17 March

Logistics

Current Zoom may change to MS Teams

Discussion board set up on VITAL

No exams in May

Important to continue to engage w/homework, computer project

office hours will pick up in same meeting rooms

Computer project

No in-person sign-off

Instead complete individually & submitted on VITAL

↳ scan of sheets & computer code

Accept code in language of preference

Not only MATLAB, also python, R, perl, ...

↳ Set up on a personal computer via site license

PC stations in library open at moment (I believe)

Friday: Reviewing diffusion

Support for MATLAB remote setup & guidance on various programming approaches

Recap

Big picture: Quantum gases as an application of grand-canonical ensemble

Grand-canonical approach

Internal energy & particle number can fluctuate

heat-bath

particle reservoir

Hide role of heat-bath & particle reservoir by working with fixed <u>temperature</u> and fixed <u>chemical potential</u>

partition function $Z_g(T,\mu) = \sum_{i=1}^{M} \exp(-\beta E_i + \beta \mu N_i)$

Grand potential $\Omega(T,\mu) = -T \ln Z_g$

$$\langle N \rangle = \frac{-\partial \Omega}{\partial \mu}$$

$$\langle E \rangle = -T^2 \frac{\partial}{\partial T}\left(\frac{\Omega}{T}\right) + \mu \langle N \rangle = \Omega + T \cdot S + \mu \langle N \rangle$$

entropy $S = \frac{-\partial \Omega}{\partial T}$

Quantum gases

- Energy levels discrete ("quantized") and <u>countable</u>

  $E_1, E_2, \dots, E_L$ possibly infinitely many

- Sum over microstates given by sum over occupation numbers n_ℓ for each energy level E_ℓ

Not classical sum over all energies each particle can have

Two types of quantum partiticles / statistics

Bosons can have $n_\ell = 0, 1, 2, \dots$

Any # of bosons in each individual state

Fermions can have only $n_\ell = 0, 1$

At most one fermion in each individual state ("exclusion principle")

Bose gas

$$Z_{bose} = \prod_{\ell=1}^{L} \frac{1}{1 - \exp\left(-\frac{E_\ell - \mu}{T}\right)}$$

$$\Omega_{bose} = -T \ln Z_{bose} = T \sum_{\ell=1}^{L} \ln\left[1 - \exp\left(-\frac{E_\ell - \mu}{T}\right)\right]$$

Converge of geometric series requires $\mu < 0$

$$\mu = \left.\frac{\partial \langle E \rangle}{\partial N_p}\right|_S < 0 \quad \rightarrow$$

When adding particles must decrease internal energy to keep entropy fixed

High-temperature limit

$T \to \infty \quad \beta = \frac{1}{T} \to 0$ while $\mu \to -\infty$

such that $\exp\left(-\frac{E_\ell - \mu}{T}\right) \ll 1$ or $-\mu \gg T \gg E_\ell$

Required to keep number of particles from diverging

$$\langle N \rangle = \frac{-\partial \Omega}{\partial \mu} = \sum_{\ell=1}^{L} \langle n_\ell \rangle \qquad \langle n_\ell \rangle = \frac{1}{\exp(\beta E_\ell - \beta\mu) - 1}$$

$$\Omega_{bose} \rightarrow -\sum_{\ell=1}^{L} \exp\left(-\frac{E_\ell - \mu}{T}\right)$$

μ can be positive or negative

$$\text{Classical} \quad Z_g = \prod_{\ell=1}^{L} \exp\left[\exp\left(-\frac{E_\ell - \mu}{T}\right)\right]$$

Conclusion: Quantum Bose gas becomes classical in the high-temperature limit $\cancel{-\mu} \; T \gg E_\ell$
$\gg$

We obtain the result

$$-\frac{\Omega_{\text{classical}}}{T} = \ln Z_{\text{classical}} = \sum_{\ell=1}^{L} \exp\left(-\frac{E_\ell - \mu}{T}\right),$$

matching the high-temperature limit of the Bose gas on page 121.

We can again compute the average particle number

$$\boxed{\begin{aligned}\langle N \rangle = -\frac{\partial \Omega}{\partial \mu} &= T \sum_{\ell=1}^{L} \frac{\partial}{\partial \mu} \exp(-\beta E_\ell + \beta\mu) \\ &= \cancel{T}\cancel{\beta} \sum_{\ell=1}^{L} \exp(-\beta E_\ell + \beta\mu) = \sum_{\ell=1}^{L} \langle n_\ell^{(cl)} \rangle\end{aligned}}$$

We again obtain $\langle N \rangle = \sum_{\ell=1}^{L} \langle n_\ell \rangle$, but now with the classical average occupation number

$$\left\langle n_\ell^{(\text{cl})} \right\rangle = \exp\left(-\beta E_\ell + \beta\mu\right).$$

Recalling the expression for the quantum Bose gas,

$$\left\langle n_\ell^{(\text{bose})} \right\rangle = \frac{1}{\exp\left(\beta E_\ell - \beta\mu\right) - 1}, \quad \to \frac{1}{\exp(\beta E_\ell - \beta\mu)} = \langle n_\ell^{(cl)} \rangle$$

we see that classical physics is recovered in the high-temperature limit where $\beta(E_\ell - \mu) \gg 1$ makes the exponential factor much greater than 1.

$$Z_{fermi} = \left(\sum_{n_1=0,1} \exp(-\beta E_1 n_1 + \beta\mu n_1)\right) \times \dots \times \left(\sum_{n_L=0,1} \exp(-\beta E_L n_L + \beta\mu n_L)\right)$$
$$= (1 + \exp(-\beta E_1 + \beta\mu)) \times \dots \times (1 + \exp(-\beta E_L + \beta\mu))$$
$$= \prod_{l=1}^{L} (1 + \exp(-\beta E_l + \beta\mu))$$

but room temperatures are usually considered to be very high. This explains the tremendous success of the classical statistics for everyday life settings.

FERMI GAS

We are now going to study a gas of fermions in a volume V. We again consider the setting of a grand-canonical ensemble. If we now sum over the micro-states, we need to take into account that there is at most one fermion per energy:

$$Z_{fremi} = \sum_{n_1=0,1} \dots \sum_{n_M=0,1} \exp\left\{-\beta, \sum_{i=1}^{M} E_i\, n_i \,+\, \beta\,\mu \sum_{i=1}^{M} n_i\right\} .$$

Following the lines above, we carry out each sum and arrive at: the co-called *Fermi Statistics*:

$$-\frac{\Omega}{T} = \ln Z_{fermi} = \sum_{i=1}^{M} \ln\left[1 + \exp\left(-\frac{E_i - \mu}{T}\right)\right] . \qquad (80)$$

μ can be positive or negative

As in the classical physics case, we arrive at a sum over all energy levels, but now with different terms (compare with (78)).

若 $\mu \to -\infty$

If we again consider the case of high temperatures $T \gg E_i$, we find:

$-\mu \gg T \gg E_l$

$$\ln Z_{fermi} = \sum_{i=1}^{M} \exp\left(-\frac{E_i - \mu}{T}\right) = \ln Z_{\text{classical}} .$$

It is quite remarkable that in the classical high temperature limit the difference between fermions and bosons disappear, which is probably one explanation why it took some time to discover this quantum feature.

8.1 Gas of photons and the Maxwell distribution

The energy of a photon is determined by its wavelength λ or by its (angular) frequency [12] $\omega = 2\pi\, c/\lambda$. Its energy is given

physics input: $$E_{ph} = \hbar\omega = \hbar\, c\sqrt{\vec{k}^2} , \qquad (81)$$

[12] c is here the vacuum speed of light, which is sometimes set to $c = 1$ by a redefinition of units.

Addendum: High-temperature limit of the Fermi gas

As before, let's compute the average particle number from the grand-canonical potential to explore the high-temperature limit of the Fermi gas ~~is a bit~~. Labelling the energy levels E_ℓ with $\ell = 1, \cdots, L$, we have

$$\Omega_{\text{fermi}} = -T \ln Z_{\text{fermi}} = -T \sum_{\ell=1}^{L} \ln\left[1 + \exp\left(-\beta E_\ell + \beta\mu\right)\right],$$

$$\boxed{\begin{aligned} \langle N \rangle = -\frac{\partial \Omega}{\partial \mu} &= T \sum_{\ell=1}^{L} \frac{\partial}{\partial \mu} \ln\left[1 + \exp\left(-\beta E_\ell + \beta\mu\right)\right] \\ &= \cancel{T}\, \frac{\cancel{\beta} \exp\left(-\beta E_\ell + \beta\mu\right)}{1 + \exp\left(-\beta E_\ell + \beta\mu\right)} \\ &= \sum_{\ell=1}^{L} \frac{1}{\exp\left(\beta E_\ell - \beta\mu\right) + 1} = \sum_{\ell=1}^{L} \langle n_\ell \rangle \end{aligned}}$$

The behaviour of the resulting average occupation numbers is very different than for the Bose gas:

$$\langle n_\ell \rangle = \frac{1}{\exp\left(\beta E_\ell - \beta\mu\right) + 1}.$$

This ranges between 0 (when the exponential factor is very large) and 1 (when the exponential factor is very small), consistent with our quantum physics input that there can be at most one fermion per energy state.

Even though there is no longer any possibility of a divergent $\langle n_\ell \rangle$, we still need $-\mu \gg T \gg E_i$ in order for the sum total $\langle N \rangle = \sum_{\ell=1}^{L} \langle n_\ell \rangle$ to satisfy the grand-canonical constraint on total particle number. In this limit we again recover the classical $\left\langle n_\ell^{(\text{cl})} \right\rangle = \exp\left(-\beta E_\ell + \beta\mu\right)$, because the $\beta(E_\ell - \mu) \gg 1$ makes the exponential factor much greater than 1.

$T \to \infty$

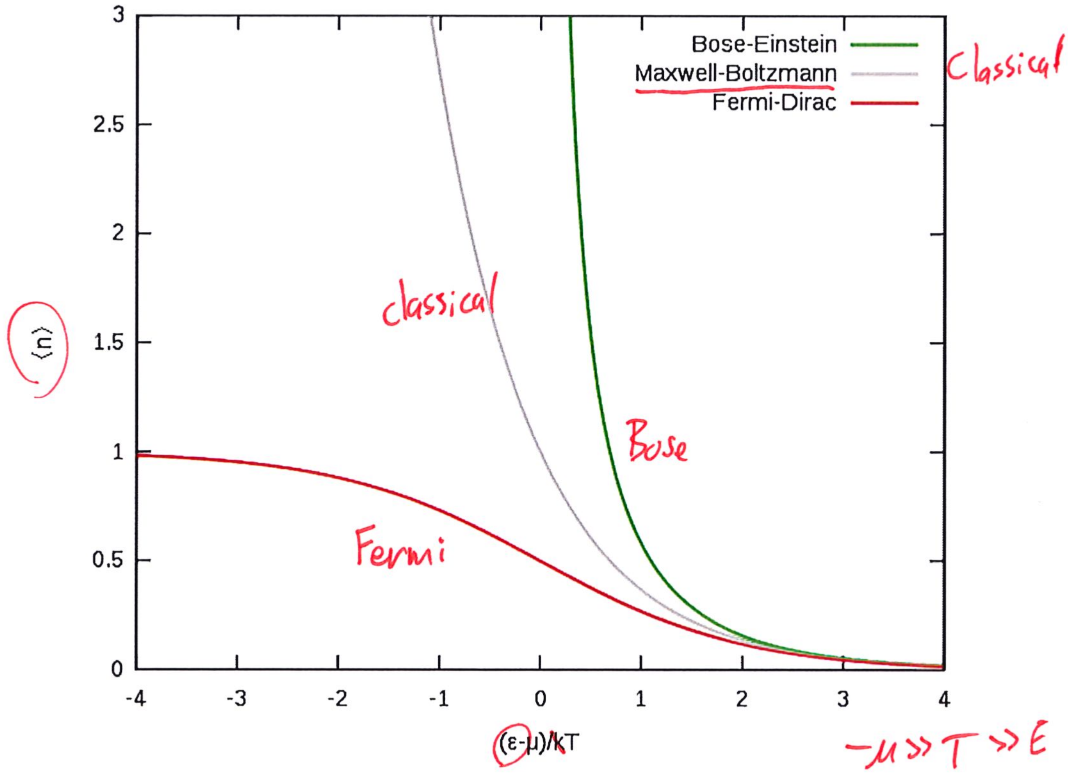
$\beta \to 0$

$\mu \to -\infty$

$\langle n_\ell \rangle \Rightarrow \exp\left(-\beta E_\ell + \beta\mu\right)$ = classical case

Energy level ε

The figure below[13] shows an average occupation number for the Bose, Fermi and classical (Maxwell–Boltzmann) gases, demonstrating how all three distributions approximately agree even when $-\mu/T$ is not all that large. (The constant k converts between units and can be set to $k = 1$.)



$-\mu \gg T \gg \varepsilon$

Classical limit: Many more states than particles (approximately unique energy for each particle)

[13]Source: commons.wikimedia.org/wiki/File:Fermi-Dirac_Bose-Einstein_Maxwell-Boltzmann_statistics.svg

momentum

where $\vec{k}$ is the wave vector. If the photons are confined to a volume V, the allowed wave vectors are

integer m_i

$$(k_x, k_y, k_z) = \left(\frac{2\pi}{L} m_1, \frac{2\pi}{L} m_2, \frac{2\pi}{L} m_3\right) , \qquad i = 1, 2, 3 , \qquad V = L^3 .$$

We have now arrived at our energy spectrum:

"ultra-relativistic" $E \propto |\vec{k}|$

vs. "non-relativistic" case in Sec. 5 $E \propto |\vec{k}|^2$

$$E_{ph,i} = \hbar\omega = \hbar c \sqrt{\vec{k}^2(m_1, m_2, m_3)} , \qquad i = (m_1, m_2, m_3) .$$

$\omega = c|\vec{k}|$

Photons have an additional quantum number, i.e., polarisation, implying that each energy level is twice degenerated.

We have already done a good deal of the calculation and can now just use the Bose Statistics (79) to get the partition function:

$$\ln Z_{ph} = -2 \sum_i \ln \left[1 - \exp\left(-\frac{E_{ph,i} - \mu}{T}\right)\right] .$$

The factor of 2 We consider large volumes so that we can approximate the sum by an integral using the leading order of a Poisson re-summation (we have studied this in detail with the exercise sheet on page 150):

$L \gg 1$

$$\ln Z_{ph} = -2 \int dm_1\, dm_2\, dm_3 \ln \left[1 - \exp\left(-\frac{E_{ph,i} - \mu}{T}\right)\right] .$$

With a simple substitution:

$$dm_i = \frac{L}{2\pi} dk_i$$

$$\ln Z_{ph} = -2 \left(\frac{L}{2\pi}\right)^3 \int dk_1\, dk_2\, dk_3 \ln\left[1 - \exp\left(-\frac{\hbar c k - \mu}{T}\right)\right]$$

$L^3 = V$

we find:

$$\ln Z_{ph} = -2\, V \int \frac{d^3k}{(2\pi)^3} \ln \left[1 - \exp\left(-\frac{\hbar c\, k - \mu}{T}\right)\right] .$$

$k>0$

The integral only depends on $k = \sqrt{\vec{k}^2}$, which suggests to use the frequency as integration variable:

$$\int_{-\pi}^{\pi} d\phi \int_{-1}^{1} d\cos\theta = 4\pi$$

$$\omega = c\,k\,, \qquad d^3k \;\to\; 4\pi\, dk\, k^2 \;=\; \frac{4\pi}{c^3}\, d\omega\, \omega^2\,.$$

Altogether, we arrive at:

$$-\frac{\Omega}{T} = \ln Z_{ph} \;=\; -\frac{V}{c^3\,\pi^2}\int_0^\infty d\omega\,\omega^2\,\ln\left[1 - \exp\left(-\frac{\hbar\omega - \cancel{\mu}\,0}{T}\right)\right]. \tag{82}$$

Physics input: Photons can be easily created e.g. by charged particles collisions. Hence, adding a photon to a box of photon a gas is generically adding a negligible amount of energy to the systems. Hence, a gas of photon is well described by a vanishing chemical potential, i.e., $\mu = 0$.

$$\mu = 0 = \left.\frac{\partial\langle E\rangle}{\partial N_p}\right|_S$$

We are now in the position to calculate thermodynamical observables. We adopt the case $\mu = 0$. ~~We leave detailed calculations to an exercise sheet.~~ Next page...

Internal energy of a photon gas:

$$\begin{aligned}\langle E\rangle \cancel{U} &= \frac{V}{c^3\pi^2}\int_0^\infty d\omega\,\omega^2\,\frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{T}\right) - 1} = \frac{V\,T^4}{\hbar^3 c^3\pi^2}\int_0^\infty dx\,\frac{x^3}{\exp\{x\}-1} \\ &= \frac{\pi^2 V T^4}{15\,\hbar^3 c^3}\,.\end{aligned} \tag{83}$$

We observe that the energy density increases like T^4 with temperature, i.e., $\langle E\rangle\,\cancel{U}/V \propto T^4$.

From which (small) frequency intervall rises the most important contribution to the internal energy of a photon gas?

To answer this question, we introduce the spectral density $P(\omega)$ by

$$\langle E\rangle \cancel{U} \;=\; \int d\omega\, P(\omega)\,, \qquad P(\omega) \;=\; \frac{\hbar V}{c^3\pi^2}\,\frac{\omega^3}{\exp\left(\frac{\hbar\omega}{T}\right) - 1}\,. \tag{84}$$

$P(\omega)$ is called the Planck spectrum.

$$\langle E\rangle = -T^2 \frac{\partial}{\partial T}\left(\frac{\Omega}{T}\right) + \cancelto{0}{\mu}\langle N\rangle = T^2 \frac{\partial}{\partial T} \ln Z_{ph}$$

$$= \frac{-T^2 V}{c^3 \pi^2} \int_0^\infty d\omega\ \omega^2 \frac{\partial}{\partial T} \ln\left[1 - \exp\left(-\frac{\hbar\omega}{T}\right)\right]$$

$$= \frac{+\cancel{T^2} V}{c^3 \pi^2} \int_0^\infty d\omega\ \omega^2 \frac{+(\hbar\omega/\cancel{T^2})\exp(-\hbar\omega/T)}{1 - \exp(-\hbar\omega/T)}$$

$$= \frac{\hbar V}{c^3 \pi^2} \int_0^\infty d\omega \frac{\omega^3}{\exp(\hbar\omega/T) - 1}$$

$$x = \frac{\hbar\omega}{T} \qquad \omega = \frac{T}{\hbar}x \qquad d\omega = \frac{T}{\hbar}dx$$

$$= \frac{V T^4}{\hbar^3 c^3 \cancel{\pi^2}} \underbrace{\int_0^\infty dx \frac{x^3}{e^x - 1}}_{\pi^4/15}$$

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

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

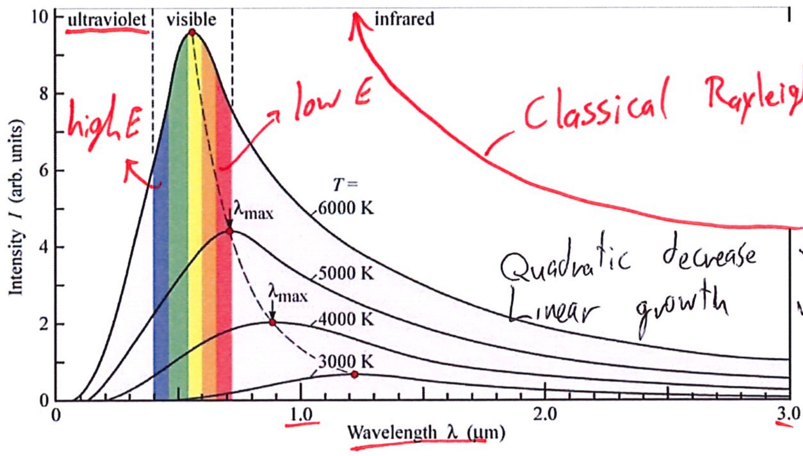
$$E_{ph} = \hbar\omega = \frac{2\pi\hbar c}{\lambda}$$

DISCUSSIONS:

The Planck spectrum as function of the wave length $\lambda = 2\pi c/\omega$:

$K \approx {}^\circ C + 273.$

$P(\lambda)$



The Planck Distribution function (Source: E. Schubert, *Light Emitting Diodes*).

COMMENTS:

Large λ → small ω $\quad \exp\left(\frac{\hbar\omega}{T}\right) - 1 \approx \frac{\hbar\omega}{T}$

spectrum at low energy → $\frac{VT}{c^3\pi^2}\omega^2 = \frac{4VT}{c\lambda^2}$ → ultraviolet catastrophe

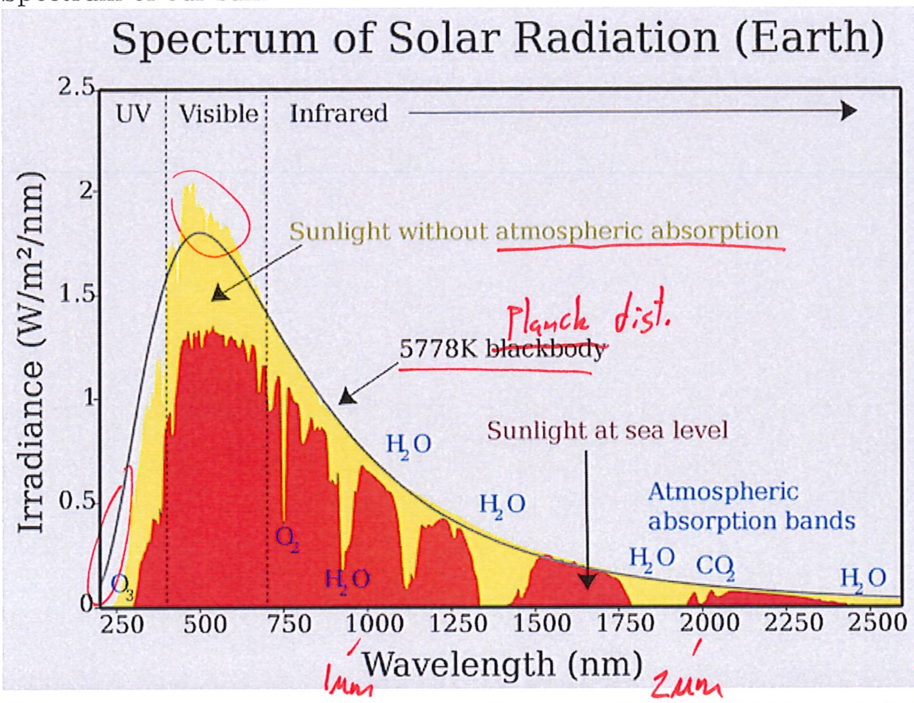
High temperatures: Rayleigh-Jeans

Short λ → high energy, large $\exp\left(\frac{\hbar\omega}{T}\right)$

$P(\omega) \to 0$

Peak intensity moves to shorter λ, higher energy as temperature increases

Spectrum of our sun:



1000 nm = μm

COMMENTS:

Sunlight approximately follows non-interacting Planck distribution

Determine effective surface tempera~~t~~ture by fitting to Planck distribution

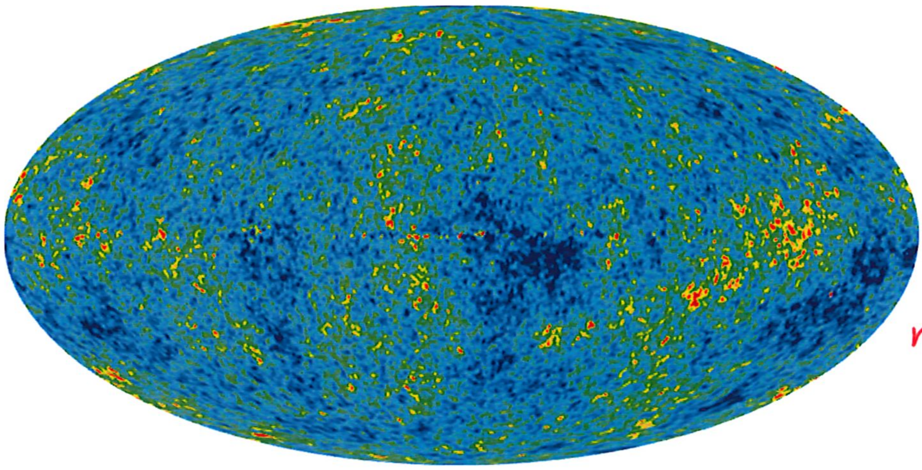
For sun ~ 6000 K

red stars $\lesssim$ 3500 K

blue stars $\gtrsim$ 10,000 K

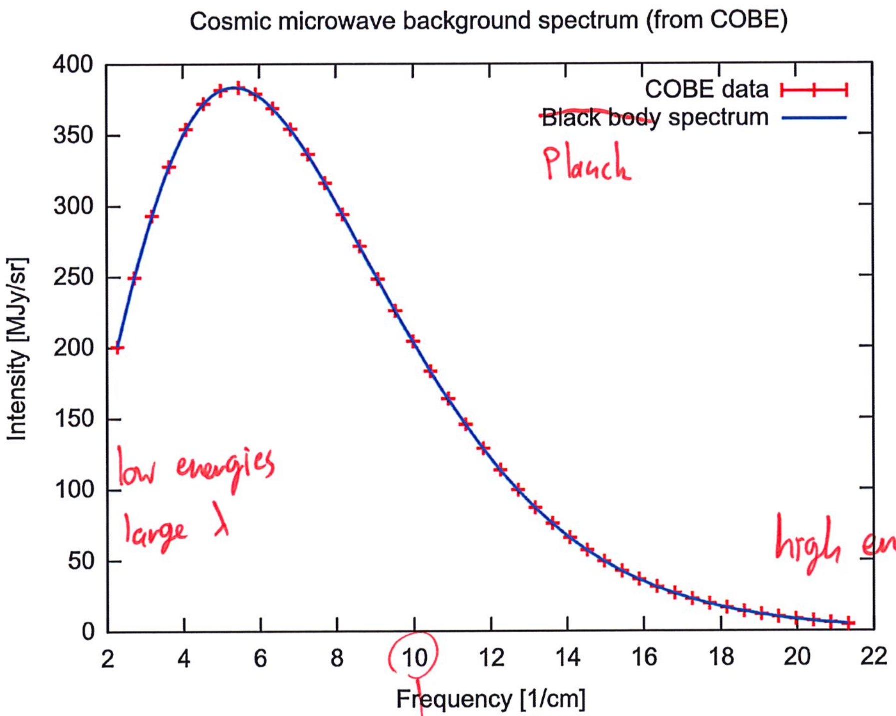
full sky subtracting sun, stars, galaxies

Spectrum of the night sky (not from the stars): The Cosmic Microwave Background temperature fluctuations from the 7-year Wilkinson Microwave Anisotropy Probe data seen over the full sky.



temperature of empty space $T \approx 2.7\,K$

red - blue : $\Delta T = 0.0002\,K$



Planck

low energies large λ

high energies, small λ

$\lambda \approx 100{,}000\,nm$

Conclusion: Non-interacting Planck distribution of photon gas good mathematical model for real physical systems