# Phys. 528 Lecture 18

## Bose systems (cont.)

### 1) Black-body radiation

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

$$N(\omega) = 2\,\frac{4\pi}{3}k^3\,\frac{V}{8\pi^3} = \frac{V\omega^3}{3\pi^2 c^3}$$

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

$$Z = \prod_{\omega} Z(\omega)$$

$$F = -k_B T \ln Z = -k_B T \sum_{\omega} \ln Z(\omega)$$

$$= -k_B T \int_0^\infty d\omega\, g(\omega) \ln Z(\omega)$$

$$Z(\omega) = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} \quad \text{(dropping zero-pt. energy)}$$

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

$$\boxed{F = +k_B T \int_0^\infty d\omega\, g(\omega) \ln\left(1 - e^{-\beta\hbar\omega}\right)}$$

compare to $\Omega$ for ideal Bose gas with $\mu = 0$. Photons are (thermal) excitations. Their # is <u>not conserved</u>.

Instead, it is determined by minimizing $F$:

$$\langle N \rangle: \quad \mu = \frac{\partial F}{\partial N}\bigg|_{T,V} = 0$$

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

let $x = \beta \hbar \omega$

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

$$= -\frac{(k_B T)^4}{3\pi^2 \hbar^3 c^3} \underbrace{\int_0^\infty dx \frac{x^3}{e^x - 1}}_{\Gamma(4)\zeta(4) = \frac{\pi^4}{15}}$$

(integrating by parts)

$$\boxed{\frac{F}{V} = -\frac{\pi^2}{45} \frac{(k_B T)^4}{\hbar^3 c^3}}$$

On the other hand,



$$E = -\frac{\partial \ln Z}{\partial \beta} = +\frac{\partial}{\partial \beta}\int_0^\infty d\omega\, g(\omega) \ln\left(1 - e^{-\beta\hbar\omega}\right)$$

$$= \int_0^\infty d\omega \frac{g(\omega)\, \hbar\omega}{e^{\beta\hbar\omega} - 1} \equiv \int_0^\infty d\omega\, g(\omega)\, \hbar\omega\, f(\omega)$$

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

$$\boxed{\frac{E}{V} = -3F = \frac{\pi^2}{15}\frac{(k_B T)^4}{\hbar^3 c^3}}$$

Also, $F = E - TS$ so $S = \dfrac{E - F}{T}$

$$\boxed{S = \frac{4}{3}\frac{E}{T} \propto VT^3}$$

$$C_V = T \left.\frac{\partial S}{\partial T}\right|_V = 3S$$

$$\boxed{P = -\left.\frac{\partial F}{\partial V}\right|_T = -\frac{F}{V} = \frac{1}{3}\frac{E}{V}}$$

$$\langle N \rangle = \int_0^\infty d\omega \, g(\omega) \, \langle n(\omega) \rangle$$

$$= \frac{V}{\pi^2 c^3} \int_0^\infty d\omega \frac{\omega^2}{e^{\beta \hbar \omega} - 1} = \frac{V}{\pi^2} \left( \frac{k_B T}{\hbar c} \right)^3 \underbrace{\int_0^\infty dx \frac{x^2}{e^x - 1}}_{\Gamma(3)\zeta(3)}$$

$$\boxed{\langle N \rangle = \frac{V}{\pi^2} \left( \frac{k_B T}{\hbar c} \right)^3 2\zeta(3)}$$

# of photons

$$\frac{S}{N k_B} = \frac{2\pi^4}{45\zeta(3)} = 3.60 \qquad \frac{\text{entropy}}{\text{photon}}$$

2) <u>Quantum sound waves (phonons)</u>

The Hamiltonian for a solid composed of $N$ atoms is

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m_i} + U(\{\vec{r}_i\})$$

For simplicity, let's take $m_i = m$ (elemental solid). Let's expand $U$ for small displacements about equilibrium positions

$$\{\vec{r}_i^{(0)}\} : \qquad \vec{r}_i = \vec{r}_i^{(0)} + \vec{x}_i$$

$$U(\{\vec{r}_i\}) \simeq \underbrace{U(\{\vec{r}_i^{(0)}\})}_{U_0} + \cancelto{0}{\sum_{i=1}^{N} \left.\frac{\partial U}{\partial \vec{r}_i}\right|_{\{\vec{r}_j^{(0)}\}}} \cdot \vec{x}_i$$

$$+ \frac{1}{2} \sum_{i,j} \vec{x}_i \cdot \underbrace{\left.\frac{\partial^2 U}{\partial \vec{r}_i \partial \vec{r}_j}\right|_{\{\vec{r}_k^{(0)}\}}}_{C_{ij}} \cdot \vec{x}_i + \cdots$$

Dropping higher-order terms yields the harmonic approximation:

$$U(\{\vec{r}_i\}) = U_0 + \frac{1}{2} \sum_{i,j} \vec{x}_i \cdot C_{ij} \cdot \vec{x}_j$$

$C_{ij}$ is a symmetric $3 \times 3$ matrix for given $i, j$.

The Hamiltonian is now quadratic in momenta and displacements, and can be diagonalized by an appropriate orthogonal transformation

$$\{\vec{x}_i\} \to \{q_\alpha\}, \qquad \{\vec{p}_i\} \to \{p_\alpha\}.$$

$$H = U_0 + \sum_{\alpha=1}^{3N} \left( \frac{p_\alpha^2}{2m} + \frac{1}{2} m \omega_\alpha^2 q_\alpha^2 \right)$$

The $\{q_\alpha\}$ are the <u>normal modes</u> of the set of coupled oscillators.

Quantum mechanically,

$$\hat{H} = U_0 + \sum_{\alpha=1}^{3N} \hbar\omega_\alpha \left( a_\alpha^\dagger a_\alpha + \frac{1}{2} \right)$$

$$E(\{n_\alpha\}) = \sum_{\alpha=1}^{3N} \hbar\omega_\alpha \left( n_\alpha + \frac{1}{2} \right) + U_0, \quad n_\alpha = 0, 1, 2, \ldots, \infty$$

$$Z = \sum_{\{n_\alpha\}} e^{-\beta E(\{n_\alpha\})}$$

$$Z = e^{-\beta U_0} \prod_\alpha Z_\alpha$$

$$Z_\alpha = \sum_{n_\alpha=0}^{\infty} e^{-\beta\hbar\omega_\alpha \left(n_\alpha + \frac{1}{2}\right)} = \frac{e^{-\beta\frac{\hbar\omega_\alpha}{2}}}{1 - e^{-\beta\hbar\omega_\alpha}}$$

$$F = -k_B T \ln Z = U_0 - k_B T \sum_\alpha \ln Z_\alpha$$

$$\boxed{\begin{aligned} F &= \underbrace{U_0 + \sum_\alpha \frac{\hbar\omega_\alpha}{2}}_{E_0} + k_B T \sum_\alpha \ln\left(1 - e^{-\beta\hbar\omega_\alpha}\right) \\ F &= E_0 + k_B T \int_0^{\omega_{max}} d\omega\, g(\omega) \ln\left(1 - e^{-\beta\hbar\omega}\right) \end{aligned}}$$

Looks just like free energy of Black-body radiation, except $\omega_{max} < \infty$ and $E_0$ is directly measureable.

## 3) Debye model

The spectrum of vibrational modes $g(\omega)$ in a crystal can be quite complex. However, all crystals have three modes with linear dispersion at long wavelengths

$$\omega_s(\vec{k}) = v_s |\vec{k}| , \quad s = 1, 2, 3.$$

These may be thought of as two transverse and one longitudinal mode(s).

In the Debye model, we set the speeds of all three modes to a single number, the speed of sound.

Then $$N(\omega) = 3 \, \frac{4\pi}{3} k^3 \frac{V}{8\pi^3} = \frac{V\omega^3}{2\pi^2 v_s^3}$$

$$g(\omega) = \frac{dN}{d\omega} = \frac{3V\omega^2}{2\pi^2 v_s^3}$$

<u>Total # of modes</u>

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

$$3N = \frac{V\omega_D^3}{2\pi^2 v_s^3}$$

$$\boxed{\omega_D = v_s \left(\frac{6\pi^2 N}{V}\right)^{1/3} \quad \text{Debye frequency}}$$

$$F = E_0 + k_B T \int_0^{\omega_D} d\omega \, \frac{3V}{2\pi^2 v_s^3} \omega^2 \ln\left(1 - e^{-\beta\hbar\omega}\right)$$

$$F = E_0 + \frac{3V}{2\pi^2 v_s^3} \frac{(k_B T)^4}{\hbar^3} \int_0^{x_D} dx \, x^2 \ln\left(1 - e^{-x}\right),$$

$x_D = \beta \hbar \omega_D$. For $T \ll \Theta_D \equiv \frac{\hbar \omega_D}{k_B}$,

the upper limit $x_D \to \infty$.

$$F \underset{T \ll \Theta_D}{\cong} E_0 + \frac{3V}{2\pi^2} \frac{(k_B T)^4}{(\hbar v_s)^3} \underbrace{\int_0^{\infty} dx \, x^2 \ln\left(1 - e^{-x}\right)}_{-\frac{1}{3}\Gamma(4)\zeta(4) = \frac{\pi^4}{45}}$$

$$F \underset{T \ll \Theta_D}{\simeq} E_0 - \frac{\pi^2}{30} \frac{V (k_B T)^4}{(\hbar v_s)^3}$$

$$S = -\left.\frac{\partial F}{\partial T}\right|_V = \frac{2\pi^2}{15} V \left(\frac{k_B T}{\hbar v_s}\right)^3 k_B = \frac{4\pi^4}{5} N k_B \left(\frac{T}{\Theta_D}\right)^3$$

$$\boxed{C_V = T \left.\frac{\partial S}{\partial T}\right|_V = \frac{12\pi^4}{5} N k_B \left(\frac{T}{\Theta_D}\right)^3}$$

The specific heat of the lattice vibrations in insulating crystals is well-described by the Debye model for $T \le \Theta_D/50$. $\Theta_D$ ranges from 38K in Cs to 2230K in diamond.

In <u>metals</u>, the Debye contribution must be added to the electronic term, giving

$$\boxed{\frac{C_V}{N k_B} = \frac{\pi^2}{2}\frac{T}{T_F} + \frac{12\pi^4}{5}\left(\frac{T}{\Theta_D}\right)^3 .}$$