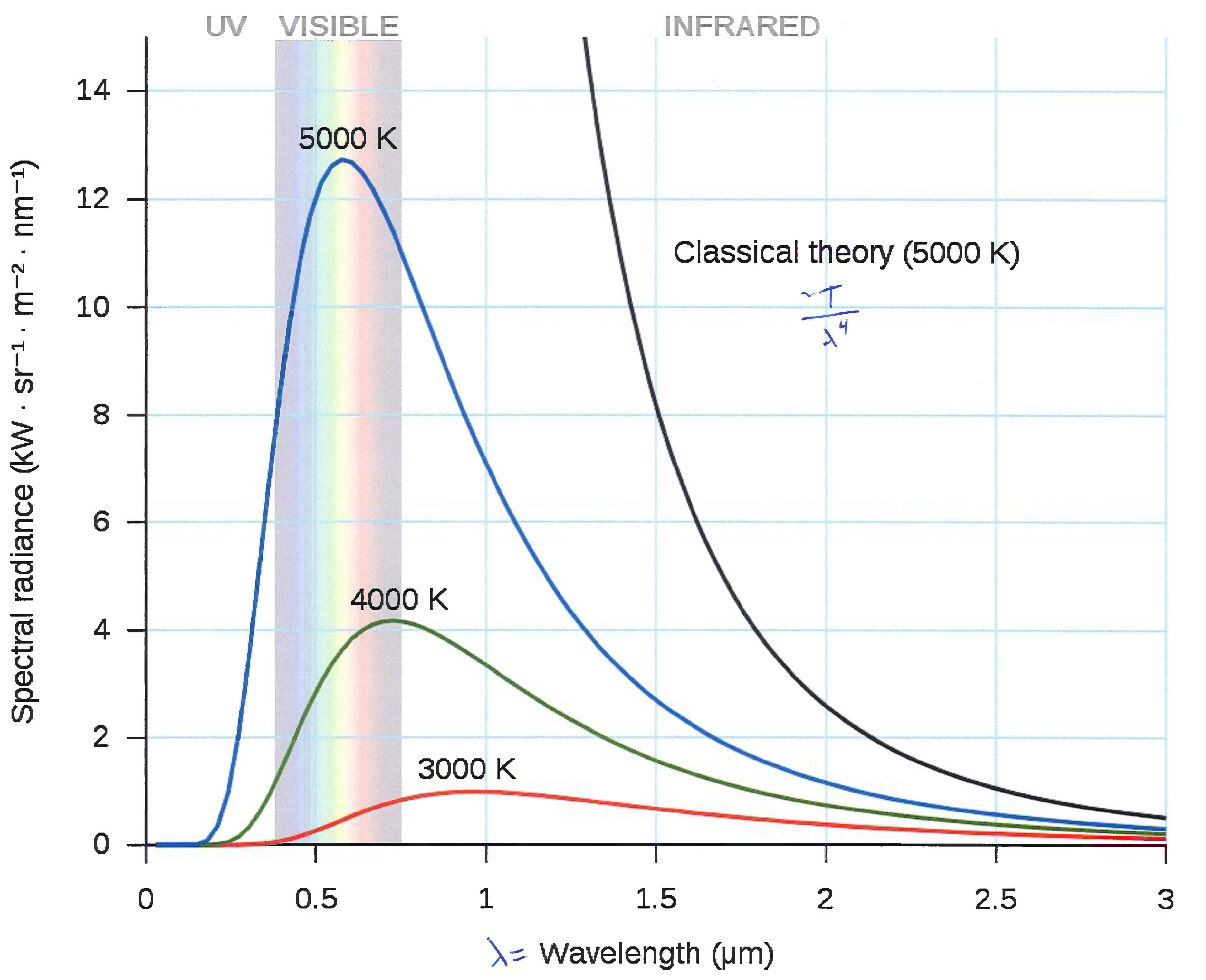
$\Delta T \approx 0.0002$ K

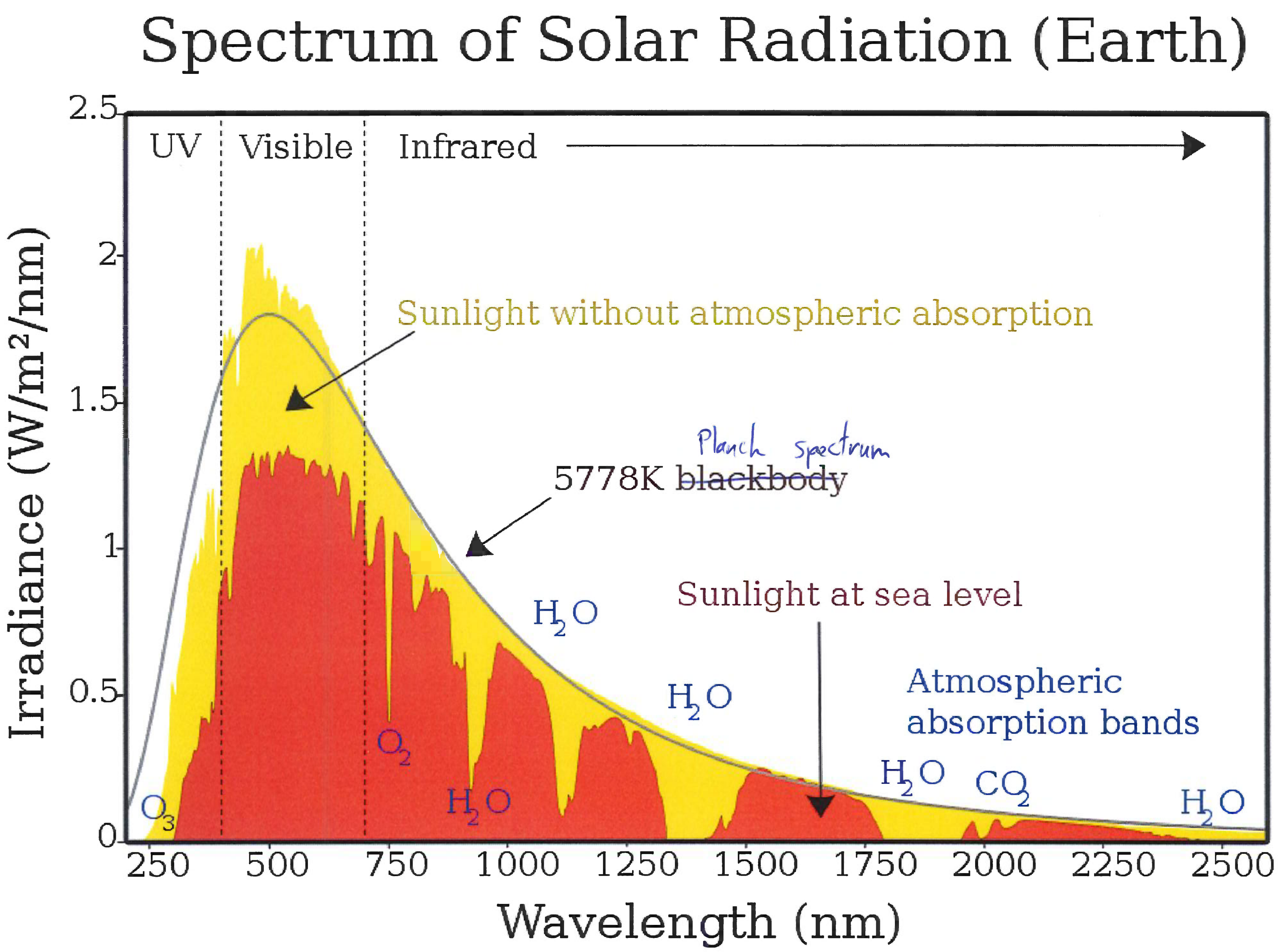
Pattern of fluctuations $\to$ dark matter

Earlier data from COBE for $P(f)$ $\quad f = \frac{\omega}{2\pi}$ $\to T_{CMB} = 2.735 \pm 0.060$

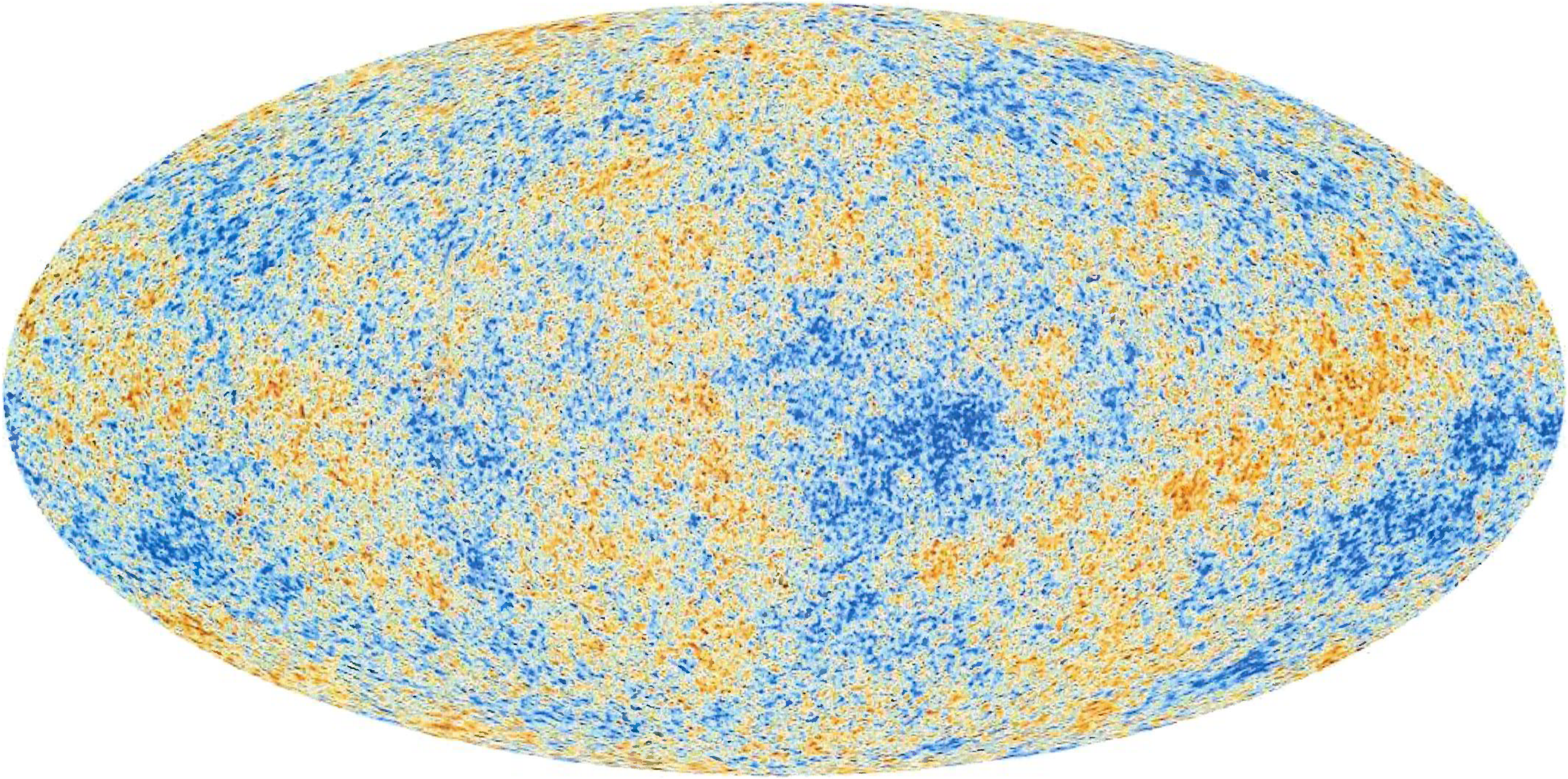
Peak around $f \sim 150$ GHz $= 1.5 \times 10^{11}$ s^{-1}

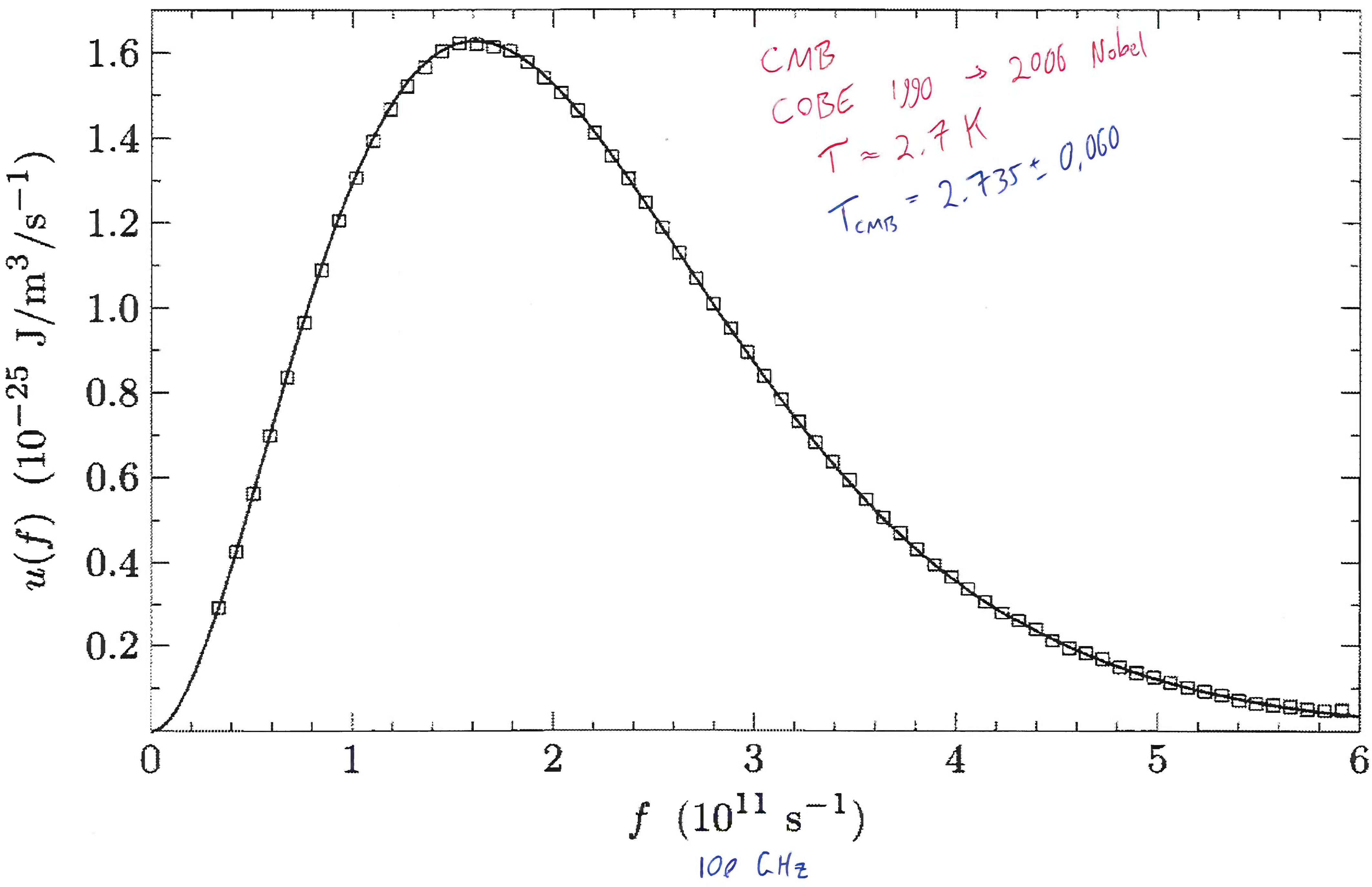
$\lambda = \frac{c}{f} \sim 2$ mm (microwave) ~ 1000x visible


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


Spectrum of Solar Radiation (Earth)
Irradiance (W/m²/nm)
2.5
2
1.5
1
0.5
0
UV
Visible
Infrared
Sunlight without atmospheric absorption
Planck spectrum
5778K ~~blackbody~~
Sunlight at sea level
Atmospheric absorption bands
O_3
O_2
H_2O
H_2O
H_2O
H_2O
CO_2
H_2O
250
500
750
1000
1250
1500
1750
2000
2250
2500
Wavelength (nm)

Planck, 2013





CMB
COBE 1990 → 2006 Nobel
T ≈ 2.7 K
T_CMB = 2.735 ± 0,060
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

Amazingly accurate descriptions given assumption of non-interacting ideal gas

Finish integrating Planck spectrum!

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

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

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

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

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

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

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

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

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

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

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

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

Now constant is $\left(\frac{\pi^2\cancel{\hbar^3c^3}}{2\zeta(3)}\right)\left(\frac{\pi^2}{15\cancel{\hbar^3c^3}}\right) = \frac{6\pi^4/90}{2\zeta(3)} = \frac{\Gamma(4)\zeta(4)}{\Gamma(3)\zeta(3)} \simeq 2.7$

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

Need constant entropy $\quad S_{ph} = \frac{1}{T}\left(\langle E \rangle_{ph} - \Phi_{ph} - \underset{\searrow 0}{\mu} \langle N \rangle_{ph}\right)$

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

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

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

$$S_{ph} = V T^3 \left(\frac{\pi^2}{\hbar^3 c^3}\right)\left(\frac{1}{15} + \frac{1}{45}\right) = \frac{4\pi^2}{45 \hbar^3 c^3} V T^3$$

constant when $T = b V^{-1/3}$

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

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EoS: $\quad P_{ph} V = \frac{\pi^4}{90\zeta(3)} \langle N \rangle_{ph} T$

$\quad\quad 0.9004$

Photon gas EoS same form as ideal gas law
$\sim 10\%$ different proportionality factor

Ideal gas of fermions

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

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

Non-relativistic regime has $p \ll mc$

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

$$\approx \underbrace{mc^2}_{\text{fixed}} + \frac{p^2}{2m}$$

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

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

Excited states:

6ε	$(2,1,1)$ 3x degen.
9ε	$(2,2,1)$ 3x degen.
11ε	$(3,1,1)$ 3x degen.
12ε	$(2,2,2)$

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

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 variables to energy $\hat{k} = \frac{L\sqrt{m}}{\pi\hbar}\sqrt{2E}$

$$d\hat{k} = \frac{L\sqrt{m}}{\pi\hbar}\frac{dE}{\sqrt{2E}}$$

$$\Phi_F \simeq -\pi T \left(\frac{L\sqrt{m}}{\pi \hbar}\right)^3 \int_0^\infty (2E) \log\left(1+e^{-\beta(E-\mu)}\right) \frac{dE}{\sqrt{2E}}$$

$$= -VT\left(\frac{\sqrt{2m^3}}{\pi^2 \hbar^3}\right)\int_0^\infty \log\left(1+e^{-\beta(E-\mu)}\right)\sqrt{E}\, dE$$

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Preview: Simplify by consider low temperature