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Blackbody Radiation (cont.)

Frequency dependence of the density of energy:

$$u(\omega)\,d\omega = \frac{\hbar\omega^3\,d\omega}{\pi^2 c^3 (e^{\beta\hbar\omega}-1)} = \frac{\hbar\, x^3 (kT)^3}{\hbar^3 \pi^2 c^3}\frac{dx\,kT}{\hbar\,(e^x-1)} =$$

$$x = \frac{\hbar\omega}{kT} \Rightarrow dx = \frac{\hbar}{kT}\,d\omega$$

$$= \frac{x^3 (kT)^4\,dx}{c^3\hbar^3\pi^2(e^x-1)} = \frac{(kT)^4}{c^3\pi^2\hbar^3}\,\tilde{u}(x)\,dx \qquad (2)$$

$$\tilde{u}(x)\,dx = \frac{x^3}{e^x-1}\,dx \qquad (1)$$

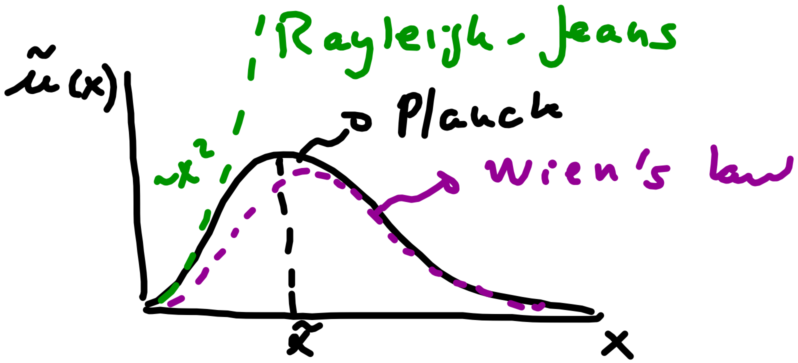
If $x \ll 1 \Rightarrow \hbar\omega \ll kT$ (low frequency)

Then

$$\tilde{u}(x) \sim \frac{x^3}{1-x-1} = x^2$$ Rayleigh-Jeans classical behavior.

If $x \to \infty \Rightarrow \hbar\omega \gg kT$

$$\tilde{u}(x) \sim x^3 e^{-x}$$ Wien's law



No ultraviolet catastrophe.

$\tilde{x} = 2.8214$

$$\int_0^\infty \tilde{u}(x)\,dx = \frac{\pi^4}{15} \approx 6.49$$

$$\int_0^\infty x^3 e^{-x}\,dx = 6 \quad \text{(Wien's law)}$$

$$\int_0^\infty x^2\,dx \longrightarrow \infty \quad \text{catastrophe.}$$

Now let's calculate U/V.

$$\frac{U}{V} = \int_0^\infty u(\omega)\, d\omega \overset{2}{=} \frac{(kT)^4}{\pi^2 c^3 \hbar^3} \underbrace{\int_0^\infty \frac{x^3\, dx}{e^x - 1}}_{\pi^4/15} =$$

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

$\frac{U}{V} \propto T^4$ Stephan-Boltzmann's law

T dependence of radiation flow:

photons will come out through effusion:

$$R = \frac{1}{4} n \langle u \rangle \longrightarrow \frac{1}{4}\frac{U}{V} c = \frac{\pi^2 k^4}{60 \hbar^3 c^2} T^4 = \sigma T^4$$

③

replace by $\frac{U}{V}$ because we care about the rate of energy that is being effused.

c (speed of the photons)

Stephan's constant.

Since $\mu = 0$ for photons it means that

$z = 1$ then

$$\ln \mathcal{Z}(V,T) = \frac{PV}{kT} = -\sum_{\varepsilon} \ln\left(1 - e^{-\varepsilon/kT}\right) \longrightarrow$$

$$\xrightarrow[\sum \to \int]{} -\int a(\varepsilon) \ln\left(1 - e^{-\varepsilon/kT}\right) d\varepsilon$$

with $a(\varepsilon) = \dfrac{2V4\pi p^2 dp}{h^3} = \dfrac{2V4\pi}{ch^3} \varepsilon^2/c^2 \, d\varepsilon =$

$$= \frac{8\pi V \varepsilon^2 d\varepsilon}{c^3 h^3} \quad (4)$$

$\varepsilon = \hbar\omega = \hbar ck = pc$

Then

$$\ln Z(V,T) \overset{④}{=} -\int_0^\infty \frac{8\pi V}{c^3h^3} \underbrace{\varepsilon^2}_{u'} \underbrace{\ln\left(1-e^{-\varepsilon/kT}\right)}_{v} d\varepsilon =$$

$$= -\frac{8\pi V}{c^3h^3}\left[\cancel{\frac{\varepsilon^3}{3}\ln\left(1-e^{-\varepsilon/kT}\right)\Big|_0^\infty} - \right.$$

$$\left. - \frac{1}{3kT}\int_0^\infty \frac{\varepsilon^3 e^{-\varepsilon/kT}}{1-e^{-\varepsilon/kT}} d\varepsilon \right] = \frac{8\pi V}{3c^3h^3kT}\int_0^\infty \frac{\varepsilon^3 \, d\varepsilon}{e^{\varepsilon/kT}-1} =$$

$$= \frac{PV}{kT} \qquad ⑤$$

From (5):

$\varepsilon / kT = x \qquad d\varepsilon = kT\,dx$

$$PV = \frac{8\pi V}{3c^3h^3}\int_0^\infty \frac{\varepsilon^3\, d\varepsilon}{e^{\varepsilon/kT}-1} = \frac{8\pi V (kT)^5}{3c^3h^3 kT}\underbrace{\int_0^\infty \frac{x^3\,dx}{e^x-1}}_{\pi^4/15} =$$

$$= \frac{8\pi^5 V (kT)^4}{45 c^3 h^3} = \frac{1}{3}\left[\frac{\pi^2 V (kT)^4}{15 c^3 h^3}\right] \overset{(3)}{=}$$

$$= \frac{1}{3} U$$

$$\therefore \quad P = \frac{1}{3}\frac{U}{V}$$

$$\boxed{F} = E - TS = \cancel{TS} - PV + \underset{=0}{\cancel{\mu}} N - \cancel{TS} = -PV$$

$$= \boxed{-\frac{U}{3}}$$

③ $U \propto VT^4$

$$S = \frac{U - F}{T} = \frac{U + \frac{U}{3}}{T} = \frac{4U}{3T} \propto VT^3$$

$$S = \gamma V T^3$$

$$c_V = T \left.\frac{\partial S}{\partial T}\right|_V = T \gamma \left.\frac{\partial V T^3}{\partial T}\right|_V = T \gamma 3 V T^2$$

$$= 3 \gamma V T^3 = 3S$$

Then if $VT^3 = \text{constant} \Rightarrow dS = 0$

adiabatic transformation.

Since $P \propto T^4 \Rightarrow T \propto P^{1/4}$

$\therefore VT^3 \propto VP^{3/4}$ or $V^{4/3} P = \text{constant}$

also $\Rightarrow \Delta S = 0$

adiabatic.

Average number of photons in the cavity:

$$\bar{N} = \int_0^\infty \frac{g(\omega)\,d\omega}{e^{\hbar\omega/kT}-1} = \int_0^\infty \frac{V\omega^2\,d\omega}{\pi^2 c^3 \left(e^{\hbar\omega/kT}-1\right)} =$$

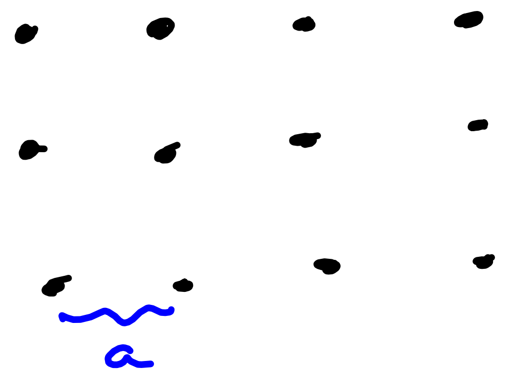
$$= \frac{V}{\pi^2 c^3}\int_0^\infty \frac{\omega^2\,d\omega}{e^{\hbar\omega/kT}-1} = \frac{V\,2\,\zeta(3)\,(kT)^3}{\pi^2\hbar^3 c^3} \propto VT^3$$

Eq. 14b App. E : $2\,\zeta(3) \simeq 2.4$

$\hbar\omega/kT = x$

$d\omega = \frac{kT}{\hbar}dx$ and $\int_0^\infty \frac{x^2\,dx}{e^x-1}$

Lattice vibrations in solids: phonons.



Solids are formed by a regular array of atoms that can vibrate about their equilibrium positions.

a: lattice constant.

The N atoms that form the solid are located at $(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_N)$.

The solid's energy ~~is~~ minimized when the atoms are at $(\bar{x}_1^{(0)}, \ldots, \bar{x}_N^{(0)})$ (equilibrium position). Let $(\bar{x}_i - \bar{x}_i^{(0)}) = \bar{u}_i$: atomic displacement

Then,

$$K = \frac{1}{2} m \sum_{i=1}^{3N} \dot{x}_i^2 = \frac{1}{2} m \sum_{i=1}^{3N} \dot{u}_i^2$$

kinetic energy

$$\Phi \equiv \Phi(\{x_i\}) = \Phi(\{\bar{x}_i^{(0)}\}) + \sum_{i=1}^{3N} \underbrace{\frac{\partial \Phi}{\partial x_i}\Big|_{x_i = x_i^{(0)}}}_{=0} (x_i - x_i^{(0)})$$

potential

$$+ \frac{1}{2} \sum_{i,j} \frac{\partial^2 \Phi}{\partial x_i \partial x_j}\Big|_{\{x_i = x_i^{(0)}\}} (x_i - x_i^{(0)})(x_j - x_j^{(0)}) + \ldots$$

$$H = \phi_0 + \left\{ \sum_i \frac{1}{2} m \dot{u}_i^2 + \sum_{i,j} \alpha_{ij} u_i u_j \right\}$$

$$\alpha_{ij} = \frac{1}{2} \frac{\partial^2 \phi}{\partial x_i \partial x_j} \Big|_{\{x_i = x_i^{(0)}\}}$$

we assume $x_i - x_i^{(0)} = u_i$ small

Notice that α_{ij} form a matrix. We can make a change of basis so that α_{ij} becomes diagonal. The eigenvectors will be linear combinations of the atomic displacement and are called "normal modes". The eigenvalues

ω_s are the normal mode frequencies.

$$q_i = \sum_{j=1}^{3N} r_j u_j$$

Now

$$H' = \phi_0 + \sum_{i=1}^{3N} \frac{1}{2} m \left(\dot{q}_i^2 + \omega_i^2 q_i^2 \right)$$

ω_i $(i = 1, 2, \ldots 3N)$ frequencies of the normal modes.

The problem has be transformed into studying the behavior of 3N non-interacting 1D harmonic oscillators.

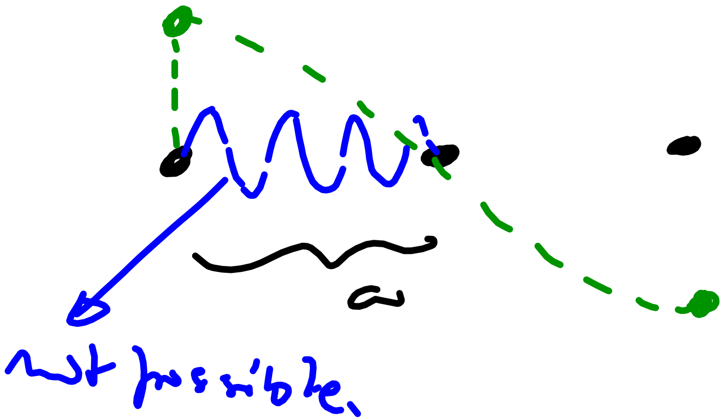
Classically: distortions of the lattice $\Rightarrow$ sound waves.

Q.M: we will call the "particles" populating the harmonic oscillators levels "phonons".

Notice: now there are 3N oscillators which means that ω_s cannot go to infinity as for photons where the number of oscillators was not determined.

But $\mu = 0$ as for photons because the number of phonons, i.e. how many particles populate each oscillator is not defined.

Phonons behave like photons at low T but when going to high T and higher frequencies are populated the behavior is different because there is a cut-off.



$\lambda = 2a$ is the smallest wave length.

Now

$$E\{n_i\} = \Phi_0 + \sum_i \left(n_i + \tfrac{1}{2}\right)\hbar\omega_i$$

occupation number of the phonon levels or state of excitation of the oscillator.

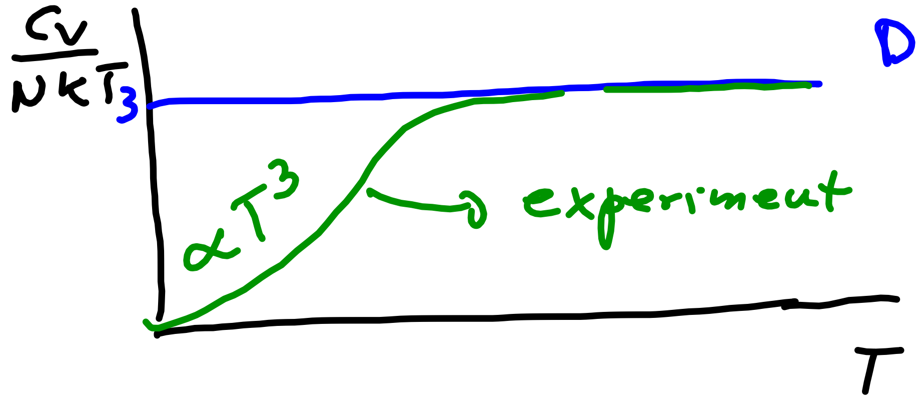
zero-point energy

$$\therefore\ U(T) = \underbrace{\left\{\Phi_0 + \overbrace{\sum_i \tfrac{1}{2}\hbar\omega_i}\right\}}_{\text{energy of the solid at } T=0}\; + \sum_i \frac{\hbar\omega_i}{e^{\hbar\omega_i/kT}-1}$$

energy of the solid at $T=0$ - Binding energy of the solids.

$$C_V(T) = \frac{\partial U}{\partial T}\Big|_V = k \sum_i \frac{(\hbar\omega_i/kT)^2 e^{\hbar\omega_i/kT}}{(e^{\hbar\omega_i/kT}-1)^2}$$

Paradox in the early 20 century:



Dulong + Petit (using equipartition for harmonic oscillators).

$C_V \propto T^3$ at low T (could not be explained.