STATISTICAL MECHANICS

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PART 5-6 Some special topics, Thermal Radiation, and Plank distribution

Equipartition theorem

- Let Xi be Pi or ri

$$
\begin{aligned}
< X_i \frac{\partial H}{\partial X_j} > &= -\frac{\tau}{Z}\int dP\cdots dr\ Xi(\frac{\partial}{\partial X_j}e^{-H/\tau}) \\
&= \frac{\tau}{Z}\int dP\cdots dr\ (\frac{\partial X_i}{\partial X_j}e^{-H/\tau})
\end{aligned}
$$

$$
< X_i \frac{\partial H}{\partial X_j} > \ = \ \tau\delta_{ij}
$$

- Generalized equipartition theorem

Special case:

- For every quadratic degree of freedom Xi in the partition function, with an energy constitution

$$E = AX_i^2$$

- We have

$$< E > = < AX_i^2 >= \frac{1}{2} < X_i \frac{\partial E}{\partial X_i} >= \frac{1}{2}\tau = \frac{1}{2}k_B T$$

- “one half $k_B T$ for every quadratic degree of freedom”
- Therefore ideal gas:

$$U = \frac{3}{2} N k_B T = 3N \frac{1}{2} k_B T$$

- 3N-- quadratic degree of freedom

Additive Hamiltonian

- If the Hamiltonian of a system is a sum of independent terms, the partition function is a product of independent terms, and thus the free energy is again a sum of independent terms.
- We used that for the ideal gas.
- Other example: Particle with translational, rotational, and vibrational degree of freedom

$$H = H_{trans} + H_{rot} + H_{vib}$$

$$\begin{aligned}
Z &= \int d \cdots \, e^{-(H_{trans}+H_{rot}+H_{vib})/\tau} \\
&= \int d \cdots \, e^{-H_{trans}/\tau} e^{-H_{rot}/\tau} e^{-H_{vib}/\tau} \\
&= \int d_{trans} \cdots \, e^{-H_{trans}/\tau} \int d_{rot} \cdots e^{-H_{rot}/\tau} \int d_{vib} \cdots e^{-H_{vib}/\tau} \\
&= Z_{trans} Z_{rot} Z_{vib}
\end{aligned}$$

$$F = F_{trans} + F_{rot} + F_{vib}$$

Partition function in generalized coordinates

- The integrals will contain the Jacobian for the transformation in generalized coordinates. We are not going to look into this very much. Let's just make one example.

- Dipole in electric field

Dipole in electric field

- The energy is

$$H = -\vec{D}\,\vec{\epsilon} = -D\epsilon cos\theta$$

- The rotational partition function is then given by

$$Z = \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta\; sin\theta\; e^{D\epsilon cos\theta/\tau}$$

- Explain why are different types of coordinates are useful.
- Jacobian from spherical coordinates, etc ...

$$z = cos\theta \Rightarrow dz = -sin\theta d\theta$$

(not really necessary to do the change of variable)

- Substitute

$$\begin{aligned} Z &= -\int_0^{2\pi} d\varphi \int_1^{-1} dz\, e^{D\epsilon z/\tau} \\ &= -2\pi\left[\frac{\tau}{D\epsilon}\, e^{D\epsilon z/\tau}\right]_1^{-1} \\ &= \frac{2\pi\tau}{D\epsilon}\left(e^{D\epsilon/\tau} - e^{-D\epsilon/\tau}\right) \\ &= \pi\frac{\tau}{D\epsilon} sinh\frac{D\epsilon}{\tau} \end{aligned}$$

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- Via parameter differentiation, we can now work out the average component of D in the direction of the field:

$$
\begin{aligned}
P &= \; < D\cos\theta > = \tau \frac{\partial \ln z}{\partial \epsilon} = -\frac{\partial F}{\partial E} \\
&= \tau \frac{\partial}{\partial \epsilon} \ln\left[\pi \frac{\tau}{D\epsilon} \sinh \frac{D\epsilon}{\tau}\right] \\
&= D\left(\frac{\cosh \frac{D\epsilon}{\tau}}{\sinh \frac{D\epsilon}{\tau}} - \frac{\tau}{D\epsilon}\right) = D\left(\coth \frac{D\epsilon}{\tau} - \frac{\tau}{D\epsilon}\right)
\end{aligned}
$$

Langevin function

- Then we define

$$\mathcal{L}(x) := \coth x - \frac{1}{x}$$

- Then we have:

$$P = D\mathcal{L}(\frac{D\epsilon}{\tau})$$

- For small arguments we have $\mathcal{L}(x) \approx \frac{1}{3}x$, hence for small electric fields we have

$$P \approx \frac{D^2}{3\tau}\epsilon$$

THERMAL RADIATION AND PLANK DISTRIBUTION

PLANK DISTRIBUTION FUNCTION

- The Plank distribution function is the first application of thermal Physics.
- It describes black body radiation and also thermal energy spectrum of lattice vibrations.

The energy states of quantum harmonic oscillator is given by

$$\varepsilon_s = s\hbar\omega$$

Where $\omega = 2\pi f$ is the frequency of radiation and s is zero or any positive integer.

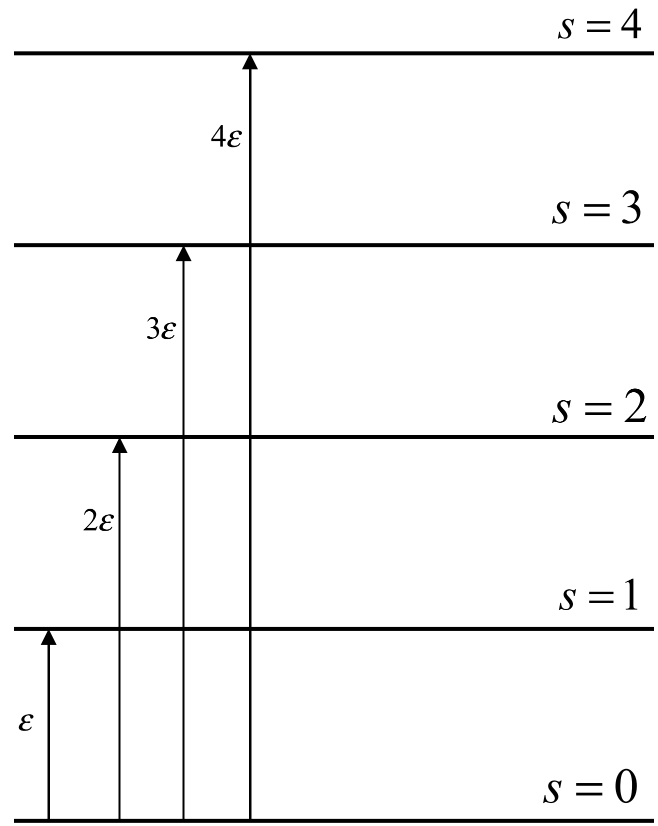
We omit the zero point energy $\frac{1}{2}\hbar\omega$.

The partition function is then given by

$$z = \sum_{s=0}^{\infty} \exp\left(-\varepsilon_s / \tau\right) = \sum_{s=0}^{\infty} \exp\left(-s\hbar\omega / \tau\right)$$

This sum is of the form $\sum x^s$

with $x = \exp(-\hbar\omega/\tau)$.



(A mode of radiation can only be exited in units of $\hbar\omega$).

Which is geometric series with x smaller than 1, thus

$$\sum x^s = 1/(1-x),$$

Which implies the partition function

$$Z = \frac{1}{1-\exp(-\hbar\omega/\tau)}.$$

Now let's calculate $\langle s \rangle$ (average excitation state).

The probability that the system is in the state s of energy $s\hbar\omega$ is given

by the Boltzmann factor:

$$P(s) = \frac{\exp(-s\hbar\omega/\tau)}{Z}$$

The thermal average value of s is

$$\langle s \rangle = \sum_{s=0}^{\infty} sP(s) = \sum_{s=0}^{\infty} \frac{s\exp(-s\hbar\omega/\tau)}{Z}$$

Chose $y \equiv \hbar\omega/\tau$,

Then we have,

$$\sum s\exp(-sy) = -\frac{d}{dy}\sum \exp(-sy)$$

$$= -\frac{d}{dy}\left(\frac{1}{1-\exp(-y)}\right) = \frac{\exp(-y)}{\left[1-\exp(-y)\right]^2}$$

Thus,

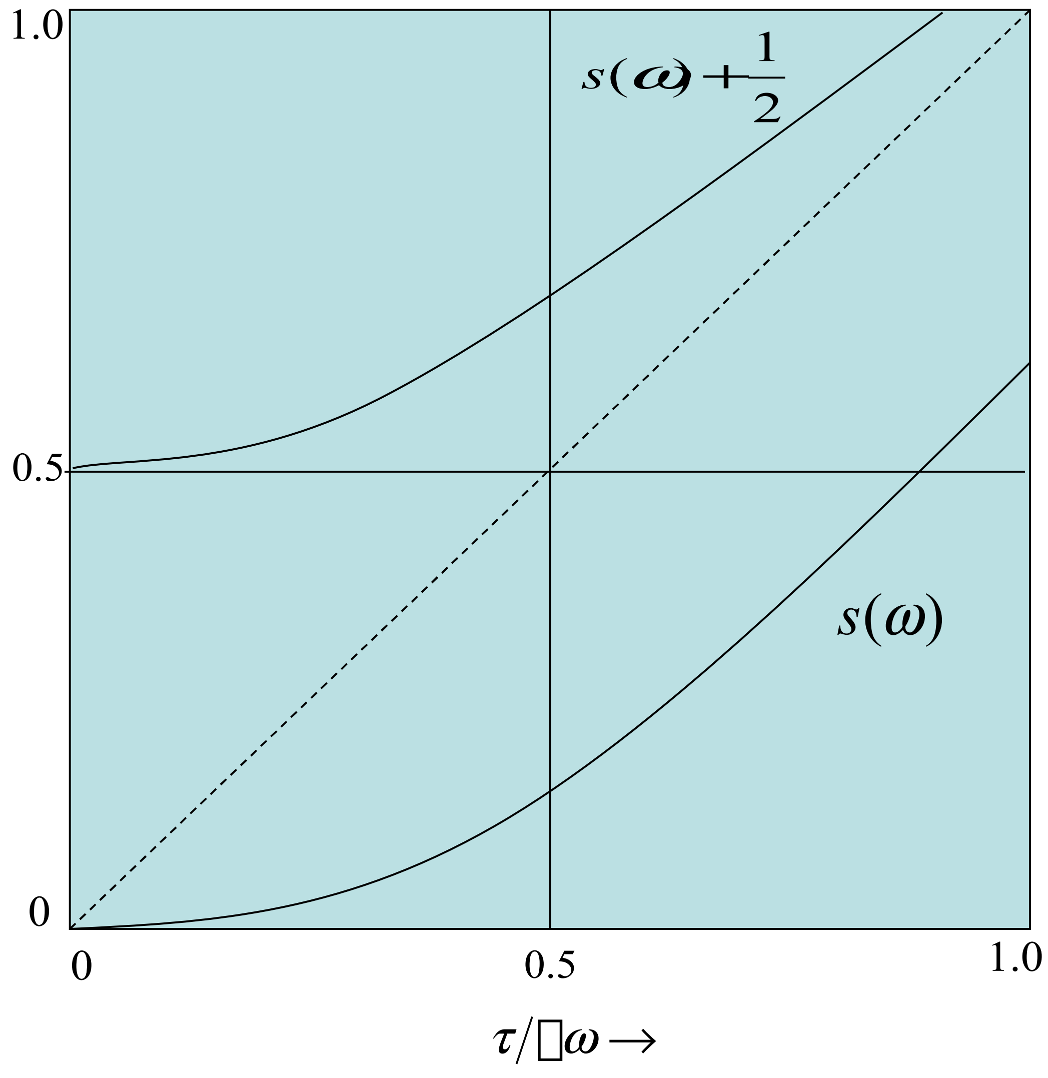
$$\langle s\rangle = \frac{\exp(-y)}{1-\exp(-y)},$$

or

$$\langle s\rangle = \frac{1}{\exp(\hbar\omega/\tau)-1}$$

This is the **Planck distribution function** for the thermal average number of photons.

Plank distribution as a function of the reduced temperature $\tau/\hbar\omega$.



PLANKS LAW AND STEFAN-BOLTZMANN LAW

- The thermal average energy in the mode is

$$\langle \varepsilon \rangle = \langle s \rangle \hbar\omega = \frac{\hbar\omega}{\exp(\hbar\omega/\tau) - 1}.$$

For high temperature limit (the classical limit): $\tau >> \hbar\omega$

Then we have the approximation $\exp(\hbar\omega) \approx 1 + \hbar\omega/\tau$

And the classical average energy is $\langle \varepsilon \rangle \approx \tau$

Now we want to find out the radiation modes confined with in a perfectly conducting cavity in the form of a cube of edge L , then there is a set of modes of the form

$$\left.\begin{aligned} E_x &= E_{x0}\sin\omega t\cos(n_x\pi x/L)\sin(n_y\pi y/L)\sin(n_z\pi z/L) \\ E_y &= E_{y0}\sin\omega t\sin(n_x\pi x/L)\cos(n_y\pi y/L)\sin(n_z\pi z/L) \\ E_z &= E_{z0}\sin\omega t\cos(n_x\pi x/L)\sin(n_y\pi y/L)\cos(n_z\pi z/L) \end{aligned}\right\} \quad \text{(i)}$$

The field must be divergence free:

$$divE = \frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} + \frac{\partial E_z}{\partial z} = 0 \quad \text{(ii)}$$

When we insert (i) into (ii)

$$E_{x0}n_x + E_{y0}n_y + E_{z0}n_z = \mathrm{E}_0.\mathrm{n}$$

Which implies that the electromagnetic field in the cavity is transversely polarized.

The modes have to satisfy the wave equation

$$c^2\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)E_z = \frac{\partial^2 E_z}{\partial t^2}$$

$$\Rightarrow c^2\pi^2\left(n_x^2 + n_y^2 + n_z^2\right) = \omega^2 L^2$$

Let $n^2 = n_x^2 + n_y^2 + n_z^2$

$$\Rightarrow \omega_n = {n\pi c}/{L}.$$

The frequencies have to satisfy certain conditions.

The total energy in the cavity is

$$U = \underbrace{\sum_n}_{\substack{\text{sum over triplet of}\\ \text{positive integers}}} \langle \varepsilon_n \rangle = \sum_n \frac{\hbar\omega_n}{\exp(\hbar\omega_n/\tau)-1}$$

Replace sum by integral over $dn_x dn_y dn_z$

$$\Rightarrow \sum_n (\ldots) = \underbrace{\left(\tfrac{1}{2}\right)^3}_{\substack{\text{because of only}\\ \text{positive space of}\\ \text{octant}}} \int_0^\infty 4\pi n^2 dn(\ldots) \bullet \underbrace{2}_{\substack{\text{for two independent}\\ \text{states of polarization}}}$$

$$\Rightarrow U = \pi \int_0^\infty dn\, n^2 \frac{\hbar\omega_n}{\exp(\hbar\omega_n/\tau)-1}$$

$$= \left(\pi^2 \hbar c \big/ L\right) \int_0^\infty dn\, n^3 \, \frac{1}{\exp(\hbar c n \pi / L\tau) - 1} \qquad (*)$$

Let $x = \pi \hbar c n \big/ L\tau$,

$$\Rightarrow \mathrm{U} = \left(\pi^2 \hbar c \big/ L\right) \left(\tau L \big/ \pi \hbar c\right)^4 \underbrace{\int_0^\infty dx \, \frac{x^3}{\exp x - 1}}_{\pi^4/15}$$

$$\Rightarrow \qquad \frac{U}{V} = \frac{\pi^2}{15 h^3 c^3} \tau^4 \qquad (**)$$

This is known as **Stefan-Boltzmann law of radiation**.

Let us write $(*)$ with the help of

u_w : energy per unit volume per unit frequency range $(\omega_n = n\pi c / L)$

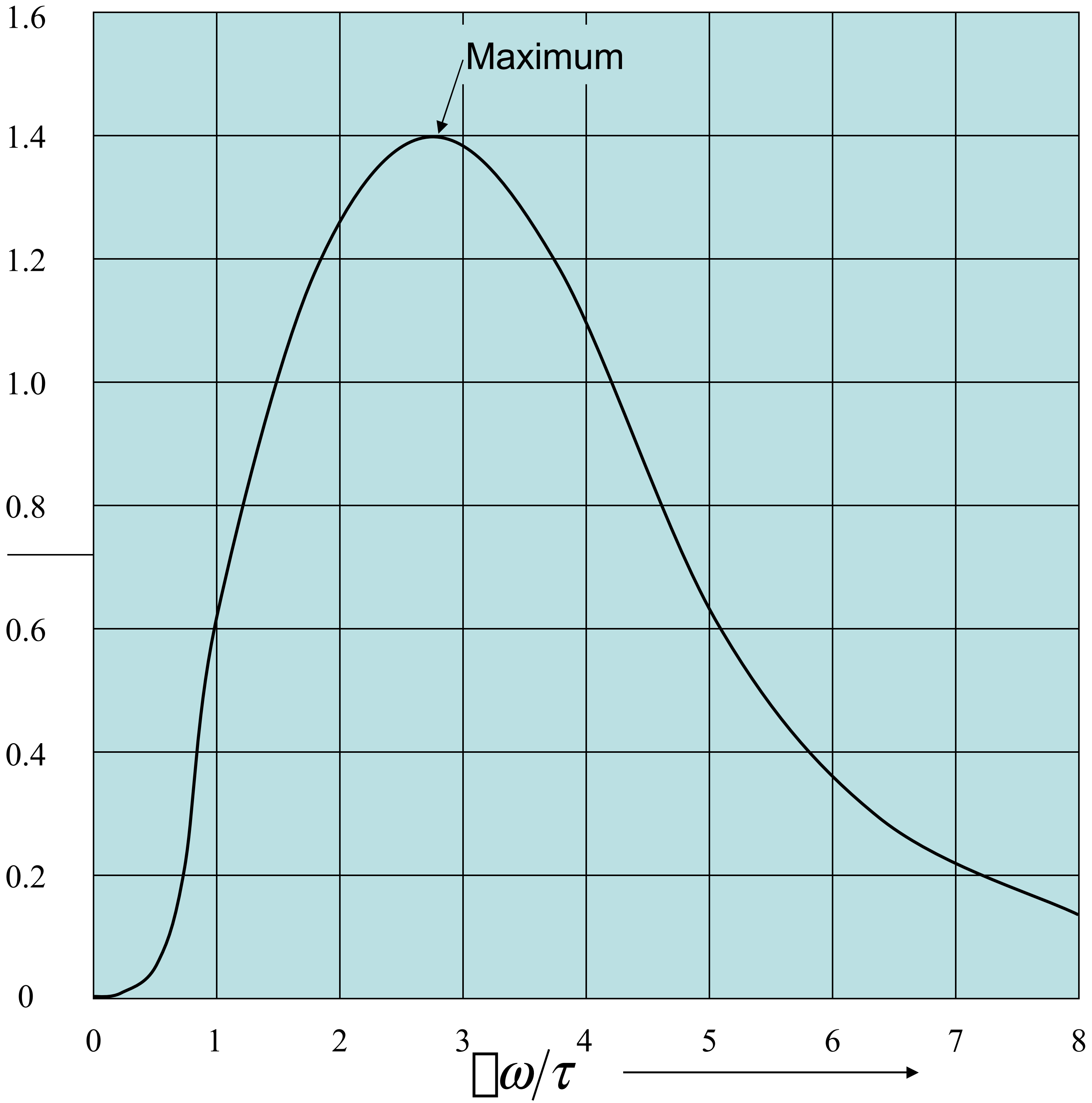
$$\frac{U}{V} = \int dw\, u_w = \left(\frac{\pi^2 \hbar c}{L} \right) \frac{1}{L^3} \int_0^\infty dw\, w^3 \frac{1}{\exp(\hbar\omega/\tau) - 1} . \left(\frac{L}{\pi c} \right)^4$$

$$= \frac{\hbar}{\pi^2 c^3} \int_0^\infty dw \frac{w^3}{\exp(\hbar\omega/\tau) - 1}$$

$$\Rightarrow \qquad u_w = \frac{\hbar}{\pi^2 c^3} \frac{w^3}{\exp(\hbar\omega/\tau) - 1}$$

This result is known as **Planck radiation law**.

Plot of $x^3/(e^x - 1)$ with $x = \omega\hbar/\tau$. This function is involved in the Plank radiation law for the spectral density u_ω. The temperature of a black body may be found from the frequency ω_{max} at which the radiant energy density is a maximum, per unit frequency range.



The entropy of the thermal photons at constant volume is

$$d\sigma = {dU}/{\tau},$$

Then from

$$d\sigma = \frac{4\pi^2 V}{15\hbar^3 c^3}\tau^2\, d\tau$$

And on integration

$$\sigma(\tau) = \left(\frac{4\pi^2 V}{45}\right)\left(\frac{\tau}{\hbar c}\right)^3.$$