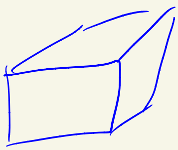
Recap : Black Body Radiation



* box w/ thermalized EM radiation

2 ways to treat

- Collection of indep HO's for each cavity mode $\vec{k},\lambda$

$$\left(H = \frac{1}{2} \sum_{\vec{k},\lambda=1,2} \left(P_{\vec{k},\lambda}^2 + \omega_k^2 Q_{\vec{k},\lambda}^2\right) \right)$$

$$= \sum_{\vec{k},\lambda} \left(n_{\vec{k},\lambda} + \frac{1}{2}\right)\hbar\omega_k$$

$$\omega_k = ck$$

- Gas of photons (massless bosons) w/ s.p.e.'s $\hbar\omega_k$ + $\mu = 0$ (non-conserved)

(i.e., the $n_{\vec{k},\lambda}$ in H can be interpreted as
- excitation level of $\vec{k},\lambda$ HO
- # of photons w/ $\vec{k},\lambda$.

$$Z = \prod_{\vec{k},\lambda} \frac{1}{1-e^{-\beta\hbar\omega_k}}$$

$$\log Z = -\sum_{\vec{k},\lambda} \log\left(1-e^{-\beta\hbar\omega_k}\right)$$

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

density of states ($\varepsilon = \hbar\omega$)

$\Downarrow$

$$\log Z = -\frac{V}{\pi^2 c^3}\int_0^\infty d\omega\, \omega^2 \log\left(1-e^{-\beta\hbar\omega}\right)$$

* using $\frac{PV}{kT} = \log Z$

$$\Rightarrow P = \frac{\pi^2}{45} \frac{(k_B T)^4}{(\hbar c)^3}$$

$$\Rightarrow E = 3PV$$

* Planck's Law

let $u(\omega) d\omega = \frac{\text{energy}}{\text{Volume}}$ radiated in $[\omega, \omega + d\omega]$

$$= \frac{\hbar \omega^3 d\omega}{\pi^2 c^3} \frac{1}{e^{\beta \hbar \omega} - 1}$$ agrees w/ experiment ⓧ

(get this from $E(\omega) \equiv \int_0^\omega d\omega' \, g(\omega') \frac{\hbar \omega'}{e^{\beta \hbar \omega'} - 1}$ = energy up to ω

$$u(\omega) = \frac{1}{V} \frac{dE(\omega)}{d\omega}$$)

Planck arrived at ⓧ by guessing EM energy was quantized in packets of $\hbar\omega$, where $\hbar$ came out of a fit to data!

Classically, one would expect

$$u(\omega) = \frac{k_B T \omega^2}{\pi^2 c^3} d\omega$$

from ET theorem, since each quadratic mode has $\frac{k_B T}{2}$ energy

and would get divergent

$$\int u(\omega) d\omega \rightarrow \infty$$

"UV catastrophe"

Planck's successful resolution of this problem was the start of QM!

Heat Capacity of Solids + Phonons

* Experimentally, $\frac{C_v}{k_B N} \propto T^3$ at low T, which disagrees w/ the classical E.T. result that $\frac{C_v}{k_B N} = \text{const.}$

* Let's model this for N atoms in some sort of lattice. Classically,

$$H = \underbrace{\sum_i \frac{m}{2} \dot{\vec{x}}_i^{\,2}}_{\text{KE}} + \underbrace{\Phi(\vec{x}_1, \vec{x}_2 \ldots \vec{x}_N)}_{\text{PE function}}$$

* Expect g.s. = config. that minimizes Φ

$$\boxed{\begin{gathered} \frac{\partial \Phi}{\partial \vec{x}_i} = 0 \quad \text{at} \quad \vec{x}_j = \vec{x}_{j,eq} \equiv \vec{x}_j^{\,0} \\ \text{where} \\ \left.\frac{\partial^2 \Phi}{\partial \vec{x}_i \partial \vec{x}_j}\right|_{\{\vec{x}_j^{\,0}\}} \geq 0 \end{gathered}}$$

Low $T \Rightarrow$ small deviations from equilibrium

$\therefore$ Let $\vec{\xi}_j = \vec{x}_j - \vec{x}_j^{\,0}$ + Taylor expand H

(Minor) notation change $\Rightarrow$ label ξ_i $i = 1 \ldots 3N$ rather than

$\vec{\xi}_i$ $i = 1 \ldots N \Rightarrow \xi_{i,\alpha}$ $i = 1 \ldots N$, $\alpha = x, y, z$

$$\therefore \boxed{\begin{aligned} H &\approx \Phi_0 + \sum_{i=1}^{3N} \frac{m}{2} \dot{\xi}_i^2 + \sum_{i,j=1}^{3N} \alpha_{ij} \xi_i \xi_j + \mathcal{O}(\xi^3) \\ \alpha_{ij} &= \frac{1}{2} \left.\frac{\partial^2 \Phi}{\partial x_i \partial x_j}\right|_{\{x_i = x_i^0\}} = 3N \times 3N \text{ matrix} \end{aligned}}$$

$\alpha_{ij} = \alpha_{ji}$ (symmetric real matrix $\Rightarrow$ diagonalizable by orthogonal matrix)

* writing in matrix notation ($\xi = \begin{pmatrix} \xi_1 \\ \vdots \\ \xi_{3N} \end{pmatrix}$ etc.)

$$H = \Phi_0 + \frac{m}{2} \dot{\xi}^T \dot{\xi} + \xi^T \alpha \xi$$

* let $$O^T \alpha O = \Lambda = \begin{pmatrix} \lambda_1 & & & 0 \\ & \lambda_2 & & \\ & & \ddots & \\ 0 & & & \lambda_{3N} \end{pmatrix}$$

where $O^T O = O O^T = \mathbb{1}_{3N \times 3N}$

* let $\left.\begin{aligned} \xi &= O q \\ \xi^T &= q^T O^T \end{aligned}\right\} \Rightarrow H = \Phi_0 + \frac{m}{2} \dot{q}^T \dot{q} + q^T O^T \alpha O q$

$$= \Phi_0 + \sum_{i=1}^{3N} \frac{m}{2} \dot{q}_i^2 + \sum_{i=1}^{3N} \lambda_i q_i^2$$

* let $\lambda_i \equiv \frac{m}{2}\omega_i^2$ (why is $\lambda_i \geq 0$? Because $\alpha_{ij} = \left.\frac{\partial^2 \Phi}{\partial x_i \partial x_j}\right|_{eq} \geq 0$)

$$\Rightarrow H = \cancel{\Phi_0} + \sum_{i=1}^{3N} \left(\frac{m}{2}\dot{q}_i^2 + \frac{m}{2}\omega_i^2 q_i^2 \right)$$

ignore
(re-define E-zero)

$\therefore$ As with the Blackbody Radiation problem, we see the complicated H for a lattice solid reduces to a sum of HO's, at least for low T where we expect small deviations from the $T=0$ ground state config.

* As before, now we quantize H + solve Sch. eqn:

$$\Rightarrow \boxed{E = \sum_{i=1}^{3N} (n_i + \tfrac{1}{2})\hbar\omega_i \equiv \sum_{i=1}^{3N} n_i \hbar\omega_i}$$

(dropping 0-pt energies)

* As with photon case,

n_i = excitation level of oscillator i

OR

= # of phonons (quantized lattice vibrations) in s.p state $\hbar\omega_i$

sound like excitation

* as with the photon BBR problem, we can either treat this problem as

1.) 3N indep HO's w/ freqs. ω_i $i = 1 \ldots 3N$

or

2) Identical bosons ("phonons") having $\mu = 0$ since they aren't conserved w/ s.p.e.'s $\hbar\omega_i$

* Some noteable differences though

1.) 3 polarizations (longitudinal + transverse)

2) finite # of HO's

* Carrying over what we've done many times now, (either using the picture of 3N HO's or of a gas of phonons of spe $\hbar\omega_i$)

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

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

etc.

* To actually make further progress, need to know the spectrum ω_i

* In general, this is hard $\Rightarrow \alpha_{ij} = 3N \times 3N$ matrix, and $N \sim O(10^{23})$. Therefore we turn to simple models

<u>Einstein model</u> : take all $\omega_i = \omega$

$$\Rightarrow E = \sum_{i=1}^{3N} \frac{\hbar\omega}{e^{\beta\hbar\omega}-1} = \frac{3N\hbar\omega}{e^{\beta\hbar\omega}-1}$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{V,N} = 3N\left(\frac{\hbar\omega}{kT}\right)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$$

$T \to \infty$

$$E = 3Nk_BT$$

$$C_V = 3Nk_B$$

(E.T. w/ 6N quadratic terms in H)

Low T ($k_BT \ll \hbar\omega$)

$$E \sim 3N\hbar\omega\, e^{-\beta\hbar\omega}$$

$$C_V \sim \frac{3N\hbar\omega}{(kT)^2} e^{-\beta\hbar\omega}$$

Does <u>not</u> agree w/ $C_V \sim T^3$ of experiment

Debye Model

* allow for continuous spectrum of ω, but only up to some UV cutoff ω_D

based on idea that
- low T dominated by low-ω oscillators
- Since lattice has finite spacing, $K_{max} \sim \frac{\pi}{a}$ a = typical spacing

  $\therefore$ assuming $\omega(K) = c_s K$ (c_s = speed of sound) there will be a cutoff

* analogous to photon case,

$$g(K)\,dK = \underbrace{3}_{\text{polarizations}} \times 4\pi V \frac{K^2 dK}{(2\pi)^3}$$

* taking $\omega_k = c_s K$ c_s = speed of sound

$\Downarrow$

$$\boxed{g(\omega)\,d\omega = V \frac{12\pi}{(2\pi c_s)^3}\omega^2 d\omega \quad \text{and} \quad \int_0^{\omega_D} g(\omega)\,d\omega = 3N}$$

*Use this to estimate ω_D

$$\int_0^{\omega_D} g(\omega)\,d\omega = 3N = \frac{V \cdot 12\pi}{(2\pi c_s)^3} \int_0^{\omega_D} \omega^2 d\omega$$

$$\Rightarrow \boxed{\omega_D = c_s \left(\frac{6\pi^2 N}{V}\right)^{1/3}}$$

* Reiterating, the introduction of ω_D makes sense, since a discrete lattice can't have waves with $\lambda \lesssim a$ where a = lattice spacing, and

$$\lambda_D \frac{\omega_D}{2\pi} = c_s$$

$$\Rightarrow \lambda_D = \left(\frac{V}{6\pi^2 N}\right)^{1/3} \propto a$$

*Now it's just a matter of applying familiar formulas to $\int_0^{\omega_D} g(\omega) \text{--}\, d\omega$

$$\log Z = -\int d\omega\, g(\omega) \log\left(1 - e^{-\beta\hbar\omega}\right)$$

$$= -\frac{12\pi V}{(2\pi c_s)^3} \int d\omega\, \omega^2 \log(\quad)$$

* use $\omega_D = c_s \left(\frac{6\pi^2 N}{V}\right)^{1/3}$

$$\Rightarrow \quad \omega_D^3 = c_s^3 \frac{6\pi^2 N}{V}$$

$$\Rightarrow \quad V = \frac{c_s^3 \, 6\pi^2 N}{\omega_D^3}$$

$$\therefore \log Z = -\frac{12\pi}{(2\pi c_s)^3} \cdot \frac{c_s^3 \, 6\pi^2 N}{\omega_D^3} \int_0^{\omega_D} \omega^2 d\omega \log(\quad)$$

$$\boxed{\log Z = \frac{9N}{\omega_D^3} \int_0^{\omega_D} d\omega \, \omega^2 \log(1 - e^{-\beta\hbar\omega})}$$

$$\Downarrow \quad E = -\frac{\partial}{\partial\beta} \log Z \qquad\qquad \beta = \frac{1}{kT}$$

$$\boxed{E = \frac{9N\hbar}{\omega_D^3} \int_0^{\omega_D} \frac{d\omega \, \omega^3}{e^{\beta\hbar\omega} - 1}}$$

$$\frac{\partial}{\partial T} = \frac{\partial\beta}{\partial T} \frac{\partial}{\partial\beta} = -\frac{1}{kT^2} \frac{\partial}{\partial\beta} = -k_B \beta^2 \frac{\partial}{\partial\beta}$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{V,N} = -k_B \beta^2 \frac{\partial}{\partial\beta} E$$

$$\boxed{C_V = \frac{9N\hbar^2}{\omega_D^3} k_B \int_0^{\omega_D} d\omega \, \omega^3 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} \cdot \frac{\hbar\omega}{(kT)^2}}$$

define Debye temperature $\Theta_D = \frac{\hbar \omega_D}{k_B}$; let $\beta \hbar \omega = x$

$$\Rightarrow \boxed{C_V = 9N\left(\frac{T}{\Theta_D}\right)^3 k_B \int_0^{\Theta_D/T} dx \, \frac{x^4 e^x}{(e^x-1)^2}}$$

<u>high T</u> : $T \gg \Theta_D$ $\Rightarrow$ upper limit $\frac{\Theta_D}{T} \ll 1$

$\therefore$ Taylor expand integrand

$$\Rightarrow C_V \approx 9N\left(\frac{T}{\Theta_D}\right)^3 k_B \cancel{\int_0^{\Theta_D/T} dx \, \frac{x^4}{x^2}} \quad \frac{1}{3}\left(\frac{\Theta_D}{T}\right)^3$$

$$= 3Nk_B$$

(as E.T. tells us!)
for 6N quadratic DOF

<u>low T</u> : take upper limit $\rightarrow \infty$

$$C_V = 9N\left(\frac{T}{\Theta_D}\right)^3 k_B \int_0^{\infty} dx \, \frac{x^4 e^x}{(e^x-1)^2}$$

$$\sim \frac{12\pi^4}{5} N k_B \left(\frac{T}{\Theta_D}\right)^3$$

Hurray! It reproduces experimental T^3 behavior.