

Blackbody radiation (photons)

and

Lattice vibrations (phonons)

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References :

Baierlein, Thermal Physics, chapter 6

Salinas, chapters 10 and 11.

Landau, chapter 5 (Sec 63) and chapter 6

For phonons, the best reference is Ashcroft and Mermin,
chapters 22 and 23.

Photons in a box

A photon is completely characterized by its wave vector \mathbf{k} and its polarization $\alpha = 1, 2$ (You can take 1 for x-polarized and 2 for y-polarized. Or you can use circular polarization, it makes no difference). The dispersion relation for photons is

$$\omega_{\mathbf{k}} = c |\mathbf{k}| \quad (1)$$

It is independent of the polarization.

Now suppose you have a bunch of photons in a box. For each state (\mathbf{k}, α) we may have $n(\mathbf{k}, \alpha)$ photons. The energy of each photon is $h\nu = \hbar\omega$. Thus the total energy will be

$$E = \sum_{\mathbf{k}, \alpha} \hbar \omega_{\mathbf{k}} n(\mathbf{k}, \alpha) \quad (2)$$

The values of $n(\mathbf{k}, \alpha)$ will depend on the conditions that you set up your electromagnetic field. Nowadays people can construct experiments where the cavity (ie, the "box") has just one photon of one wave vector. We would write that as

$$n(\mathbf{k}, \alpha) = \begin{cases} 1 & \mathbf{k} = \mathbf{k}_0, \alpha = \alpha_0 \\ 0 & \text{otherwise} \end{cases}$$

of course, you can imagine building cavities with all sorts of photon configurations. But here we will be interested in thermal configurations

We are going to assume that the walls of our cavity are in thermal equilibrium at a given temperature T . Consequently, the $n(\mathbf{k}, \alpha)$ will become random variables: there will be a continuous creation and annihilation of photons due to the thermal agitation of the atoms in the wall.

What we want to ask, therefore, is what is the average photon number $\langle n(\mathbf{k}, \alpha) \rangle$? Well this is easy: this problem is mathematically analogous to the quantum harmonic oscillator.

Recall

$$E_n = \hbar \omega n \quad n = 0, 1, 2, 3, \dots$$

$$\Rightarrow Z_n = \sum_{m=0}^{\infty} e^{-\beta \hbar \omega m} = \frac{1}{1 - e^{-\beta \hbar \omega}} \quad (3)$$

$$\langle n \rangle = \frac{1}{e^{\beta \hbar \omega} - 1} \quad (4)$$

Thus, the average occupation number $\langle n(\mathbf{k}, \alpha) \rangle$ will be

$$\langle n(\mathbf{k}, \alpha) \rangle = \frac{1}{e^{\beta \hbar \omega_{\mathbf{k}}} - 1} \quad (5)$$

We may now write all thermodynamic quantities we want. For instance, the internal energy will be

$$U = \sum_{\mathbf{k}, \alpha} \hbar \omega_{\mathbf{k}} \langle n(\mathbf{k}, \alpha) \rangle = \sum_{\mathbf{k}, \alpha} \frac{\hbar \omega_{\mathbf{k}}}{e^{\beta \hbar \omega_{\mathbf{k}}} - 1} \quad (6)$$

We can also go beyond: the total number of photons will be

$$N = \sum_{k, \alpha} \langle n(k, \alpha) \rangle = \sum_{k, \alpha} \frac{1}{e^{\beta \hbar \omega_k} - 1} \quad (7)$$

The partition function will be a product of the individual partition functions

$$Z = \prod_{k, \alpha} \left[\frac{1}{1 - e^{-\beta \hbar \omega_k}} \right] \quad (8)$$

Thus, the free energy will be a sum

$$F = -k_B T \ln Z = k_B T \sum_{k, \alpha} \ln(1 - e^{-\beta \hbar \omega_k}) \quad (9)$$

If we have F , then we can compute the entropy as

$$S = \frac{U - F}{T} \quad (10)$$

and even the pressure as

$$p = - \frac{\partial F}{\partial V} \quad (11)$$

This is the radiation pressure. Yes, radiation also exerts a pressure

The density of states for electromagnetic radiation

If you look back you will see that all thermodynamic quantities have the form

$$\sum_{\mathbf{k}, \alpha} f(\omega_{\mathbf{k}})$$

where f is an arbitrary function. It is convenient to convert this into an integral:

$$\sum_{\mathbf{k}, \alpha} f(\omega_{\mathbf{k}}) \rightarrow \int_0^{\infty} d\omega g(\omega) f(\omega) \quad (12)$$

The quantity $g(\omega)$ is called the density of states (DOS). The procedure to find it is similar to the one we used when we discussed the ideal gas.

First we note that $\omega_{\mathbf{k}}$ does not depend on α (the polarization)

$$\sum_{\mathbf{k}, \alpha} f(\omega_{\mathbf{k}}) = 2 \sum_{\mathbf{k}} f(\omega_{\mathbf{k}}) \quad (13)$$

Next, we note that since the photons are in a box, the \mathbf{k} 's are quantized as

$$k_i = \frac{2\pi m_i}{L}, \quad m_i = 0, \pm 1, \pm 2, \dots \quad (14)$$

[\mathbf{k} 's are always quantized like this]. Thus $\Delta k_i = \frac{2\pi}{L}$

We use this to conveniently insert a "1";

$$2 \sum_{\mathbf{k}} f(\omega_{\mathbf{k}}) = 2 \left(\frac{L}{2\pi} \right)^3 \sum_{\mathbf{k}} \Delta k_x \Delta k_y \Delta k_z f(\omega_{\mathbf{k}})$$

This now has the form of a Riemann sum, so we may write
($V=L^3$)

$$2 \sum_{\mathbf{k}} f(\omega_{\mathbf{k}}) = 2 \frac{V}{(2\pi)^3} \int d^3k f(\omega_{\mathbf{k}})$$

Now we note that $\omega_{\mathbf{k}} = c|\mathbf{k}|$ depends only on $k = |\mathbf{k}|$. We therefore change to spherical coordinates

$$d^3k = k^2 dk d\Omega$$

The integral over $d\Omega$ gives 4π so

$$2 \sum_{\mathbf{k}} f(\omega_{\mathbf{k}}) = 2 \frac{V}{(2\pi)^3} 4\pi \int_0^{\infty} dk k^2 f(\omega_{\mathbf{k}})$$

Finally, we change the integration variable from k to $\omega = ck$. We will then have

$$k^2 dk = \left(\frac{\omega}{c} \right)^2 \frac{d\omega}{c} = \frac{\omega^2 d\omega}{c^3}$$

Thus

$$2 \sum_{\mathbf{k}} f(\omega_{\mathbf{k}}) = \frac{V}{\pi^2 c^3} \int_0^{\infty} d\omega \omega^2 f(\omega)$$

We therefore conclude that the density of states will be

$$g(\omega) = \frac{V}{\pi^2 c^3} \omega^2$$

(15)

The Planck distribution

Now that we know $g(\omega)$ we are ready to compute any k_B -sum we want. We start with the internal energy, E_T (6):

$$U = \sum_{\omega, k, \alpha} \frac{\hbar \omega_{k\alpha}}{e^{\beta \hbar \omega_{k\alpha}} - 1} = \int_0^{\infty} d\omega g(\omega) \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \quad (16)$$

or

$$U = \frac{V}{\pi^2 c^3} \int_0^{\infty} d\omega \frac{\hbar \omega^3}{e^{\beta \hbar \omega} - 1} \quad (17)$$

We will do this integral in a minute. But first I want to analyze the integrand. We may write this formula as

$$U = V \int_0^{\infty} d\omega \rho(\omega) \quad (18)$$

where

$$\rho(\omega) = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{\beta \hbar \omega} - 1} \quad (19)$$

this quantity gives an energy per unit frequency. It is the fraction of the total energy which has frequency ω . Eq. (19) is known as the Planck distribution. It was proposed by Max Planck in 1900 and marks the birth of quantum mechanics.

It is more common to make plots as a function of the wavelength λ (oops! this is not the polarization)

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

We will then have:

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

so

$$\int_0^{\infty} d\omega \rho(\omega) = -2\pi c \int_{\infty}^0 \frac{d\lambda}{\lambda^2} \rho(\omega(\lambda)) = \int_0^{\infty} \frac{2\pi c d\lambda}{\lambda^2} \rho(\omega(\lambda))$$

Thus

$$\rho(\lambda) d\lambda = \rho(\omega) d\omega$$

and

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

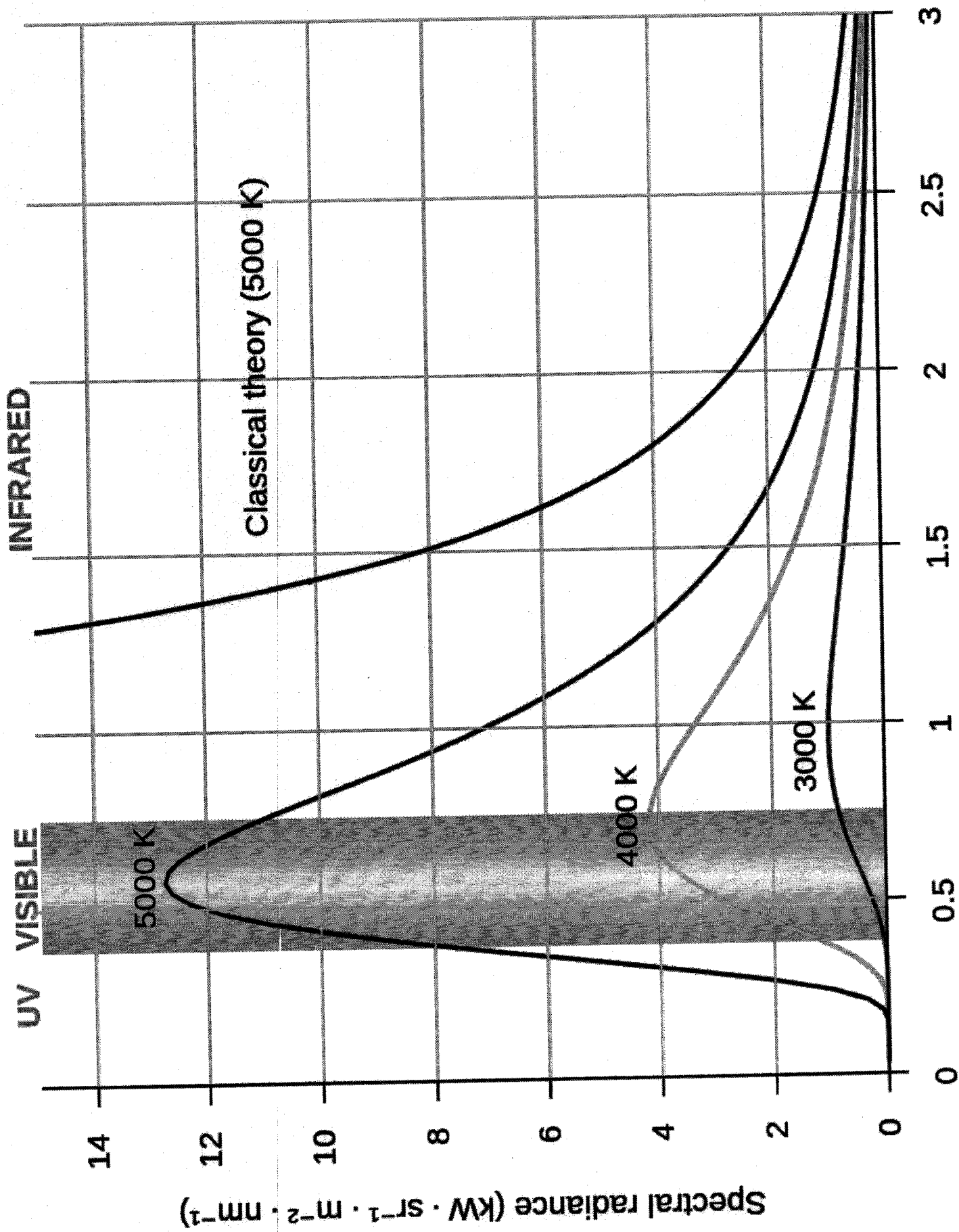
organizing a bit:

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

(20)

this is plotted in the next page for different temperatures.

Any body at $T \neq 0$ emits radiation over a continuous spectrum. We (310K) emit most around the infrared. Light bulbs get hot and start emitting a bit around the visible. The sun is very hot and emits a lot in the visible spectrum.



Source: Wikipedia

Thermodynamic quantities

Now let us compute the main thermodynamic quantities.

Internal energy

$$U = \frac{V}{\pi^2 c^3} \int_0^{\infty} d\omega \frac{\hbar \omega^3}{e^{\beta \hbar \omega} - 1} \quad x = \beta \hbar \omega \quad dx = \beta \hbar d\omega$$

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

This integral is tabled (you can use Mathematica)

$$\int_0^{\infty} dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{15} \quad (20)$$

Thus

$$U = \frac{V}{\pi^2 c^3} \frac{k_B^4 T^4}{\hbar^3} \frac{\pi^4}{15} = \frac{\pi^2 k_B^4}{15 \hbar^3 c^3} VT^4$$

For historical reasons, we introduce the Stefan-Boltzmann constant

$$\sigma = \frac{\pi^2 k_B^4}{60 \hbar^3 c^2} = 5.67 \times 10^{-8} \frac{\text{J}}{\text{m}^2 \text{s K}} \quad (21)$$

We then finally get

$$U = \frac{4\sigma}{c} VT^4 \quad (22)$$

The total energy in the radiation field scales with T^4 , which is a very sharp dependence.

Number of photons in the cavity, Eq (7)

$$N = \sum_{k, \alpha} \frac{1}{e^{\beta \hbar \omega_k} - 1} = \int_0^{\infty} d\omega g(\omega) \frac{1}{e^{\beta \hbar \omega} - 1}$$

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

$$x = \beta \hbar \omega$$

$$= \frac{V}{\pi^2 c^3} \frac{1}{(\beta \hbar)^3} \underbrace{\int_0^{\infty} dx \frac{x^2}{e^x - 1}}_{2.404}$$

$$N = \frac{2.404}{\pi^2 c^3 \hbar^3} k_B^3 V T^3$$

(23)

Plugging the numbers we get

$$N = (2.028 \times 10^7) V T^3$$

[for V in m^3 and T in K]. Thus, for $T = 300 K$ we find

$$\frac{N}{V} = 5.47 \times 10^{14} \text{ photons}/m^3 \quad (T = 300K)$$

But for $T = 6000K$

$$\frac{N}{V} = 4.38 \times 10^{18} \text{ photons}/m^3$$

The average energy per photon will be

$$\frac{U}{N} = \frac{\pi^2 k_B^4 V T^4}{15 h^3 c^3} = \frac{\pi^4}{2.404 \times 15} k_B T$$

$$\frac{2.404 k_B^3 V T^3}{\pi^2 c^3 h^3} \quad \underbrace{\quad}_{2.7}$$

thus

$$\boxed{\frac{U}{N} = 2.7 k_B T}$$

(25)

Heat capacity

$$C = \frac{\partial U}{\partial T} = \frac{16 \sigma V T^3}{c}$$

(26)

Free energy, Eq (9)

$$F = k_B T \sum_{k, \alpha} \ln(1 - e^{-\beta \hbar \omega_k}) = k_B T \int_0^{\infty} d\omega g(\omega) \ln(1 - e^{-\beta \hbar \omega})$$

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

$$x = \beta \hbar \omega$$

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

$$= \frac{V}{\pi^2 c^3} \frac{k_B^4 T^4}{h^3} \int_0^{\infty} dx x^2 \ln(1 - e^{-x})$$

we may compute this integral by parts

$$\int u dv = uv - \int v du$$

choose $dv = x^2 dx$, $u = \ln(1 - e^{-x})$. then

$$\begin{aligned} \int_0^{\infty} dx x^2 \ln(1 - e^{-x}) &= \underbrace{\frac{x^3}{3} \ln(1 - e^{-x})}_0^{\infty} - \int_0^{\infty} dx \frac{x^3}{3} \frac{(+e^{-x})}{1 - e^{-x}} \\ &= \frac{1}{3} \int_0^{\infty} dx \frac{x^3}{e^x - 1} \quad \left[\text{Eq (20')} \right] \end{aligned}$$

thus

$$F = -\frac{V}{\pi^2 c^3} \frac{k_B^4 T^4}{h^3} \frac{1}{3} \frac{\pi^4}{15}$$

$$= -\frac{\pi^2 k_B^4}{45 h^3 c^3} V T^4$$

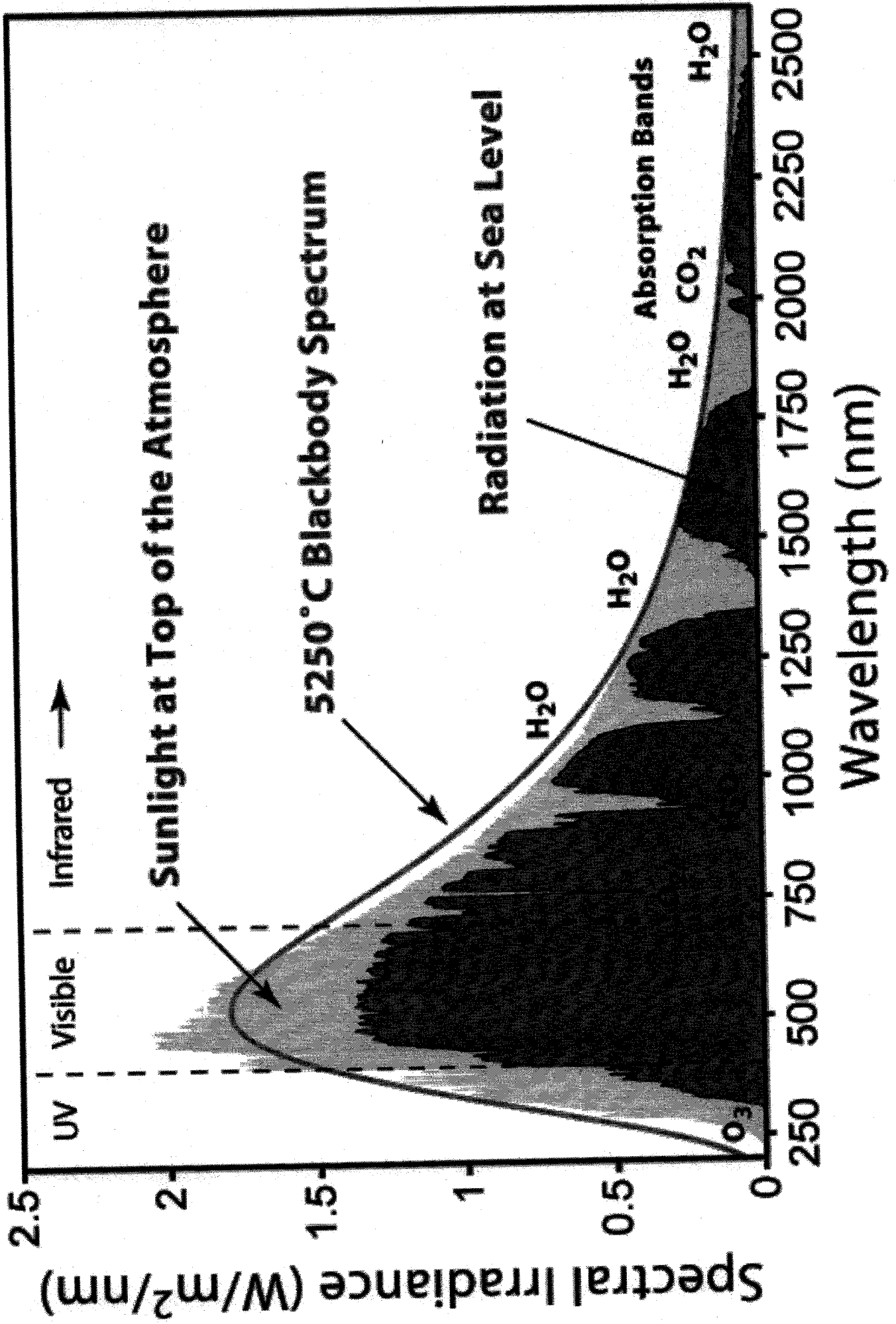
$$\frac{4\sigma}{3c}$$

$$\therefore \boxed{F = -\frac{4\sigma}{3c} V T^4} \quad (27)$$

Radiation pressure

$$\boxed{P = -\frac{\partial F}{\partial V} = \frac{4\sigma}{3c} T^4 = \frac{U}{3V}} \quad (28)$$

Solar Radiation Spectrum



Random topic: equilibrium in the state which minimizes the free energy $F = U - TS$. (19)

Sorry, I completely forgot to discuss an important interpretation of thermal states. Suppose you have a system with some probabilities P_m . You don't know what they are. They may or may not be equilibrium probabilities.

We can always define the average energy as

$$U = \sum_m E_m P_m \quad (29)$$

and the entropy as

$$S = -k_B \sum_m P_m \ln P_m \quad (30)$$

then we may also define the free energy as

$$F = U - TS = \sum_m E_m P_m + k_B T \sum_m P_m \ln P_m \quad (31)$$

This is just a definition. It is true whether or not the P_m are the Gibbs probabilities.

Now comes the cool part: the equilibrium state is exactly that state which minimizes F . So let's prove this: we minimize F by setting

$$\frac{\partial F}{\partial P_m} = 0 \quad (32)$$

we will then show that the P_m which solve these equations are the Gibbs probabilities $e^{\beta E_m} / Z$.

But there is a catch: the P_m must be normalized. This is a constrained minimization problem. To deal with that we introduce a Lagrange multiplier

$$F = \sum_m (E_m + k_B T \ln P_m) P_m + \alpha \left(1 - \sum_m P_m \right) \quad (33)$$

We then fix α so as to ensure that $\sum_m P_m = 1$.

Now we can compute $\partial F / \partial P_m$:

$$\begin{aligned} \frac{\partial F}{\partial P_m} &= \frac{\partial}{\partial P_m} \left\{ \sum_e (E_e + k_B T \ln P_e) P_e + \alpha \left(1 - \sum_e P_e \right) \right\} \\ &= \frac{\partial}{\partial P_m} \left[(E_m + k_B T \ln P_m) P_m \right] - \alpha \\ &= E_m + k_B T \ln P_m + k_B T \frac{P_m}{P_m} - \alpha \\ &= 0 \end{aligned}$$

thus we get

$$k_B T \ln P_m = -E_m + k_B T - \alpha$$

$$\ln P_m = -\beta E_m + 1 - \beta \alpha$$

$$P_m = e^{-\beta E_m} \underbrace{(e^{1 - \beta \alpha})}_{\substack{= 1 \\ Z}}$$

The constant α , or $1/Z$, must be set to ensure that $\sum_m P_m = 1$. It will then be the partition function

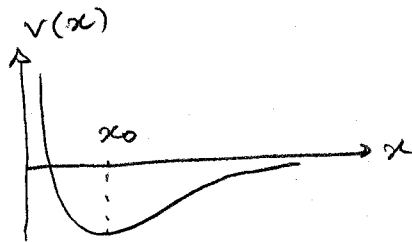
$$(34) \quad \begin{aligned} P_m &= \frac{e^{-\beta E_m}}{Z} \\ Z &= \sum_m e^{-\beta E_m} \end{aligned}$$

At $T=0$ the system tends to the ground state. So to find the state at $T=0$ we minimize the energy U .
At $T \neq 0$ we must minimize the free energy $F = U - TS$

Lattice vibrations

Now I want to discuss the vibrations of atoms in a solid. I will show you that, in many aspects, these vibrations are quite similar to electromagnetic radiation.

The potential energy of interaction between two atoms in a solid looks like this



It is usually attractive, except when the atoms get so close that their electronic clouds start repelling each other. This competition creates a minimum at a certain point x_0 . This is the equilibrium separation.

But due to thermal fluctuations the atoms will not stand still, but will vibrate around their mean equilibrium positions. Unless we are at high temperatures, these vibrations will generally be small, so we may expand $v(x)$ around their equilibrium positions:

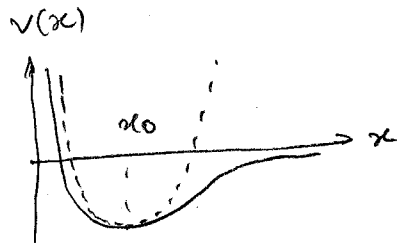
$$v(x) \approx v(x_0) + \underbrace{v'(x_0)}_{=0 \text{ because } x_0 \text{ is a minimum}} (x-x_0) + \frac{v''(x_0)}{2} (x-x_0)^2 + \dots \quad (35)$$

$\left\{ \begin{array}{l} v''(x_0) > 0 \end{array} \right.$

Let us define $v''(x_0) := g > 0$. This is a constant. It is related to the curvature of the potential at the bottom. We then get

$$v(x) \approx v(x_0) + \frac{g}{2} (x-x_0)^2 \quad (36)$$

This is the harmonic approximation: we approximate the bottom of the potential by a parabola

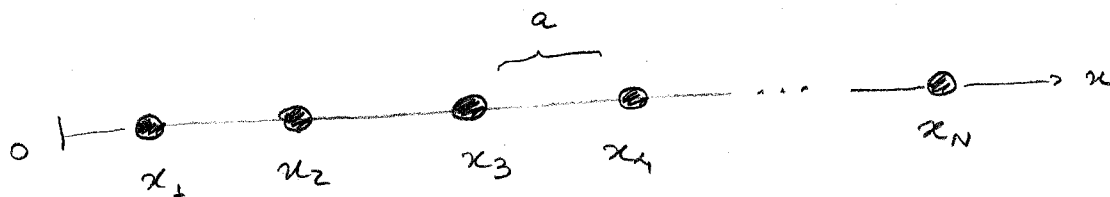


The harmonic approximation allows us to solve the problem exactly. With the full potential we would only be able to tackle the problem numerically.

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The 1D harmonic chain

Now consider the following problem:



We have a "1D crystal" of N atoms. We denote by x_n the equilibrium position of each atom. So if we define the lattice spacing a , then

$$x_n = a n \quad \begin{cases} x_1 = a \\ x_2 = 2a \\ \vdots \end{cases}$$

The x_n are fixed. They are the positions the atoms would have if they were standing still. We now let X_n be the actual position.

We assume that each atom interacts only with its two nearest neighbors. So atom n will interact with $n-1$ and $n+1$. The interaction has the form

$$V(X_n - X_{n+1}) \approx V(a) + \frac{g}{2} (X_n - X_{n+1} - a)^2$$

It is more convenient to define the relative displacement

$$q_n = X_n - x_n$$

then we may write

$$V(X_n - X_{n+1}) \approx V(a) + \frac{g}{2} (q_n - q_{n+1})^2 \quad (37)$$

The first term is just a constant potential. Energies are always defined up to a constant, so we don't have to worry about it

