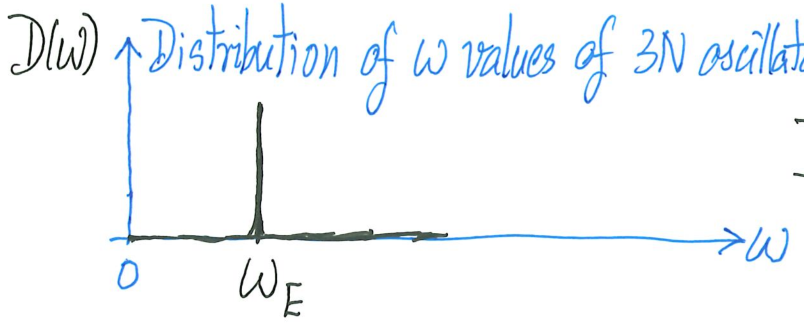
Application B: Heat Capacity of Insulators

[Collection of Oscillators and Debye Model]

B. Heat Capacity of Insulators: Revisited

Einstein's Model: 3N oscillators, all with $\omega = \omega_E$ (same angular frequency)

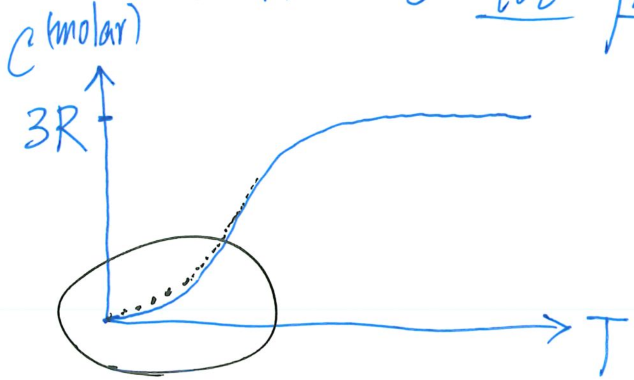
Mathematically,



$$D_{Einstein}(\omega) = 3N\,\delta(\omega - \omega_E)$$

Consequences

- $E(T) = 3N \dfrac{\hbar\omega_E}{e^{\hbar\omega_E/kT} - 1} + 3N\dfrac{\hbar\omega_E}{2}$; $C(T)$ that goes to zero as $T \to 0$
- But $C(T) \to 0$ too fast when compared with experimental data!



Data say: $C \sim \underbrace{T^3}$ at low temperatures

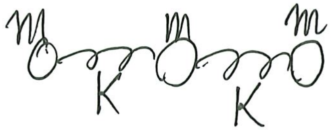
not predicted by Einstein's Model

Here, we re-do the Statistical Mechanical Problem of Harmonic Oscillators, and introduce the Debye Model

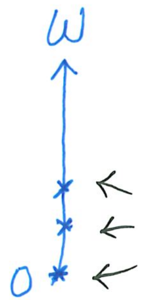
Collection of Independent Oscillators with Different Angular Frequencies

Motivation: Atoms are bonded in a solid

3 atoms in 1D



3 normal mode frequences



plot normal-mode frequencies

4 atoms

4 normal modes

10 atoms

10 nomal modes

N atoms
1D

N normal modes

N normal mode frequencies

A Normal mode : an oscillation that involves all atoms with a single frequency

Normal modes are independent of each other

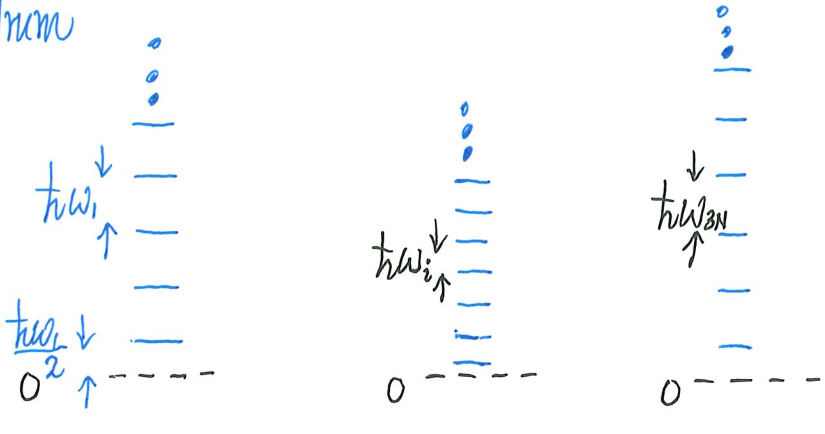
[called phonon modes]

$\therefore$ Einstein's Model is not quite right!

Consider 3N independent oscillators : ω_i = freq. of i^{th} oscillator $(i=1,\dots,3N)$

Oscillator # :	1	…	i	…	3N
Frequency :	ω_1	…	ω_i	…	ω_{3N}

Energy spectrum



"3N oscillators problem"

$\Updownarrow$

"3N particles problem"

$$Z = \sum_{\substack{\text{all 3N-oscillator} \\ \text{states } i}} e^{-E_i/kT}$$

E_i = energy of 3N oscillator state i

- A 3N-oscillator state : Specify how each oscillator is excited

  ∴ a string $\{n_1, n_2, \cdots, n_i, \cdots, n_{3N}\}$ specifies a 3N-oscillator state

  "n_i" means the i^{th} oscillator is excited to the energy $(n_i + \frac{1}{2})\hbar\omega_i$

- How many 3N-oscillator states are there?

  Infinitely many! (Each n_i can run from 0 to ∞)

- Energy of a 3N-oscillator state $\{n_1, n_2, \cdots, n_i, \cdots n_{3N}\}$

$$E(\{n_i\}) = (n_1+\tfrac{1}{2})\hbar\omega_1 + (n_2+\tfrac{1}{2})\hbar\omega_2 + \cdots + (n_i+\tfrac{1}{2})\hbar\omega_i + \cdots + (n_{3N}+\tfrac{1}{2})\hbar\omega_{3N}$$

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

short-hand for a given state

- **What is summing over 3N-oscillator states?**

$$\sum_{\text{all 3N-oscillator states}} (\cdots) = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_i=0}^{\infty}\cdots\sum_{n_{3N}=0}^{\infty} (\cdots)$$

all strings $\{n_i\}$ are included (must understand this point)

$$Z = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_i=0}^{\infty}\cdots\sum_{n_{3N}=0}^{\infty} e^{-\beta\left[(n_1+\frac{1}{2})\hbar\omega_1 + (n_2+\frac{1}{2})\hbar\omega_2 + \cdots + (n_i+\frac{1}{2})\hbar\omega_i + \cdots (n_{3N}+\frac{1}{2})\hbar\omega_{3N}\right]} \qquad (B1)$$

$$= \underbrace{\left(\sum_{n_1=0}^{\infty} e^{-\beta(n_1+\frac{1}{2})\hbar\omega_1}\right)}_{z_1}\underbrace{\left(\sum_{n_2=0}^{\infty} e^{-\beta(n_2+\frac{1}{2})\hbar\omega_2}\right)}_{z_2}\cdots\underbrace{\left(\sum_{n_i=0}^{\infty} e^{-\beta(n_i+\frac{1}{2})\hbar\omega_i}\right)}_{z_i}\cdots\underbrace{\left(\sum_{n_{3N}=0}^{\infty} e^{-\beta(n_{3N}+\frac{1}{2})\hbar\omega_{3N}}\right)}_{z_{3N}}$$

$$= z_1 \, z_2 \cdots z_i \cdots z_{3N}$$

$$= \prod_{i=1}^{3N} z_i$$ (factorized into product of single-oscillator partition functions) (B2)

where $$z_i = \sum_{n_i=0}^{\infty} e^{-\beta(n_i+\frac{1}{2})\hbar\omega_i}$$ (can be evaluated) (B3)

↑ over all single-oscillator states

Factorization comes from independent and distinguishability of the oscillators

[Train yourself to "see through" a problem on whether Z can be factorized]

$$F = -kT\ln Z = -kT\ln\left[\prod_{i=1}^{3N} z_i\right] = -kT\sum_{i=1}^{3N}\ln z_i = \sum_{i=1}^{3N}\underbrace{\left(-kT\ln z_i\right)}_{\text{Helmholtz free energy of } i^{th} \text{ oscillator}} \qquad \text{(B4)}$$

SUM over oscillators

[make sense! F is extensive]

z_i = partition function of one (the i^{th}) oscillator

$$= \sum_{n_i=0}^{\infty} e^{-\beta n_i \hbar\omega_i} e^{-\beta\frac{\hbar\omega_i}{2}} = e^{-\beta\frac{\hbar\omega_i}{2}}\sum_{n_i=0}^{\infty} e^{-\beta\hbar\omega_i n_i} = \frac{e^{-\beta\frac{\hbar\omega_i}{2}}}{1-e^{-\beta\hbar\omega_i}} \qquad \left(\because \frac{1}{1-x} = \sum_{n=0}^{\infty} x^n\right)$$

(B5)

$$\langle E\rangle = -\left(\frac{\partial \ln Z}{\partial\beta}\right) = -\frac{\partial}{\partial\beta}\left(\sum_{i=1}^{3N}\ln z_i\right) = -\sum_{i=1}^{3N}\left(\frac{\partial}{\partial\beta}\ln z_i\right) = -\sum_{i=1}^{3N}\frac{\partial}{\partial\beta}\ln\left(\frac{e^{-\frac{\beta\hbar\omega_i}{2}}}{1-e^{-\beta\hbar\omega_i}}\right)$$

$$= -\sum_{i=1}^{3N}\frac{\partial}{\partial\beta}\left[-\frac{\beta\hbar\omega_i}{2} - \ln\left(1-e^{-\beta\hbar\omega_i}\right)\right]$$

$$= \sum_{i=1}^{3N}\left(\frac{\hbar\omega_i}{2} + \frac{\hbar\omega_i e^{-\beta\hbar\omega_i}}{1-e^{-\beta\hbar\omega_i}}\right)$$

$$= \sum_{i=1}^{3N}\left(\underbrace{\frac{\hbar\omega_i}{e^{\beta\hbar\omega_i}-1} + \frac{1}{2}\hbar\omega_i}_{\langle e_i\rangle}\right) \qquad \text{(B7)}$$

Done!

ground state energy of i^{th} oscillator (just a constant)

$\langle e_i\rangle$ ← mean energy of i^{th} oscillator (temperature dependence in $\frac{\hbar\omega_i}{kT}$)

Physics here!

$$\langle E \rangle = \sum_{i=1}^{3N} \left(\frac{\hbar\omega_i}{e^{\beta\hbar\omega_i} - 1} + \frac{1}{2}\hbar\omega_i \right)$$

compares with

$$\sum_{i=1}^{3N} \left(\langle n_i \rangle \hbar\omega_i + \frac{1}{2}\hbar\omega_i \right)$$

$\langle n_i \rangle$: average/mean excitation of i^{th} oscillator (when it is in equilibrium with heat bath at temp. T)

$$\langle n_i \rangle = \frac{1}{e^{\beta\hbar\omega_i} - 1} = \frac{1}{e^{\frac{\hbar\omega_i}{kT}} - 1} \tag{B8}$$

- $\langle n_i \rangle$ is generally NOT an integer (allowed n_i's are integers)
  (thermal contact with bath $\Rightarrow$ energy exchange with bath $\Rightarrow$ energy of oscillator(s) is not fixed $\Rightarrow$ (as time evolves) oscillator sometimes excited to $n_i = 3$, sometimes to $n_i = 5, \ldots$, the average is NOT an integer
- $\hbar\omega_i / kT$ appears: same temp. T, an oscillator with big ω_i will have a small $\langle n_i \rangle$ than an oscillator with small ω.

[this is important when oscillators have different ω's]

$$F = -kT\ln Z = \sum_{i=1}^{3N}\left(-kT\ln z_i\right) = \sum_{i=1}^{3N}\left[kT\ln\left(1-e^{-\frac{\hbar\omega_i}{kT}}\right) + \frac{\hbar\omega_i}{2}\right] \qquad (B9)$$

$$S = -\frac{\partial F}{\partial T} = k\sum_{i=1}^{3N}\left[\frac{\frac{\hbar\omega_i}{kT}}{e^{\hbar\omega_i/kT}-1} - \ln\left(1-e^{-\frac{\hbar\omega_i}{kT}}\right)\right] \qquad (B10)\ (Ex.)$$

- All results are general
- Work for all $\omega_i = \omega_E$ (Einstein's Model) and when there are different ω_i's among oscillators (Debye Model)

Debye Model

- 3D (dimensions matter) monatomic solids $\underbrace{\overbrace{\text{[N atoms in a 3D lattices]}}^{N\sim 10^{23} \text{ for } V\sim cm^3}}_{3N \text{ oscillators}}$
- The $\underbrace{\text{normal modes}}_{3N \text{ of them}}$ are independent

3N of them ($\omega_1, \omega_2, \cdots, \omega_i, \cdots \omega_{3N}$) [finite #, despite large]

angular frequency

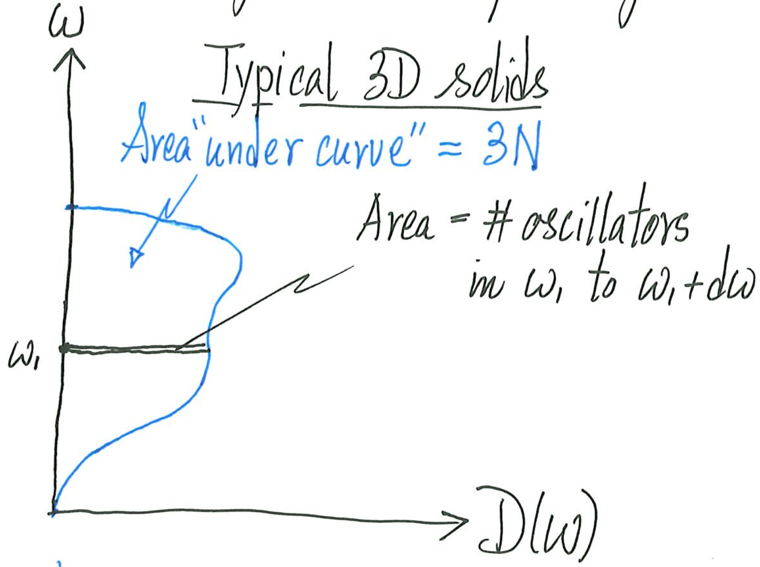
3N values of ω's for the 3N normal modes

values are densely packed!

each normal mode of angular freq. ω is an oscillator of angular freq. ω

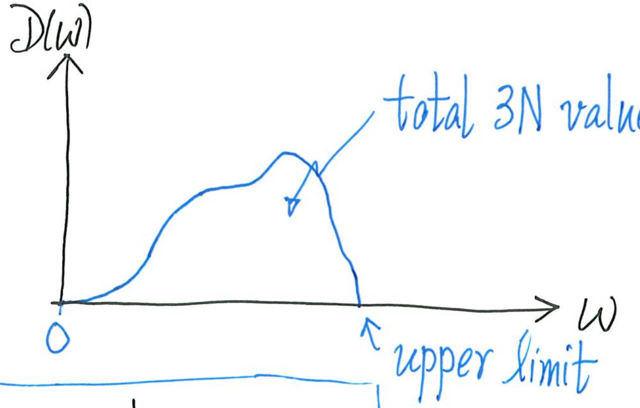
Use a buffer $d\omega$ to count

(B11) $\boxed{D(\omega)\,d\omega \equiv \text{\# of oscillators with angular freq. in interval } \omega \text{ to } \omega + d\omega}$

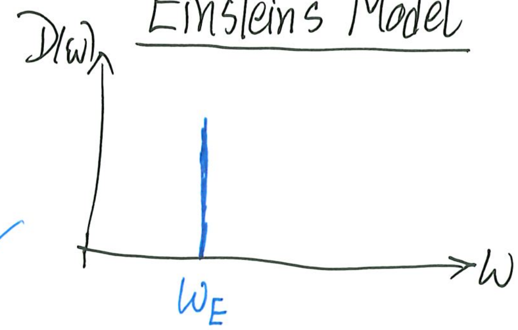


May call $D(\omega)$ the Density of normal-mode frequencies

Rotate the picture :



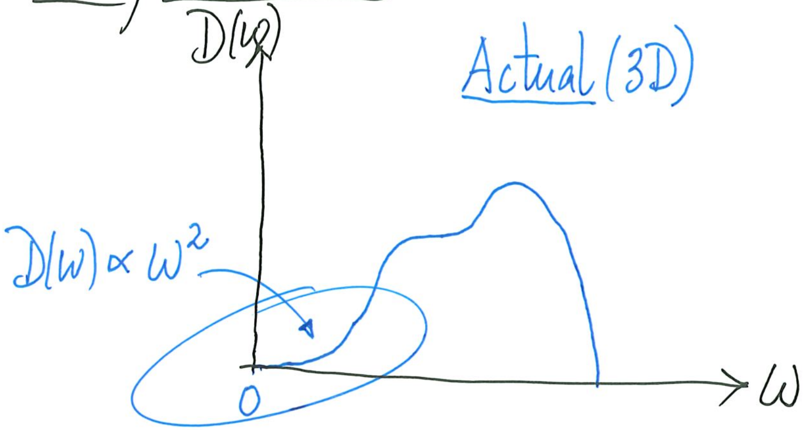
Einstein's Model



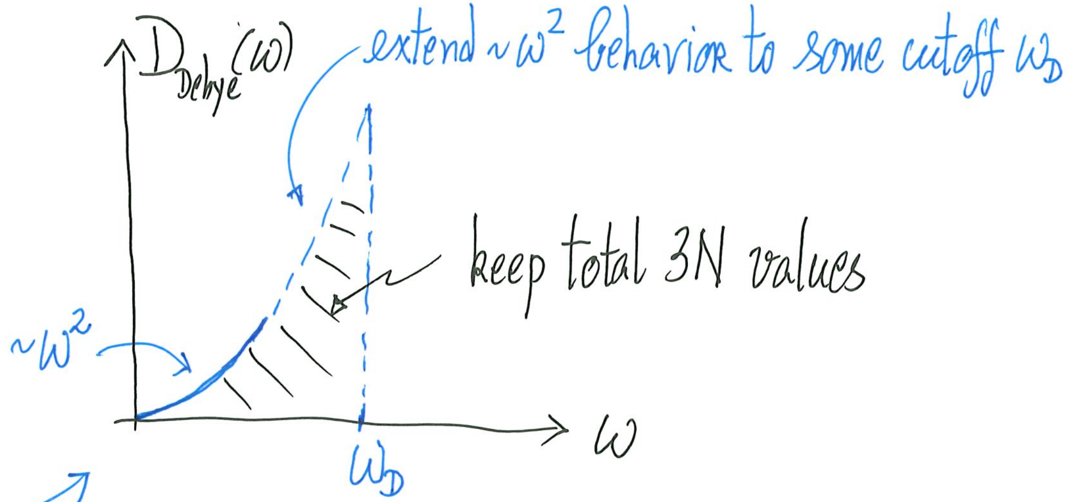
What Einstein's model missed is that low-freq oscillators, as only these oscillators matter at low temp.

Missed the low-temp physics of $C_V(T)$

Debye Model



capture this part accurately



Debye frequency (the only parameter in Debye Model)

$$D_{Debye}(\omega) = A\omega^2 \quad \text{for } 0 < \omega < \omega_D$$ (3D solids)

$$\int_0^{\omega_D} D_{Debye}(\omega)\,d\omega = A\int_0^{\omega_D} \omega^2\,d\omega = \frac{A\omega_D^3}{3} = \underbrace{3N}_{\text{Total \# of normal mode frequencies}} \Rightarrow A = \frac{9N}{\omega_D^3}$$

$$\therefore \boxed{D_{Debye}(\omega) = \frac{9N}{\omega_D^3}\cdot\omega^2} \qquad (B11)$$

$$\langle E\rangle = \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\hbar\omega_i/kT}-1} + \sum_{i=1}^{3N}\frac{1}{2}\hbar\omega_i$$

$$= \int_0^{\omega_D} \frac{\hbar\omega}{e^{\hbar\omega/kT}-1} D(\omega)\,d\omega + \int_0^{\omega_D} \frac{1}{2}\hbar\omega\, D(\omega)\,d\omega$$

Recall:
$D(\omega)d\omega$ = # of oscillators with angular frequencies in $\omega \to \omega + d\omega$

$$= \underbrace{\frac{9N}{\omega_D^3}\int_0^{\omega_D} \frac{\hbar\omega\cdot\omega^2}{e^{\hbar\omega/kT}-1}\,d\omega}_{\text{should have seen a similar (not identical) integral in black-body radiation (Stefan-Boltzmann Law)}} + \underbrace{\frac{9N}{8}\hbar\omega_D}_{\text{just a constant (total GS energy)}}$$

$$\langle E \rangle = \frac{9N}{\omega_D^3} \underbrace{\int_0^{\omega_D} \frac{\hbar\omega\ \omega^2}{e^{\hbar\omega/kT}-1}\, d\omega}\ +\ \text{GS energy}$$

$x \equiv \hbar\omega/kT$, $\omega = \frac{kT}{\hbar}x$, $d\omega = \frac{kT}{\hbar}dx$, $\omega^3 = \left(\frac{kT}{\hbar}\right)^3 x^3$ (change of variable)

$$\sim \left(\frac{kT}{\hbar}\right)^4 \int_0^{\frac{\hbar\omega_D}{kT}} \frac{x^3\, dx}{e^x - 1}$$

low-temp behavior

$\Rightarrow \frac{\hbar\omega_D}{kT} \gg 1$ (put upper limit to ∞)

$$\sim T^4 \underbrace{\int_0^{\infty} \frac{x^3\, dx}{e^x-1}}$$

→ just a number (can be evaluated)

$$\therefore \langle E \rangle(T) \sim A T^4 + \text{GS energy}$$

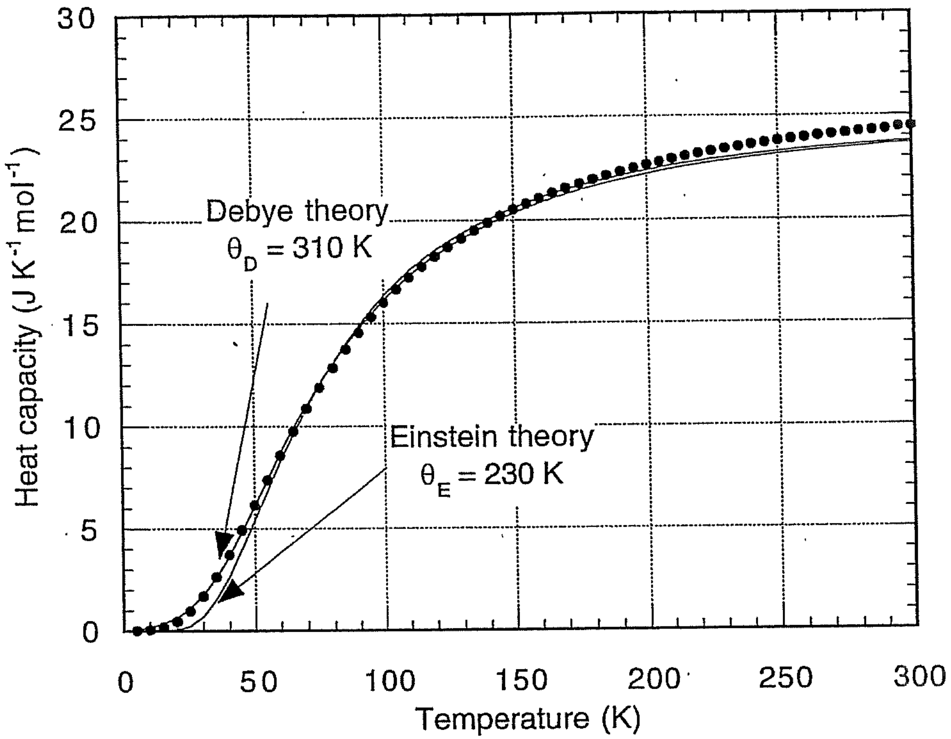
$$C_V = \frac{\partial \langle E \rangle}{\partial T} \sim \underbrace{T^3}$$ low-temperature behavior!

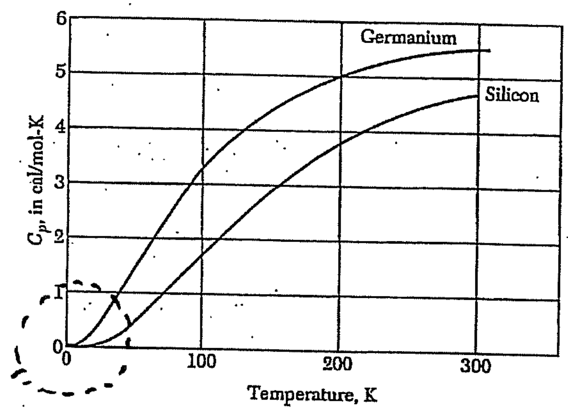
observed in experiments, drop to zero slower than Einstein's model

Note: Could formal obtain $C_V(T)$ by $\frac{\partial \langle E \rangle}{\partial T}$ and then find low-temperature behavior.

CE - B14

The Debye prediction for the heat capacity of copper compared with the Einstein prediction





$\Theta_D = \frac{\hbar\omega_D}{k}$, $\Theta_E = \frac{\hbar\omega_E}{k}$ Debye Model works

$C_V \sim T^3$ behavior is also observed in Ge, Si (semiconductors)

Remarks

- See how the calculation of Z avoids counting $W_S(E,V,N)$
- Related topics in Solid State Physics
  - How does $D(\omega)$ relate to dimension?
  - Low temperature physics → low ω modes → low wavenumber modes → long wavelength vibrations → "sound modes" → $\omega \sim \underbrace{v_s}_{\text{sound speed}} \underbrace{q}_{\text{wave-number } = \frac{2\pi}{\lambda}}$

    How do (a) dimension (3D) and (b) $\omega = v_s q$ give
    $$D(\omega)\,d\omega \sim \omega^2 d\omega \,?$$
  - How about 1D? 2D?
  - Gas of phonons (same system, different viewpoints)