12: Bose Systems

First goal: $U \overset{?}{=} \# \, PV$

- relationship this simple?
- if yes, what is #?

12.1: Photons

Photons: $\underbrace{\text{massless bosons}}_{\substack{\text{move with} \\ \text{velocity } c \\ (c\text{ : speed of light})}}$ of spin $\hbar$

result on p. 278

Photons are transverse excitations of the electromagnetic field polarized perpendicular to the direction of propagation

$$\underbrace{\vec{\varepsilon} \cdot \vec{k} = 0}$$

$\vec{k}$ wave vector

$\vec{\varepsilon}$ polarization vector

$\vec{E}$ electric field vector

follows from transversality of the electric field:

$$\vec{\nabla} \cdot \vec{E} = 0$$

$$\vec{E} \propto \hat{\varepsilon}$$

$\hat{\varepsilon}$ determines direction of electric field

$\vec{k}$ determines direction of propagation

Two polarization vectors : The two polarizations of circularly polarized light are clockwise and counter-clockwise

A photon in a definite spin state corresponds to a plane electromagnetic wave that is either right- or left-circularly polarized.

Alternatively, superimpose two photons with definite spins and obtain a photon state that is not an eigenstate of the spin operator.

In either case, we have two fields to quantize:

$$\hat{\mathcal{H}} = \sum_{\vec{k},\varepsilon} \hbar c k \underbrace{\hat{a}^{+}_{\vec{k},\varepsilon} \hat{a}_{\vec{k},\varepsilon}}$$

this is the modes' number operator with eigenvalue $n_{\vec{k},\varepsilon} = 0, 1, 2, \ldots$

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

$ck = \omega$

ε takes two different values corresponding to the two different polarizations

energy $\hbar\omega$

$$\Rightarrow \text{energy} = \sum_{\vec{k},\varepsilon} \hbar c k \, n_{\vec{k},\varepsilon}$$

Before we calculate the partition function, let us think a bit about relativistic quantum mechanics.

$\rightsquigarrow$ $v = c$ $\Rightarrow$ we are dealing with relativistic framework

In relativistic q.m., particles can be created and destroyed and the number of particles can change.

In general, the chemical potentials of the different particle species is constrained by conservation laws, such as electric charge conservation. $\rightsquigarrow$ e.g., e^+ and e^- creation as pair.

However: If particle production / destruction not constrained by conservation law, then the chemical potential is zero.

Photon number is not constrained a priori in photon gas at thermal equilibrium.

$\Rightarrow$ N should be viewed as an

internal variable to be determined by minimizing the Helmholtz free energy:

$$\underbrace{\frac{\partial}{\partial N} A(N,V,T)\Big|_{V,T}}_{\mu \text{ (by def.)}} = 0$$

$$\Rightarrow \boxed{\mu = 0}$$

So: $\mu = 0 \Rightarrow$ no Lagrange multiplier.

neither $n_{\vec{k},\varepsilon}$ nor $\sum_{\vec{k},\varepsilon} n_{\vec{k},\varepsilon}$ conserved.

energy $E\{n_{\vec{k},\varepsilon}\}$

$$\Rightarrow Q = \sum_{\{n_{\vec{k},\varepsilon}\}} e^{-\beta E\{n_{\vec{k},\varepsilon}\}}$$

$\uparrow$

no restriction

$$\Rightarrow \quad Q = \prod_{\vec{k},\varepsilon} \left(1 - e^{-\beta \hbar c k}\right)^{-1}$$

Let $Q_1(\hbar c k)$

$$= \sum_{n=0}^{\infty} e^{-\beta \hbar c k n}$$

$$= \left(1 - e^{-\beta \hbar c k}\right)^{-1}$$

$$\Rightarrow \quad \log Q = -\sum_{\vec{k},\varepsilon} \log\left(1 - e^{-\beta \hbar c k}\right)$$

summing over ε

$$= -2 \sum_{\vec{k}} \log\left(1 - e^{-\beta \hbar c k}\right)$$

Average occupation number of photons with momentum $\vec{k}$, regardless of polarization, is

$$\langle n_{\vec{k}} \rangle = -\frac{1}{\beta} \frac{\partial}{\partial(\hbar c k)} \log Q$$

$$= \frac{2}{e^{\beta \hbar \omega} - 1} = \frac{2}{e^{\beta \hbar c k} - 1}$$

Recall $Q = e^{-\beta A}$ and $A - U - T\frac{\partial A}{\partial T} = 0$

$$\Rightarrow \quad U = -\frac{\partial}{\partial \beta} \log Q$$

also: $P = -\left(\frac{\partial A}{\partial V}\right)_T \rightsquigarrow P = \frac{1}{\beta}\frac{\partial}{\partial V}\log Q$

Thus: $$U = -\frac{\partial}{\partial\beta}\log Q = \sum_{\vec{k}} \hbar c k \langle n_{\vec{k}} \rangle \quad (*)$$

$$P = \frac{1}{\beta}\frac{\partial}{\partial V}\log Q = \frac{1}{3V}\sum_{\vec{k}} \hbar c k \langle n_{\vec{k}}\rangle \quad (**)$$

using
$$\vec{k} = \frac{2\pi \vec{n}}{L}$$

$$\Rightarrow k = 2\pi |\vec{n}| V^{-1/3}$$

$$\Rightarrow \log Q = -2\sum_{\vec{n}} \log\left(1 - e^{-\beta\hbar c 2\pi|\vec{n}|V^{-\frac{1}{3}}}\right)$$

Comparing (*), (**)
$$\Rightarrow \boxed{PV = \frac{1}{3}U}$$ E-o-S of photon gas (obtained w/o ever performing the sum)

recall, for non-relativistic gas: $PV = \frac{2}{3}U$

To obtain an explicit result for the internal energy U, we need to evaluate the sum over $\vec{k}$.

$$U = 2 \sum_{\vec{k}} \frac{\hbar c k}{e^{\beta \hbar c k} - 1}$$

$$= 2 \int_0^\infty D(\varepsilon) \frac{\varepsilon}{e^{\beta\varepsilon} - 1} \, d\varepsilon$$

we are now working in a box

note: ε is energy here, not polarization

$D(\varepsilon)$: density of states

$$k_x, k_y, k_z = \frac{2\pi n_x, n_y, n_z}{L}$$

$$\sum_{\vec{k}} \rightsquigarrow \frac{1}{\left(\frac{2\pi}{L}\right)^3} \int \ldots d^3k \rightsquigarrow V \frac{1}{(2\pi)^3} 4\pi \int \ldots k^2 dk$$

assuming integrand depends on k and not $\vec{k}$

now: $\hbar c k = \varepsilon \Rightarrow k = \frac{1}{\hbar c} \varepsilon$

$$k^2 dk = \left(\frac{1}{\hbar c}\right)^3 \varepsilon^2 d\varepsilon$$

So: $\sum_{\vec{k}} \rightsquigarrow V \frac{1}{(2\pi)^3} 4\pi \left(\frac{1}{\hbar c}\right)^3 \int \dots \varepsilon^2 \, d\varepsilon$

$$\mathcal{D}(\varepsilon) = \frac{4\pi V}{(2\pi\hbar c)^3}\, \varepsilon^2$$

$$\Rightarrow U = 2V \frac{4\pi}{(2\pi\hbar c)^3} \underbrace{\int_0^\infty \frac{\varepsilon^3}{e^{\beta\varepsilon} - 1}\, d\varepsilon}_{\frac{\pi^4}{15\beta^4}}$$

$$\rightarrow \boxed{\frac{U}{V} = \frac{\pi^2}{15} \frac{(kT)^4}{(\hbar c)^3} \quad \propto T^4 \quad \text{(Stefan's law)}}$$

Specific heat per unit volume.

$$c_v = \frac{4\pi^2 k^4 T^3}{15(\hbar c)^3}$$

$$c_v = \frac{\partial (U/V)}{\partial T}$$

$\rightsquigarrow$ not bounded as $T \to \infty$ because the number of photons in the cavity is not bounded

If there is a small opening in the walls of the cavity, the photons will effuse through it. Net rate of flow of radiation per unit area of opening $= \frac{1}{4}\frac{U}{V} c = \sigma T^4$, where $\sigma = \frac{\pi^2 k^4}{60 \hbar^3 c^2}$.

Look at internal energy per volume again:

$$\frac{U}{V} \underset{\mathcal{E}=\hbar k c}{=} \int_0^\infty \frac{1}{\pi^2 \hbar^3 c^3} \frac{(\hbar c k)^3}{e^{\beta \hbar c k}-1}\, d(\hbar c k)$$

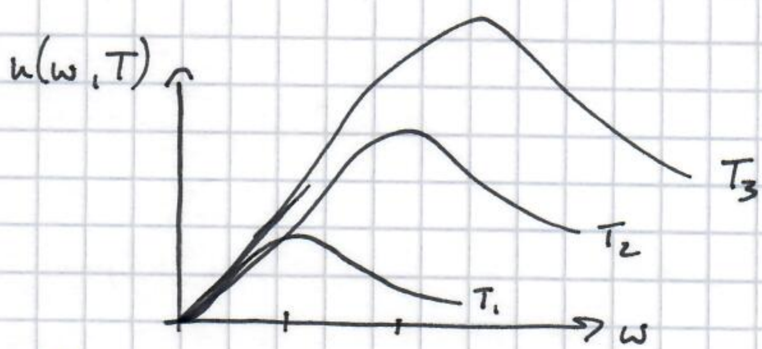
$$\underset{\omega = ck}{=} \int_0^\infty \underbrace{\frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta \hbar \omega}-1}}_{u(\omega, T)}\, d\omega$$

integrand:

$$\sim \frac{x^3}{e^x - 1} dx$$

$$x = \frac{\hbar \omega}{kT}$$

$T_3 > T_2 > T_1$



spectral distribution of energy in the black body radiation

$$\omega_{max} = 2.821 \frac{kT}{\hbar}$$

Wien's displacement law

The sun is a nearly perfect "black body".

Black body: absorbs all radiation that's incident upon it.

12.2: Phonons in solids

Phonons: quanta of sound waves in a macroscopic body

Let us consider a solid consisting of N unit cells (for simplicity, think of 1 atom per unit cell).

Each atom is represented by harmonic oscillator (this is a low-energy theory).

$\rightsquigarrow$ $\underbrace{\text{normal modes}}_{\text{this is what we did in classical mechanics}}$ that describe lattice oscillation

In quantum theory, the normal modes give rise to quanta called phonons.

Crystal lattice near ground state is specified by enumerating all the phonons present.

At low T: solid $\widehat{=}$ volume containing gas of non-interacting phonons

Sound wave $\vec{\varepsilon}\, e^{i(\vec{k}\cdot\vec{r}-\omega t)}$

$|\vec{k}| = \frac{\omega}{c}$ $\rightsquigarrow$ $\underbrace{c}$ $\hat{=}$ velocity of sound

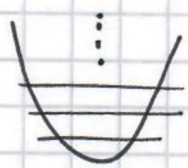
assume: c independent of $\vec{\varepsilon}$

(not really true)

$\vec{\varepsilon}$: three directions → one longitudinal mode of compression wave

→ two transverse modes of shear wave

harmonic oscillator $\rightsquigarrow$ any number of quanta



phonons obey Bose statistics;

no conservation of their total number

N atoms → $3N$ normal modes

$\omega_1, \omega_2, \ldots, \omega_{3N}$ characteristic frequencies

Einstein: N_E distinct normal modes, all with frequency ω_E
(applies to optical phonons)

internal oscillation of each cell as present in NaCl

Debye: not all frequencies are equal
(applies to acoustical phonons)

↳ one longitudinal and two transverse

Let's start with Einstein theory:

N_E distinct modes with common frequency ω_E

$$\Rightarrow Q = \left(\frac{1}{1-e^{-\beta\hbar\omega_E}}\right)^{N_E}$$

same calculation as in case of photons

$$\Rightarrow U = N_E\,\hbar\omega_E\,\frac{1}{e^{\beta\hbar\omega_E}-1}$$

specific heat:

$$C_V(T) = k N_E \left(\frac{x(T)}{\sinh(x(T))} \right)^2$$

$$C_V(T) = \left(\frac{\partial U}{\partial T} \right)_V$$

where $x(T) = \frac{\hbar \omega_E}{2kT}$

high T : $\propto k$ per oscillator

low T : $\underbrace{\propto \exp\left(- \hbar\omega_E / 2kT\right)}_{\text{too abrupt to explain measured behavior (in general)}}$

Let's move on to Debye's theory:

$$k = \frac{\omega}{c}$$

Calculate:

$$\underbrace{f(\omega)\, d\omega}_{\substack{\#\text{ of normal modes} \\ \text{with frequency betw.} \\ \omega \text{ and } \omega + d\omega}} = 3 \frac{1}{\left(\frac{2\pi}{L}\right)^3} 4\pi k^2 \, dk$$

3 possible polarizations

Maximum frequency ω_m determined by requirement

$$\int_0^{\omega_m} f(\omega)\, d\omega = 3N$$

$$\Rightarrow \omega_m = c \left(\frac{6\pi^2}{v} \right)^{1/3} \qquad \text{where } v = V/N$$

$$\lambda_m = \frac{2\pi}{k_m} = \frac{2\pi c}{\omega_m} = \underbrace{\left(\frac{4}{3} \pi v \right)^{1/3}}$$

this is of the order of the inter-particle distance

→ makes sense:

if wave length shorter than λ_m, it becomes meaningless

or: Debye sphere ≈ same volume as Brillouin zone

$$\Rightarrow E\{n_i\} = \sum_{i=1}^{3N} n_i \hbar \omega_i \quad \leftarrow \text{overall energy shift neglected}$$

$$\Rightarrow \log Q = -\sum_{i=1}^{3N} \log\left(1 - e^{-\beta\hbar\omega_i}\right)$$

$$\langle n_i \rangle = \frac{1}{e^{\beta\hbar\omega_i} - 1}$$

$$U = \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i} - 1}$$

$$\frac{U}{N} = 3kT \; \mathcal{D}\left(T_D/T\right)$$

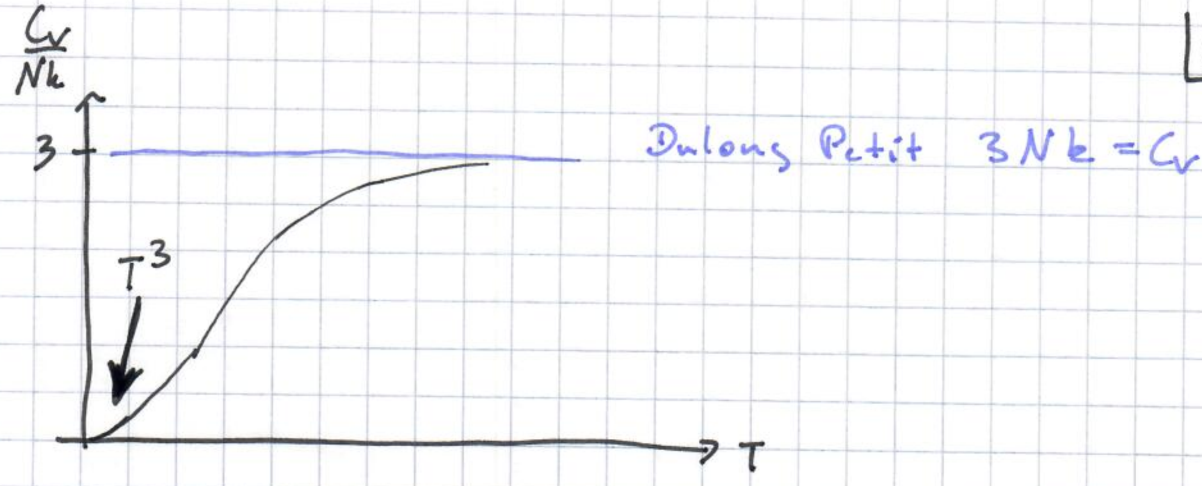
$V \to \infty$
limit
(sum $\to$ integral)

where $kT_D = \hbar\omega_m = \hbar c \left(\frac{6\pi^2}{v}\right)^{1/3}$

$$\mathcal{D}(x) = \frac{3}{x^3}\int_0^x \frac{t^3}{e^t - 1}\, dt$$

$$\frac{C_V}{Nk} = 3\mathcal{D}\left(T_D/T\right) + 3T\frac{d\mathcal{D}\left(T_D/T\right)}{dT}$$

$$= 3\left[4\mathcal{D}(\lambda) - \frac{3\lambda}{e^\lambda - 1}\right]$$



$T_D \sim 200\,K$ for many solids

at very large T: model breaks down since the lattice melts

melting can be thought of as being introduced by anharmonic forces

↳ or said differently: phonons do, in fact, interact and the interactions get larger at higher temperature