

# Analogy with the theory of BLACKBODY radiation

phonons  
elementary vibrational  
excitations in solids

$$\omega_s(\vec{k})$$

$$s = 1 \dots 3p$$

3 acoustic modes  
3p-3 optical

for  $\forall \vec{k} \in 1st \text{ BZ}$

transverse  $\vec{k} \perp \vec{u}$   
longitudinal  $\vec{k} \parallel \vec{u}$   
for high-symmetry directions

$$U = \sum_{s=1}^{3p} \int_{\text{BZ}} \frac{d^3k}{(2\pi)^3} \frac{\hbar \omega_s(\vec{k})}{e^{\beta \hbar \omega_s(\vec{k})} - 1}$$

phonons

$$U = 2 \int \frac{d^3k}{(2\pi)^3} \cdot \frac{\hbar c k}{e^{\beta \hbar c k} - 1}$$

photons

photons  
quanta of EM  
field

$$\omega = c k$$

$$(c \approx 3 \times 10^{10} \text{ cm/sec})$$

$\vec{k}$  arbitrary

2 transverse  
 $\vec{k} \perp \vec{E}$   
modes  
(in vacuum)

Analogy  $\overbrace{\text{photons} \leftrightarrow \text{phonons}}$   
 becomes especially close  
 in the Debye approximation

$$\omega_s(k) = ck \quad s=1,2,3$$

$$|\vec{k}| < k_D \quad c - \text{mean speed of sound}$$

- cut-off  $k_D \sim 1/a$
- 3 modes
- no cut-off
- 2 modes

density of states

$$g(\omega) = \frac{\omega^2}{2\pi^2 c^3} * (\# \text{ of modes})$$

Internal energy

$$dE_\omega = \hbar\omega \cdot g(\omega) \cdot \frac{1}{\exp(\hbar\omega/k_B T) - 1} d\omega$$

(M. Planck 1900)

Classical theory //  $k_B T \gg \hbar\omega$  //

$$dE_\omega = k_B T g(\omega) d\omega$$

Rayleigh-Jeans  
catastrophe

$$E = \int_0^\infty \frac{d\omega}{2\pi} k_B T \cdot \frac{2\omega^2}{2\pi^2 c^3} = \infty$$

# Thermodynamics of a black-body radiation ( $\Leftrightarrow$ phonons)

Partition function  $Z = \sum_i \exp(-\frac{E_i}{k_B T})$

Free energy  $F = -k_B T \ln Z = F(T, V)$

$$dF = - \underbrace{S}_{\text{entropy}} dT - \underbrace{P}_{\text{pressure}} dV$$

$N$  normal modes  $\equiv N$  independent oscillators

$$Z = \prod_{k=1}^N Z_k \quad E_i = \sum_{k=1}^N \hbar \omega_k (n_k + 1/2)$$

$i \equiv \{n_k\}$

Neglect energy of zero-point oscillations

$$Z_k = \sum_{n=0}^{\infty} \exp(-\frac{\hbar \omega_k n}{k_B T}) = \frac{1}{1 - \exp(-\frac{\hbar \omega_k}{k_B T})}$$

$$F = -k_B T \ln \prod_{k=1}^N \frac{1}{1 - \exp(-\frac{\hbar \omega_k}{k_B T})}$$

$$F = + k_B T \cdot \sum_{k=1}^N \ln \left( 1 - \exp(-\frac{\hbar \omega_k}{k_B T}) \right)$$

$\sum_{\text{modes}} \dots \rightarrow \int_0^{\infty} d\omega g(\omega)$

$$F = V \cdot k_B T \int_0^{\infty} \ln \left[ 1 - e^{-\frac{\hbar \omega}{k_B T}} \right] \frac{\omega^2}{\pi^2 c^3} d\omega$$

Black-body radiation (2 modes)  $\rightarrow g(\omega) * V$

$$\frac{\hbar \omega}{k_B T} = x$$

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

$$J = \int_0^{\infty} d\left(\frac{x^3}{3}\right) \ln [1 - e^{-x}] =$$

$$= \int_0^{\infty} d\left(\frac{x^3}{3} \ln [1 - e^{-x}]\right) - \int_0^{\infty} dx \cdot \frac{x^3}{3} \cdot \frac{e^{-x}}{1 - e^{-x}}$$

$\frac{1}{3} \frac{\pi^4}{15}$

$$\frac{x^3}{3} \ln [1 - e^{-x}] \Big|_0^{\infty} = 0$$

$$F = - \frac{\pi^2 (k_B T)^4}{45 (hc)^3} \cdot V = F(T, V)$$

✓  $U = U(S, V) = -3F$  internal energy

$$P = - \left( \frac{\partial F}{\partial V} \right)_T = \frac{\pi^2 (k_B T)^4}{45 (hc)^3}$$

pressure

# Anharmonic effects in crystals

ionic interaction energy

$$U(\{\vec{R}_i + \vec{u}_i\}) = U^{eq}(\{\vec{R}_i\}) + U^{harm} + U^{anh}$$

$\sim u^2$        $\sim u^3, u^4, \dots$

$$U^{anh} = \sum_{n=3}^{\infty} \frac{1}{n!} \sum_{\vec{R}_1, \dots, \vec{R}_n} D_{\mu_1 \dots \mu_n}^{(n)}(\vec{R}_1, \dots, \vec{R}_n) \cdot u_{\mu_1}(\vec{R}_1) \dots u_{\mu_n}(\vec{R}_n)$$

$$D_{\mu_1 \dots \mu_n}^{(n)}(\vec{R}_1, \dots, \vec{R}_n) = \frac{\partial^n U}{\partial u_{\mu_1}(\vec{R}_1) \dots \partial u_{\mu_n}(\vec{R}_n)}$$

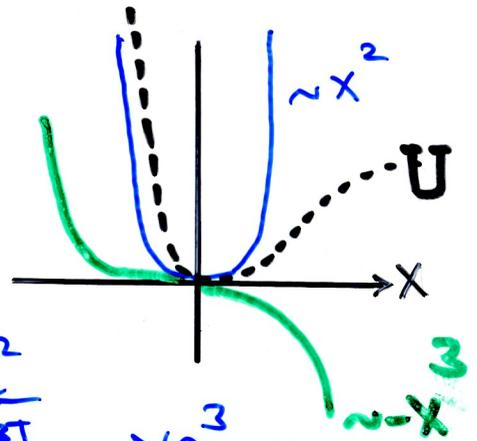
Cubic  $u^3$  and quartic terms  $u^4$  are usually considered

Anharmonicity  $\rightarrow$  thermal expansion  
 $\searrow$  finite thermal conductivity

# Thermal expansion: a simple 1D model

Anharmonic oscillator

$$U(x) = \frac{1}{2}Kx^2 - \frac{1}{3}\gamma x^3$$



Boltzmann distribution

$$f(x) = A \cdot \exp\left\{-\frac{U}{k_B T}\right\} \approx A \cdot e^{-\frac{Kx^2}{2k_B T}} \left[1 + \frac{\gamma x^3}{3k_B T}\right]$$

treated as a correction

$$A: \int_{-\infty}^{\infty} dx f(x) = 1 \quad \text{normalization constant}$$

$$A \cdot \int_{-\infty}^{\infty} dx \exp\left\{-\frac{Kx^2}{2k_B T}\right\} \left[1 + \frac{\gamma x^3}{3k_B T}\right] = A \cdot \sqrt{\frac{2\pi k_B T}{K}}$$

$$I_0(\alpha) = \int_{-\infty}^{\infty} dx e^{-\alpha x^2} = \sqrt{\frac{\pi}{\alpha}}$$

$$f(x) = \sqrt{\frac{K}{2\pi k_B T}} \exp\left\{-\frac{Kx^2}{2k_B T}\right\} \left[1 + \frac{\gamma x^3}{3k_B T}\right]$$

distribution function

Mean displacement

$$\bar{x} = \int_{-\infty}^{\infty} dx f(x) x$$

$$\bar{x} = \int_{-\infty}^{\infty} dx \sqrt{\frac{K}{2\pi k_B T}} e^{-\frac{Kx^2}{2k_B T}} \left[ 1 + \frac{\gamma x^3}{3k_B T} \right] x$$

only contributes

$$I_4(x) = \int_{-\infty}^{\infty} dx x^4 e^{-ax^2} = \frac{3}{4} \sqrt{\frac{\pi}{a^5}}$$

$$\bar{x} = \frac{\gamma k_B T}{K^2} \sim \frac{\gamma}{K^2} \quad \text{anharmonic effect}$$

Coefficient of thermal expansion

$$\alpha = \frac{\bar{x}}{a \cdot T} = \frac{\gamma k_B}{a K^2} \sim \gamma$$

lattice constant

# A simple illustrating example

estimate of  $\alpha$  for the ionic crystal

$$U(r) = -\frac{e^2}{r} + \frac{C}{r^9}$$

(order of magnitude,  $\Rightarrow$  Madelung constant  $\rightarrow 1$ )

Equilibrium:  $\frac{\partial U}{\partial r} \Big|_{r=a} = 0 \Rightarrow C = e^2 a^8 / 9$

Near equilibrium:  $U(a+x) \rightarrow$  expand in  $x$

$$U(a+x) \approx U(a) + \frac{1}{2} \cdot \frac{\partial^2 U}{\partial r^2} \Big|_{r=a} \cdot x^2 + \frac{1}{3!} \cdot \frac{\partial^3 U}{\partial r^3} \Big|_{r=a} \cdot x^3$$

$$K = 8 \frac{e^2}{a^3}$$

$$\frac{1}{2}\gamma = \frac{104 e^2}{a^4}$$

Coeff. of thermal expansion

$$\alpha = \frac{\gamma k_B}{a K^2} = \frac{52 a k_B}{64 e^2} = 1.5 \times 10^{-5} \text{ K}^{-1}$$

$$a = 3 \times 10^{-8} \text{ cm}$$

$$k_B = 1.38 \times 10^{-16} \text{ erg/K}$$

$$e = 4.8 \times 10^{-10} \text{ CGSE}$$

correct order of magnitude

at  $T \gg \Theta_D/4$ !

$$\text{LiF } \alpha = 3.3 \times 10^{-5} \text{ K}^{-1} \text{ at } T = 283 \text{ K}$$

## Thermal expansion coefficient

$$\alpha \begin{cases} \sim \text{constant} & T \gg \Theta_D/4 \\ \sim T^3 & T \ll \Theta_D/4 \end{cases}$$

same as  $C_V$   $T$ -dependence

Grüneisen law:

ratio  $\frac{\alpha}{C_V}$  does not depend on  $T$

Grüneisen parameter  $\gamma$  (usually  $\gamma \approx 2$ )

$$\alpha = \frac{\gamma}{3B} C_V$$

$$B = -V \left( \frac{\partial P}{\partial V} \right)_T = \frac{1}{\kappa} \leftarrow \begin{array}{l} \text{only weakly} \\ \text{depends on } T \end{array}$$

bulk modulus  $\uparrow$  compressibility

$$\gamma = - \frac{V}{\omega_D} \cdot \frac{\partial \omega_D}{\partial V} = - \frac{\partial \ln \omega_D}{\partial \ln V}$$

anharmonic effects  $\Rightarrow$  dependence of  
Debye temperature  
on equilibrium volume

# Equation of state of a crystal

≡ dependence between  $P$ ,  $V$ , and  $T$ .

A direct approach: calculate free energy

$$F = F(T, V) = -k_B T \ln Z$$

Partition function  $F = \sum_i \exp(-E_i/k_B T)$

$$dF = -SdT - PdV$$

entropy                  pressure

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = P(V, T) : \text{our goal}$$

Use Debye approximation:  
vibrations as acoustic modes  $|k| < k_D$  →  
≡ a set of independent oscillators

$$Z_{\text{osc}} = e^{-\frac{\hbar\omega}{2k_B T}} \cdot \frac{1}{1 - \exp(-\frac{\hbar\omega}{k_B T})}$$

$$F_{\text{osc}} = \frac{\hbar\omega}{2} + k_B T \ln \left(1 - \exp\left[-\frac{\hbar\omega}{k_B T}\right]\right)$$

one oscillator of frequency  $\omega$

$F = \sum F_{osc}$  for independent oscillators

Debye approximation:

$$F = \int_0^{\infty} d\omega \cdot V g_D(\omega) \cdot F_{osc}(\omega)$$

$$g_D(\omega) = \begin{cases} 0, & \omega > \omega_D \\ \frac{3\omega^2}{2\pi^2 c^3}, & \omega < \omega_D \end{cases}$$

$$F = \mathcal{E}_0 + k_B T \cdot V \cdot \frac{3}{2\pi^2 c^3} \int_0^{\omega_D} d\omega \ln\left(1 - e^{-\frac{\hbar\omega}{k_B T}}\right) \cdot \omega^2$$

$T$ -independent part

$$\mathcal{E}_0 = \sum \frac{\hbar\omega}{2} = \mathcal{E}_0(V) \quad \text{zero-point energy}$$

$$\omega \rightarrow \frac{\hbar\omega}{k_B T} = x, \quad \Theta_D = \frac{\hbar c}{k_B} \cdot (6\pi^2 n)^{1/3}$$

$$F = \mathcal{E}_0 + 9 k_B T \cdot n V \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} dx x^2 \ln(1 - e^{-x})$$

$N$ , number of ions in a crystal

The  $T$ -dependent part depends on  $V$  only through the  $\Theta_D(V)$  dependence

$$P = - \left( \frac{\partial F}{\partial V} \right)_T = - \frac{\partial \mathcal{E}_0}{\partial V} - 3Nk_B T \mathcal{D} \left( \frac{\Theta_D}{T} \right) \cdot \frac{1}{\Theta_D} \frac{\partial \Theta_D}{\partial V}$$

where  $\mathcal{D}(x) = \frac{3}{x^3} \int_0^x \frac{t^3 dt}{e^t - 1}$  ← Debye function

Grüneisen parameter

$$\gamma = - \frac{V}{\Theta_D} \frac{\partial \Theta_D}{\partial V} = - \frac{\partial \ln \omega_D}{\partial \ln V}$$

$$P = - \left( \frac{\partial F}{\partial V} \right)_T = - \frac{\partial \mathcal{E}_0}{\partial V} + \gamma \frac{\mathcal{E}_T}{V}$$

$$\mathcal{E}_T = 3Nk_B T \mathcal{D} \left( \frac{\Theta_D}{T} \right) : \text{T-dependent part of internal energy}$$

Pressure due to phonons  $P_{ph} = \gamma \frac{\mathcal{E}_T}{V}$

Anharmonic effect!