## D. Harmonic Oscillator [Quantum]

- Harmonic Oscillators are almost everywhere in physics!
  - lattice vibrations in a solid
    [phonons = normal modes of lattice vibrations]
  - Vibrational modes in a molecule
  - photons (oscillating EM fields)

The following treatment can thus be applied to:

- solids (heat capacity)
- molecules (a gas of diatomic molecules)
- light (black-body radiation)

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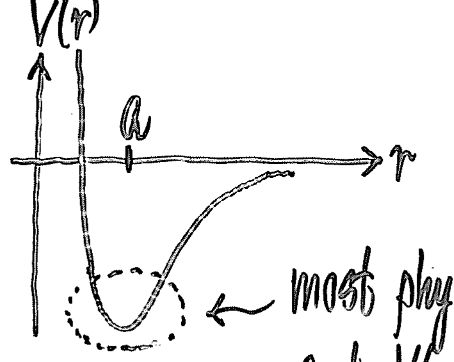
Whenever something (atoms, ions) has an equilibrium (mechanical) position, it is under a potential energy function of the form



a repulsive part
+ an attractive part

most physics happens here and V(r) looks like

parabolic potential

e.g. chemical bond length
of a diatomic molecule

∴ harmonic oscillator

## General Set up

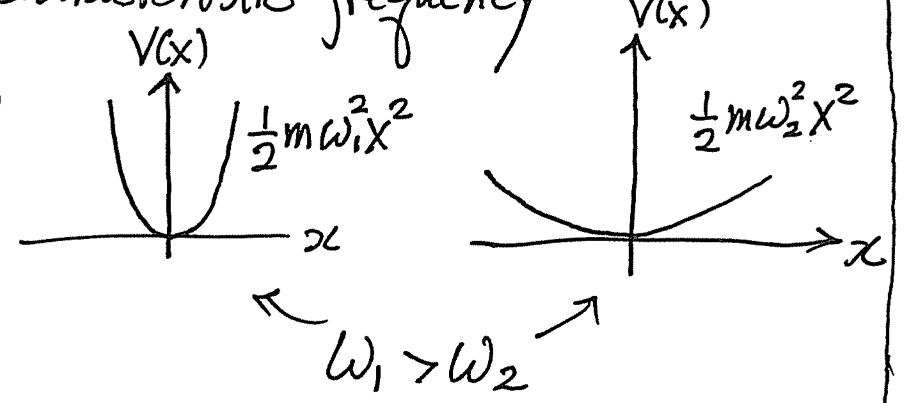
- N independent distinguishable harmonic oscillators
- $i^{th}$ oscillator: characteristic angular frequency $\omega_i$

### Essential Quantum Physics

- for a harmonic oscillator $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2$

$\omega$ = characteristic frequency

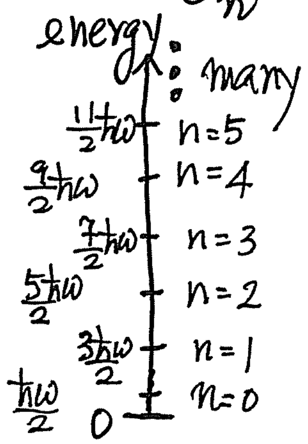
$\overset{\Uparrow}{\text{gives}}$ V(x)



$\hat{H}\psi = \varepsilon\psi$ gives energy eigenvalues

$$\varepsilon_n = \left(n+\frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, 2, \cdots$$

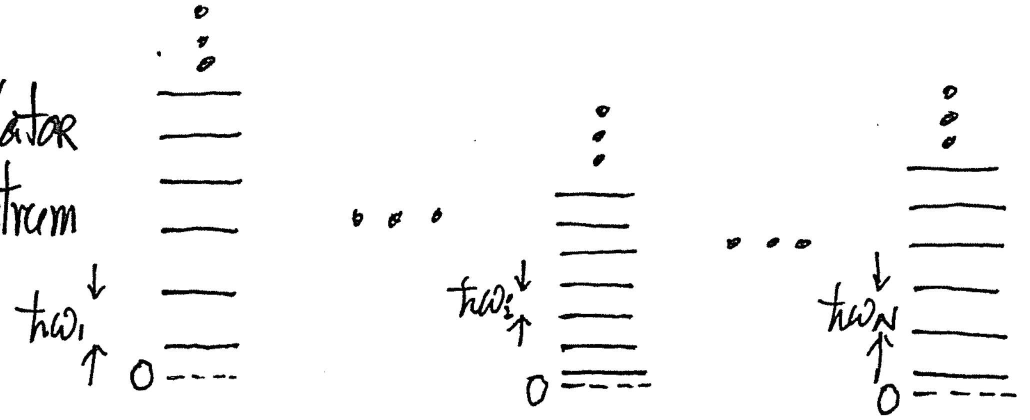
(no ceiling)



A single oscillator has an unbounded energy spectrum

| Oscillator # | $1$ | $\cdots$ | $i$ | $\cdots$ | $N$ |
|---|---|---|---|---|---|
| Characteristic freq. | $\omega_1$ | $\cdots$ | $\omega_i$ | $\cdots$ | $\omega_N$ |

Single-oscillator energy spectrum



- A state of the N-oscillator system is specified by a string $\{n_1, n_2, \cdots, n_i, \cdots, n_N\}$
  with $n_i$ = excitation of the $i^{th}$ oscillator
- All N-oscillator states are all possible strings
  $\{n_1, n_2, \cdots, n_i, \cdots, n_N\}$
  with $n_i = 0, 1, 2, \cdots$ for every $i$ (every oscillator)

Given a particular string $\{n_1, \cdots, n_i, \cdots, n_N\}$, the energy of the N-oscillator state is

$$E(\{n_i\}) = (n_1+\tfrac{1}{2})\hbar\omega_1 + \cdots + (n_i+\tfrac{1}{2})\hbar\omega_i + \cdots + (n_N+\tfrac{1}{2})\hbar\omega_N$$

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

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$$Z = \sum_{\substack{\text{All N-particle}\\ \text{states } i}} e^{-\beta E_i} \qquad \text{(definition)}$$

$$Z = \underbrace{\sum_{n_1=0}^{\infty}\cdots\sum_{n_i=0}^{\infty}\cdots\sum_{n_N=0}^{\infty}}_{\substack{\text{summing over all}\\ \text{N-oscillator states}}} e^{-\beta\overbrace{\left[(n_1+\frac{1}{2})\hbar\omega_1+\cdots+(n_i+\frac{1}{2})\hbar\omega_i+\cdots+(n_N+\frac{1}{2})\hbar\omega_N\right]}^{E(\{n_i\})}}$$

(Done!)

$$= \underbrace{\left(\sum_{n_1=0}^{\infty} e^{-\beta(n_1+\frac{1}{2})\hbar\omega_1}\right)}_{z_1}\cdots\underbrace{\left(\sum_{n_i=0}^{\infty} e^{-\beta(n_i+\frac{1}{2})\hbar\omega_i}\right)}_{z_i}\cdots\underbrace{\left(\sum_{n_N=0}^{\infty} e^{-\beta(n_N+\frac{1}{2})\hbar\omega_N}\right)}_{z_N}$$

$$= z_1 \cdots z_i \cdots z_N$$

$$= z_1 \cdot z_2 \cdots z_i \cdots z_N \qquad \left[\underline{Z \text{ is factorized}}\right] \quad \left(\begin{array}{c}\text{independent}\\ \text{distinguishable}\end{array}\right)$$

$$= \prod_{i=1}^{N} \underbrace{z_i}_{\uparrow} \qquad \text{(Key result)}$$

single-oscillator partition function ($i^{th}$ oscillator)

with $$z_i = \underbrace{\sum_{n_i=0}^{\infty}}_{\uparrow} e^{-\beta(n_i+\frac{1}{2})\hbar\omega_i}$$

over single-oscillator states

$$F = -kT\ln Z = -kT\ln\left(\prod_{i=1}^{N} z_i\right) = \sum_{\substack{i=1\\ \uparrow}}^{N}\Big(\overbrace{-kT\ln z_i}^{i^{th}\text{ oscillator's contribution}}\Big)$$

sum over oscillators

## Statistical physics of one oscillator: Canonical Ensemble

- All we need to do is to evaluate $z$ of one oscillator
- Let $\omega$ be the characteristic frequency

$$z = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega}$$

single-oscillator partition function

Work it out...

$$z = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n}\, e^{-\frac{\beta\hbar\omega}{2}} = e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n}$$

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

$$\therefore \boxed{z = \frac{e^{-\frac{\beta\hbar\omega}{2}}}{1-e^{-\beta\hbar\omega}}}$$

Done! Exact!

- Mean energy of one oscillator

$$\langle E\rangle_{\text{one oscillator}} = -\frac{1}{z}\frac{\partial z}{\partial \beta} = -\frac{\partial}{\partial \beta}\ln z$$

$$= \frac{1}{2}\hbar\omega + \underbrace{\frac{\hbar\omega}{e^{\beta\hbar\omega}-1}} \equiv \frac{1}{2}\hbar\omega + \overbrace{\langle n\rangle}\hbar\omega$$

$\uparrow$ Ground state (zero-point) energy (must be there)

average excitation energy of an oscillator of freq. $\omega$ at temp. $T$

$$\boxed{\langle n\rangle \equiv \frac{1}{e^{\beta\hbar\omega}-1}}$$

$\uparrow$ mean excitation of an oscillator at temp. $T$

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

$\uparrow$ mean excitation of an oscillator of freq. $\omega$ at temp. $T$

- Not an integer, what does it mean?
- look familiar? Saw it in black-body radiation formula (not surprising: EM fields are oscillating)
- look familiar? (Bose-Einstein distribution with $\mu=0$)

- Heat capacity contributed by one oscillator

$$C_{\text{one oscillator}} = \frac{\partial}{\partial T}\langle E\rangle_{\text{one oscillator}} = \frac{\partial}{\partial T}\left(\frac{\hbar\omega}{e^{\frac{\hbar\omega}{kT}}-1}\right) \quad \text{(Why?)}$$

$$= \frac{\hbar^2\omega^2}{kT^2}\frac{e^{\frac{\hbar\omega}{kT}}}{\left(e^{\frac{\hbar\omega}{kT}}-1\right)^2} \quad \text{(Ex.)}$$

$$= k\left(\frac{\hbar\omega}{kT}\right)^2 \underbrace{\frac{e^{\frac{\hbar\omega}{kT}}}{\left(e^{\frac{\hbar\omega}{kT}}-1\right)^2}}_{\text{function of }\left(\frac{\hbar\omega}{kT}\right)\text{ only}}$$

$\uparrow$ right units

$$E(x) = \frac{x^2 e^x}{(e^x-1)^2} \equiv \text{Einstein's function}$$

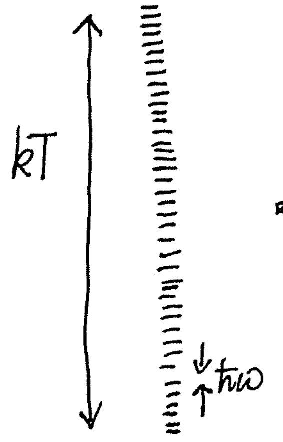
- One oscillator ($\omega$): High temp. vs Low temp.

## (a) High temperatures

$kT \gg \hbar\omega$ thermal energy $\gg$ energy scale ($\hbar\omega$) set by oscillator

discrete nature of spectrum becomes unimportant

$\Rightarrow$ classical limit



($kT \gg \hbar\omega$)

Physical Sense

- Oscillator has access to many excited states, about $\left(\frac{kT}{\hbar\omega}\right)$ of them.

$\frac{\hbar\omega}{kT} \ll 1$

$$\Rightarrow e^{\frac{\hbar\omega}{kT}} - 1 \approx 1 + \frac{\hbar\omega}{kT} - 1 = \frac{\hbar\omega}{kT}$$

$$\therefore \langle E \rangle_{\text{one oscillator}} = \underbrace{\frac{1}{2}\hbar\omega}_{\text{ground state energy}} + \frac{\hbar\omega}{e^{\frac{\hbar\omega}{kT}}-1} \approx \underbrace{\frac{1}{2}\hbar\omega}_{\text{tiny compared with } kT} + kT \approx kT$$

$$\langle E \rangle_{\text{one oscillator}} = \underbrace{kT = 2\cdot\left(\frac{1}{2}kT\right)}_{\text{an example of equipartition theorem in classical statistical mechanics}}$$

> Equipartition of Energy
>
> For every term which enters quadratically into the energy, its average value is $\frac{1}{2}kT$ in the high-temperature (classical) limit.

Meaning: Oscillator

$$H = \underbrace{\frac{p^2}{2m}}_{\text{quadratic}} + \frac{1}{2}m\omega^2 \overset{\text{quadratic}}{x^2}$$

$$\frac{1}{2}kT + \frac{1}{2}kT = kT$$

in classical limit.

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It follows that at high temperatures

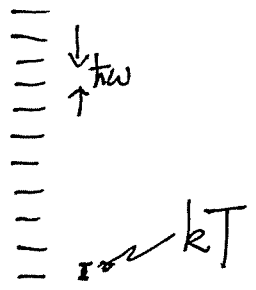
$$C_{\text{one-oscillator}} = \frac{\partial}{\partial T}(kT) = k$$

- Contributes $k$ to heat capacity at high temperature
- a constant contribution

[look familiar? Contributes $R = N_A k$ to $C_{\text{molar}}$ in a gas of diatomic molecules (due to vibrations)]

## (b) Low temperatures

$kT \ll \hbar\omega$ or $\frac{\hbar\omega}{kT} \gg 1$



$kT \ll \hbar\omega$ hard to access excited states

$$\langle E \rangle_{\text{one oscillator}} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\frac{\hbar\omega}{kT}}-1}$$

$$\approx \frac{1}{2}\hbar\omega + \underbrace{\hbar\omega\, e^{-\frac{\hbar\omega}{kT}}}_{\text{exponentially small}^{\dagger}}$$

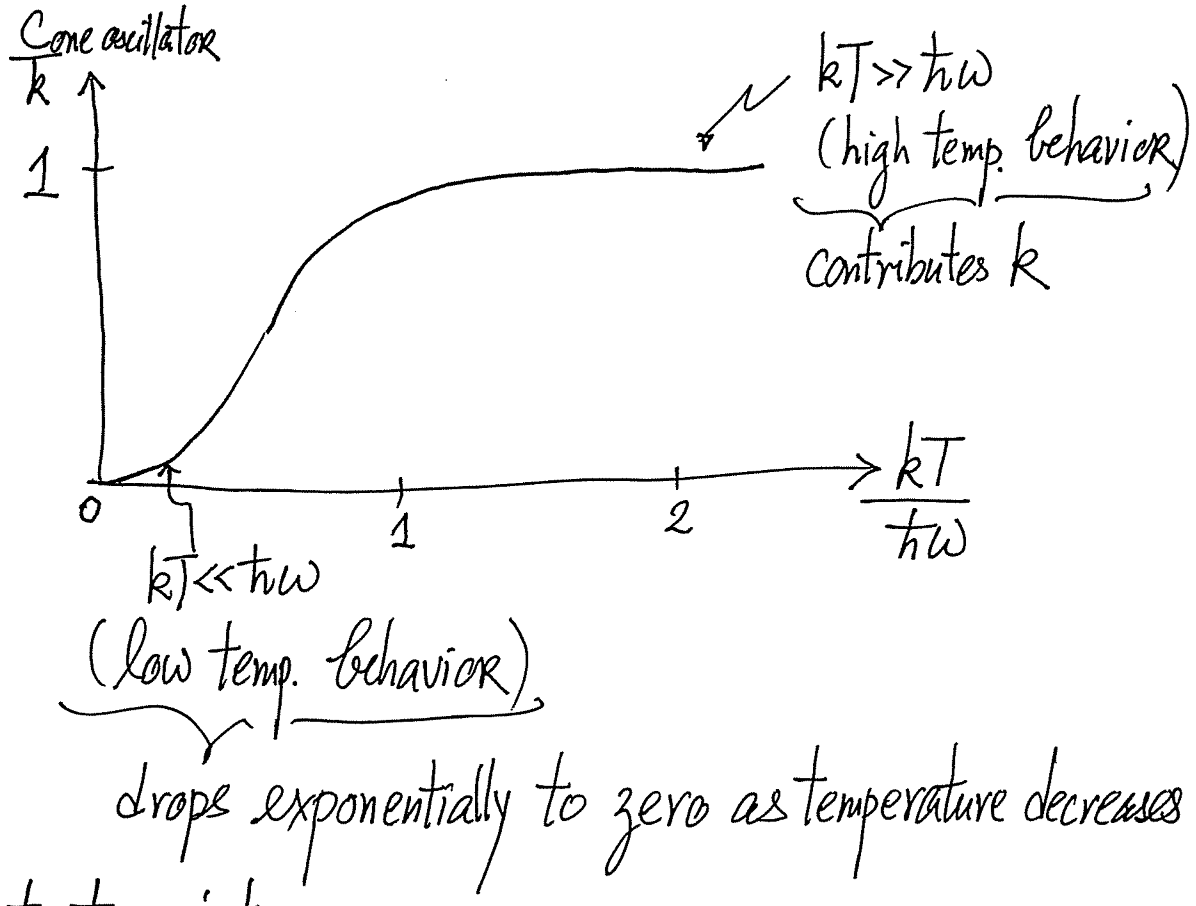
$$C_{\text{one oscillator}} = \frac{\partial}{\partial T}\left(\hbar\omega e^{-\frac{\hbar\omega}{kT}}\right)$$

$$= \underset{\text{right units}}{k} \left(\frac{\hbar\omega}{kT}\right)^2 \underbrace{e^{-\frac{\hbar\omega}{kT}}}_{\text{dominating behavior}} \rightarrow 0 \text{ as } T \rightarrow 0$$

(as $e^{-\frac{\hbar\omega}{kT}} \rightarrow 0$ faster)

† Here, the discrete nature of spectrum is important. $\langle E \rangle_{\text{one oscillator}}$ and $C_{\text{one oscillator}}$ drop because oscillator can't access excited states!

$$C_{\text{one oscillator}} = k\left(\frac{\hbar\omega}{kT}\right)^2 \frac{e^{\frac{\hbar\omega}{kT}}}{\left(e^{\frac{\hbar\omega}{kT}}-1\right)^2}$$



Important points

- Given oscillator, thus $\hbar\omega$, there exists temperatures $kT \ll \hbar\omega$ that the oscillator ceases to contribute to the heat capacity
- For $kT \gg \hbar\omega$, an oscillator contributes a constant $k$ to the heat capacity

- Helmholtz Free Energy of one oscillator

$$F_{\text{one oscillator}} = -kT\ln z = -kT\left[\ln\left(e^{-\frac{\beta\hbar\omega}{2}}\right) - \ln\left(1-e^{-\beta\hbar\omega}\right)\right]$$

$$= \underset{\substack{\uparrow \\ \text{ground state} \\ \text{energy}}}{\frac{\hbar\omega}{2}} + \underbrace{kT\ln\left(1-e^{-\frac{\hbar\omega}{kT}}\right)}_{\text{due to excitation}} \quad [\text{General}]$$

- Entropy of one oscillator

$$S_{\text{one oscillator}} = -\frac{\partial F_{\text{one oscillator}}}{\partial T}$$

$$= k\left[\frac{\frac{\hbar\omega}{kT}}{e^{\frac{\hbar\omega}{kT}}-1} - \ln\left(1-e^{-\frac{\hbar\omega}{kT}}\right)\right]$$

[General]

High Temperatures ($kT \gg \hbar\omega$)

$$S_{\text{one oscillator}} \to k\ln\left(\frac{kT}{\hbar\omega}\right)$$

Why? Physical Meaning?

Low Temperatures ($kT \ll \hbar\omega$)

$$S_{\text{one oscillator}} \to k\left(\frac{\hbar\omega}{kT}\right)e^{-\frac{\hbar\omega}{kT}} \to \underset{\substack{\uparrow \\ \text{as required by 3rd law}}}{0} \quad \left(\text{as } e^{-\frac{\hbar\omega}{kT}} \to 0 \text{ faster}\right)$$

## What about a collection of N oscillators?

- $$Z = \prod_{i=1}^{N} z_i = \underbrace{\prod_{i=1}^{N}}_{\text{Product over oscillators}} \frac{e^{-\frac{\beta\hbar\omega_i}{2}}}{1-e^{-\beta\hbar\omega_i}}$$

- Mean Energy

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z = \underbrace{\sum_{i=1}^{N}}_{\text{sum over oscillators}}\left[\frac{1}{2}\hbar\omega_i + \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i}-1}\right] = \sum_{i=1}^{N}\left[\frac{1}{2}\hbar\omega_i + \langle n_i\rangle\hbar\omega_i\right]$$

- Heat Capacity

$$C = \frac{\partial\langle E\rangle}{\partial T} = \underbrace{\sum_{i=1}^{N}}_{\text{sum over oscillators}} k\left(\frac{\hbar\omega_i}{kT}\right)^2 \frac{e^{\frac{\hbar\omega_i}{kT}}}{\left(e^{\frac{\hbar\omega_i}{kT}}-1\right)^2}$$

- Helmholtz Free energy

$$F = -kT\ln Z = \underbrace{\sum_{i=1}^{N}}_{\text{sum over oscillators}}\left[\frac{\hbar\omega_i}{2} + kT\ln\left(1-e^{-\frac{\hbar\omega_i}{kT}}\right)\right]$$

- Entropy

$$S = -\frac{\partial F}{\partial T} = \frac{\langle E\rangle - F}{T} = \underbrace{\sum_{i=1}^{N}}_{\text{sum over oscillators}} k\left[\frac{\frac{\hbar\omega_i}{kT}}{e^{\frac{\hbar\omega_i}{kT}}-1} - \ln\left(1-e^{-\frac{\hbar\omega_i}{kT}}\right)\right]$$

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## Apply the results to Heat Capacity of Solids

- A famous and practical problem
- N atoms forming an array (Solid)

Data show...

High temperature limit (See data)

$C_{\text{molar}}$ = molar heat capacity $\simeq 25\ \mathrm{J\,K^{-1}\,mol^{-1}}$

(Dulong-Petit "law" 1819)

Why?

High-temp. limit: $k$ for one oscillator

An atom could vibrate along $x, y, z$ directions

$\Rightarrow 3k$

N atoms: $C = 3Nk$

$$C_{\text{molar}} = 3\underbrace{N_A k}_{} = 3R = 24.94\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

As T drops, C drops

Why?

What is the behavior of $C(T)$ at low temperature?

VI-㊽

- $C_p$ of elements at 25°C (room temperature)
- Some are not in solid form at 25°C

Extracted from *Understanding the properties of matter* by Michael de Podesta.

For more details see **www.physicsofmatter.com**

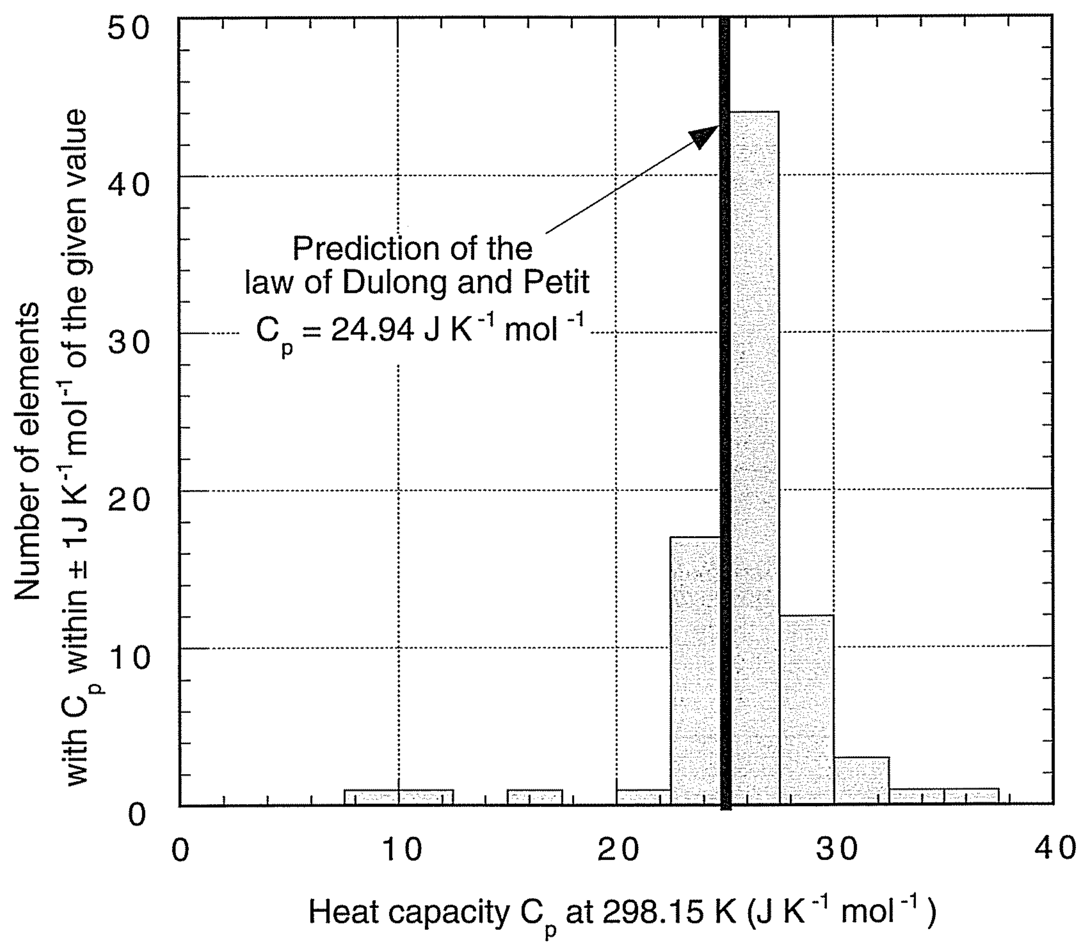
**Table 7.10** The molar heat capacity at constant pressure $C_P$ of the elements at room temperature 25 °C (298.15K). The shaded data are elements that are either liquids or gases at this temperature.

| Z | Element | A | $\rho$ (kg $m^{-3}$) | $C_P$ (J K $mol^{-1}$) | Z | Element | A | $\rho$ (kg $m^{-3}$) | $C_P$ (J K $mol^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Hydrogen, H | 1.008 | 89 | 28.824 | 49 | Indium, In | 114.8 | 7290 | 26.74 |
| 2 | Helium, He | 4.003 | 120 | 20.786 | 50 | Tin, Sn | 118.7 | 7285 | 26.99 |
| 3 | Lithium , Li | 6.941 | 533 | 24.770 | 51 | Antimony, Sb | 121.7 | 6692 | 25.23 |
| 4 | Beryllium, Be | 9.012 | 1846 | 16.44 | 52 | Tellurium, Te | 127.6 | 6247 | 25.73 |
| 5 | Boron, B | 10.81 | 2466 | 11.09 | 53 | Iodine, I | 126.9 | 4953 | 54.438 |
| 6 | Carbon (graphite), C | 12.01 | 2266 | 8.53 | 54 | Xenon, Xe | 131.3 | 3560 | 20.786 |
| 6 | Carbon (diamond), C | 12.01 | 3513 | 6.11 | 55 | Caesium, Cs | 132.9 | 1900 | 32.17 |
| 7 | Nitrogen, N | 14.01 | 1035 | 29.125 | 56 | Barium, Ba | 137.3 | 3594 | 28.07 |
| 8 | Oxygen, O | 16.00 | 1460 | 29.355 | 57 | Lanthanum, La | 138.9 | 6174 | 27.11 |
| 9 | Fluorine, F | 19.00 | 1140 | 31.300 | 58 | Cerium, Ce | 140.1 | 6711 | 26.94 |
| 10 | Neon, Ne | 20.18 | 1442 | 20.786 | 59 | Praseodymium, Pr | 140.9 | 6779 | 27.20 |
| 11 | Sodium, Na | 22.99 | 966 | 28.24 | 60 | Neodymium, Ne | 144.2 | 7000 | 27.45 |
| 12 | Magnesium, Mg | 24.31 | 1738 | 24.89 | 61 | Promethium, Pm | 145.0 | 7220 | 26.81 |
| 13 | Aluminium, Al | 26.98 | 2698 | 24.35 | 62 | Samarium, Sm | 150.4 | 7536 | 29.54 |
| 14 | Silicon, Si | 28.09 | 2329 | 20.0 | 63 | Europium, Eu | 152.0 | 5248 | 27.66 |
| 15 | Phosphorus, P | 30.97 | 1820 | 23.84 | 64 | Gadolinium, Gd | 157.2 | 7870 | 37.03 |
| 16 | Sulphur, S | 32.06 | 2086 | 22.64 | 65 | Terbium, Tb | 158.9 | 8267 | 28.91 |
| 17 | Chlorine, Cl | 35.45 | 2030 | 33.907 | 66 | Dysprosium, Dy | 162.5 | 8531 | 28.16 |
| 18 | Argon, Ar | 39.95 | 1656 | 20.786 | 67 | Holmium, Ho | 164.9 | 8797 | 27.15 |
| 19 | Potassium, K | 39.10 | 862 | 29.58 | 68 | Erbium, Er | 167.3 | 9044 | 28.12 |
| 20 | Calcium, Ca | 40.08 | 1530 | 25.31 | 69 | Thulium, Th | 168.9 | 9325 | 27.03 |
| 21 | Scandium, Sc | 44.96 | 2992 | 25.52 | 70 | Ytterbium, Yb | 173.0 | 6966 | 26.74 |
| 22 | Titanium, Ti | 47.90 | 4508 | 25.02 | 71 | Lutetium, Lu | 175.0 | 9842 | 26.86 |
| 23 | Vanadium, V | 50.94 | 6090 | 24.89 | 72 | Hafnium, Hf | 178.5 | 13276 | 25.73 |
| 24 | Chromium, Cr | 52.00 | 7194 | 23.35 | 73 | Tantalum, Ta | 180.9 | 16670 | 25.36 |
| 25 | Manganese, Mn | 54.94 | 7473 | 26.32 | 74 | Tungsten, W | 183.9 | 19254 | 24.27 |
| 26 | Iron, Fe | 55.85 | 7873 | 25.10 | 75 | Rhenium, Re | 186.2 | 21023 | 25.48 |
| 27 | Cobalt, Co | 58.93 | 8800 | 24.81 | 76 | Osmium, Os | 190.2 | 22580 | 24.70 |
| 28 | Nickel, Ni | 58.70 | 8907 | 26.07 | 77 | Iridium, Ir | 192.2 | 22550 | 25.10 |
| 29 | Copper, Cu | 63.55 | 8933 | 24.44 | 78 | Platinum, Pt | 195.1 | 21450 | 25.86 |
| 30 | Zinc, Zn | 65.38 | 7135 | 25.40 | 79 | Gold, Au | 197.0 | 19281 | 25.42 |
| 31 | Gallium, Ga | 69.72 | 5905 | 25.86 | 80 | Mercury, Hg | 200.6 | 13546 | 27.98 |
| 32 | Germanium, Ge | 72.59 | 5323 | 23.35 | 81 | Thallium, Th | 204.4 | 11871 | 26.32 |
| 33 | Arsenic, As | 74.92 | 5776 | 24.64 | 82 | Lead, Pb | 207.2 | 11343 | 26.44 |
| 34 | Selenium, Se | 78.96 | 4808 | 25.36 | 83 | Bismuth, Bi | 209.0 | 9803 | 25.52 |
| 35 | Bromine, Br | 79.90 | 3120 | 75.69 | 84 | Polonium, Po | 209 | 9400 | 25.75 |
| 36 | Krypton, Kr | 83.80 | 3000 | 20.79 | 85 | Astatine, At | 210 |  |  |
| 37 | Rubidium, Rb | 85.47 | 1533 | 31.06 | 86 | Radon, Rn | 222 | 4400 | 20.786 |
| 38 | Strontium, Sr | 87.62 | 2583 | 26.40 | 87 | Francium, Fr | 223 | 2410 | 31.70 |
| 39 | Yttrium, Y | 88.91 | 4475 | 26.53 | 88 | Radium, Ra | 226 | 5000 | 25.76 |
| 40 | Zirconium, Zr | 91.22 | 6507 | 25.36 | 89 | Actinium, Ac | 227 | 10060 | 27.20 |
| 41 | Niobium, Nb | 92.91 | 8578 | 24.60 | 90 | Thorium, Th | 232 | 11725 | 27.32 |
| 42 | Molybdenum, Mo | 95.94 | 10222 | 24.06 | 91 | Protractinium, Pa | 231 | 15370 | 27.20 |
| 43 | Technetium, Tc | 97 | 11496 | 25.88 | 92 | Uranium, U | 238 | 19050 | 27.66 |
| 44 | Ruthenium, Ru | 101.1 | 12360 | 24.06 | 93 | Neptunium, Np | 237 | 20250 | 29.62 |
| 45 | Rhodium, Rh | 102.9 | 12420 | 24.98 | 94 | Plutonium, Pu | 244 | 19840 | 32.80 |
| 46 | Palladium, Pd | 106.4 | 11995 | 25.98 | 95 | Americium, Am | 243 | 13670 | 25.86 |
| 47 | Silver, Ag | 107.9 | 10500 | 25.35 | 96 | Curium, Cm | 247 | 1330 | 27.70 |
| 48 | Cadmium, Cd | 112.4 | 8647 | 25.98 |  |  |  |  |  |

More than 50% with $C_p \sim 25\ J\,K^{-1}mol^{-1}$ (range: 22-32 $J\,K^{-1}mol^{-1}$)

# Data at 25°C plotted in a histogram

**Figure 7.23** Histogram of the heat capacities at constant pressure $C_P$ of the solid elements in J $K^{-1}$ $mol^{-1}$ at room temperature 25 °C = 298.15 K (also shown as Figure 7.18). The bold line shows the prediction of Equation (7.42) for the heat capacity of all elements.



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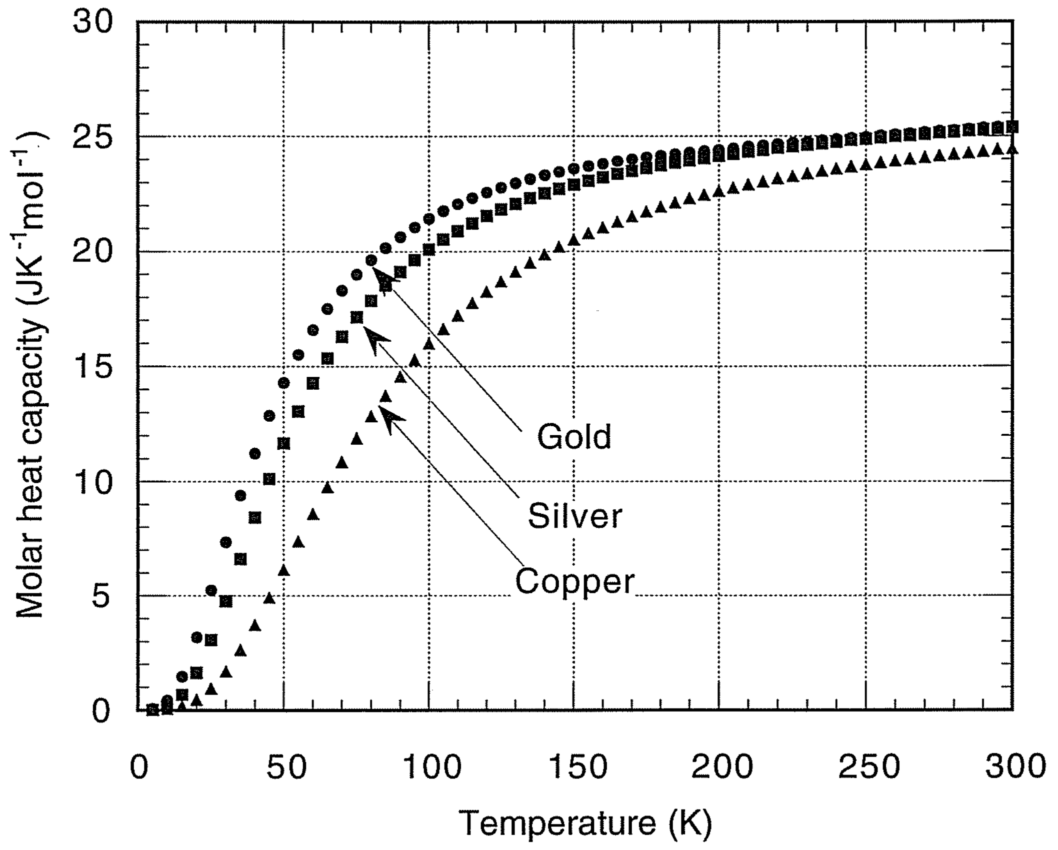
# Temperature dependence

**Figure 7.19** The variation with temperature of the molar heat capacity of copper, silver and gold. All three curves tend to a value ≈ 25J $K^{-1}$ $mol^{-1}$ at high temperatures in accord with the results of Table 7.10 and Figure 7.18. At low temperatures all three curves tend to zero.



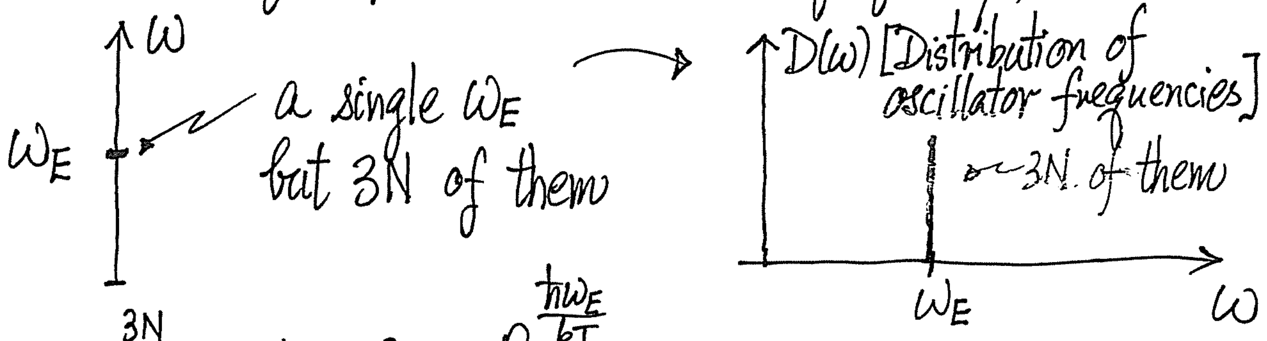
Question:

- What is the physics behind C(T)?

Statistical physics of a collection of oscillators!

## (a) Einstein's model (1907)

- 3N oscillators (N atoms in 3D solid)
- All oscillators have the same angular frequency $\omega_E$ ("Einstein frequency")



$$C = \sum_{i=1}^{3N} k\left(\frac{\hbar\omega_E}{kT}\right)^2 \frac{e^{\frac{\hbar\omega_E}{kT}}}{\left(e^{\frac{\hbar\omega_E}{kT}}-1\right)^2}$$

$$= 3Nk\left(\frac{\hbar\omega_E}{kT}\right)^2 \frac{e^{\frac{\hbar\omega_E}{kT}}}{\left(e^{\frac{\hbar\omega_E}{kT}}-1\right)^2}$$

$$= 3Nk\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{\left(e^{\theta_E/T}-1\right)^2}$$

$$\theta_E \equiv \frac{\hbar\omega_E}{k}$$

{Einstein's temperature
a material's parameter

Does it work?

Einstein's model: For insulators
(Metals: need to include contributions by electrons)

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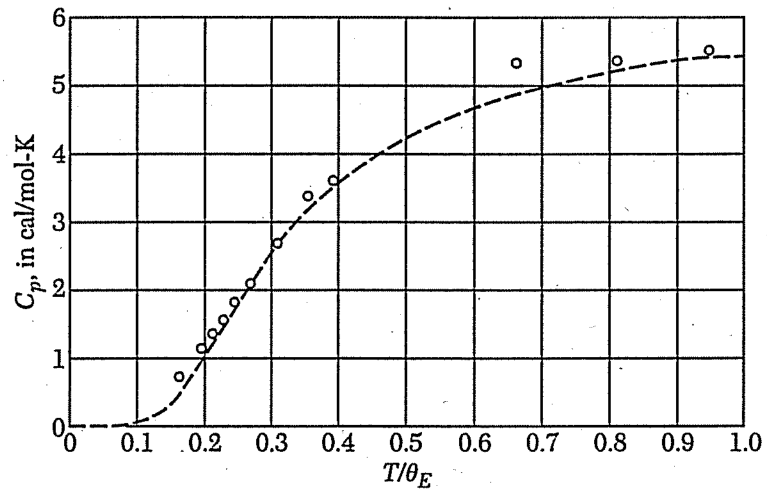
Once Upon a time...

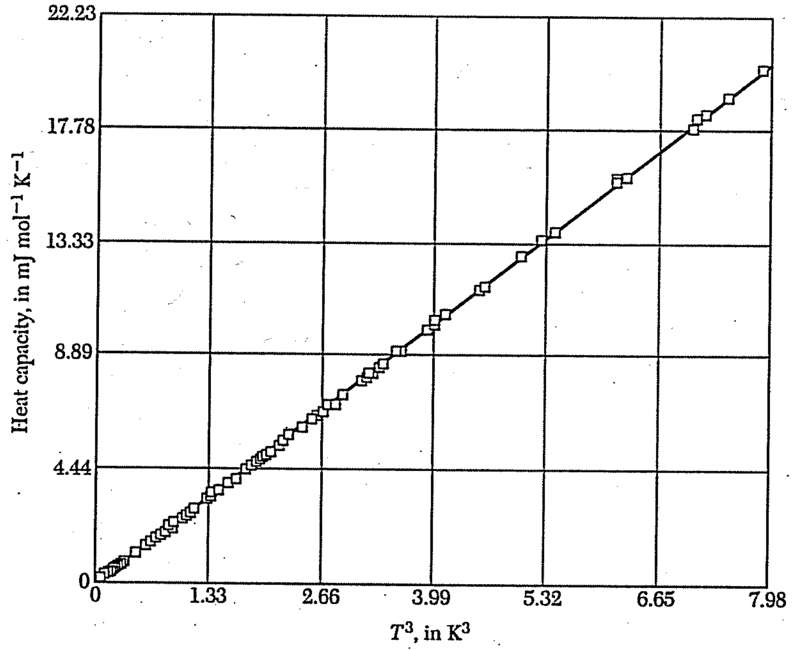


- Diamond Heat capacity
- Line: Eintein's theory (1907)
- Data (1875)

Line fitted to data using $\hbar\omega_E/k = 1320$ K

Looks "OK". BUT...

Later experiments found



- Solid Argon
  But better data at low temp. show that C drops to 0 as $T^3$ at low temp.

i.e. low temperature behavior is $C \sim T^3$ instead of exponential.

Figures taken from Kittel, "Introduction to Solid State Physics".

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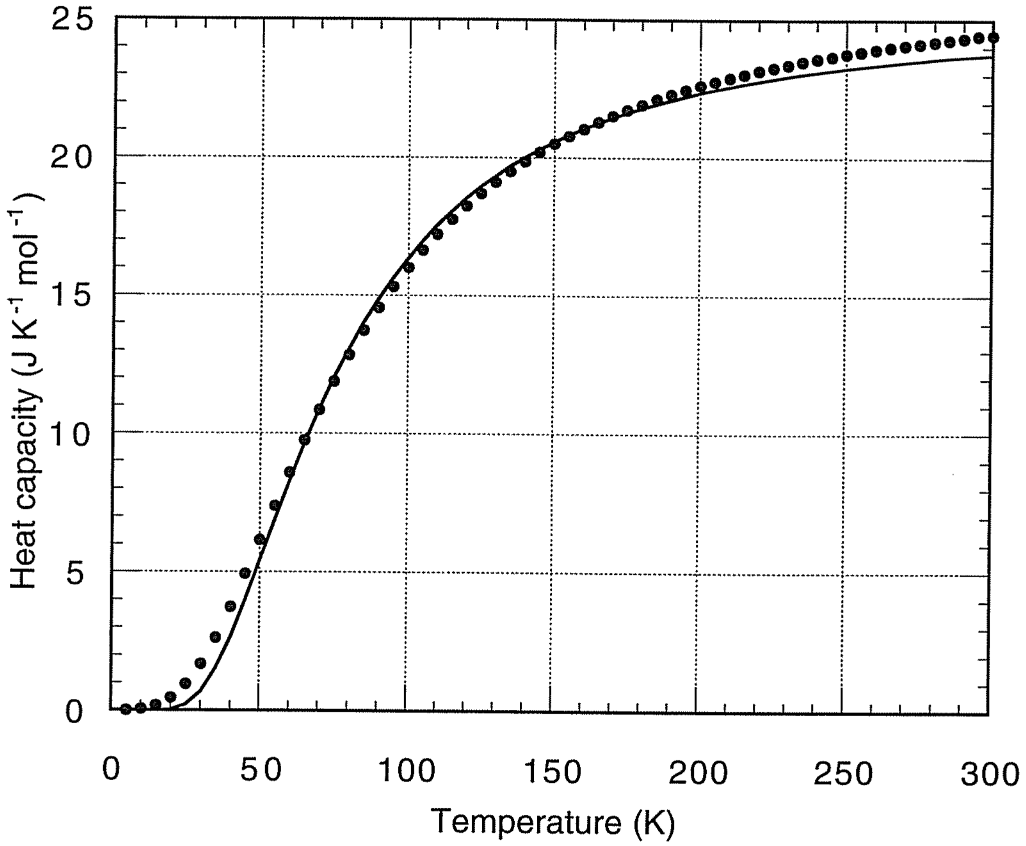
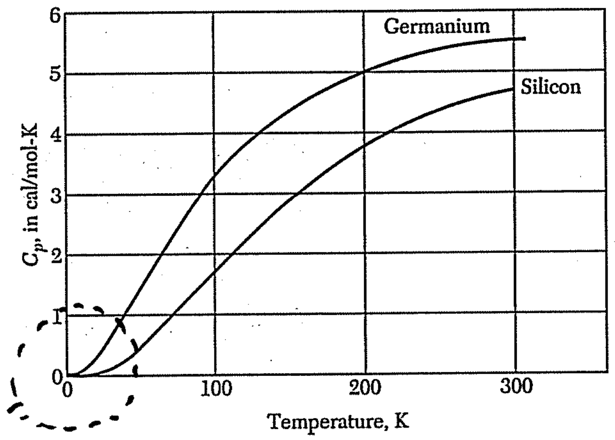
**Figure 7.25** The heat capacity of copper from Figure 7.19 plotted together with the Einstein prediction for the heat capacity based on $\Theta_E = 230$ K. The predicted Einstein temperature corresponds to a spring constant of $K = 2.423$ J m$^{-2}$, and a frequency of vibration of $f_0 = 4.79 \times 10^{12}$ Hz It is clear that the theory captures the trend of the data. However, careful examination shows that the agreement between the theory and experiment becomes poor at low temperatures. **Note:** The Einstein theory prediction is for $C_V$, but the data with which it is compared is based on $C_P$.



- Data — Line (Einstein model)
- Not bad! Capture the trend quite well!
- But Einstein's theory <u>drops too rapidly</u> with temperature at low temperatures when compared with data.
- What's wrong? (See Debye Model)



Ge, Si
(Semiconductors)

Detail analysis shows $C \sim T^3$ at low temperatures

<u>What's right?</u>

Einstein's model → $C_{\text{molar}} \to 3R$ at high temp. (Dulong-Petit)
→ $C \to 0$ as $T \to 0$

Einstein's model was the first model of this behavior

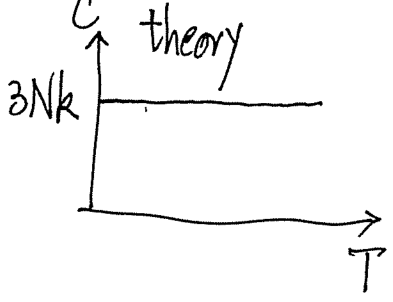
<u>What's wrong?</u>

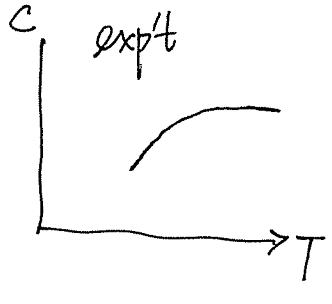
- $C \to 0$ as $T \to 0$ too fast

[All oscillators cease to contribute when $kT \ll \hbar\omega_E$]

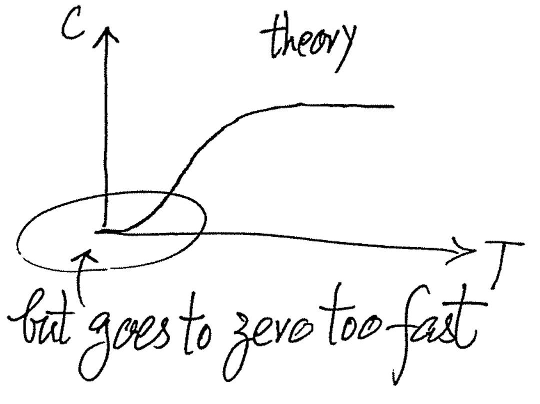
Observed experimentally: $C(T) \sim T^3$

Before Einstein's Model





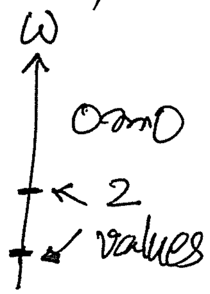
With Einstein's model



## (b) Debye Model (Key ideas) (1912)

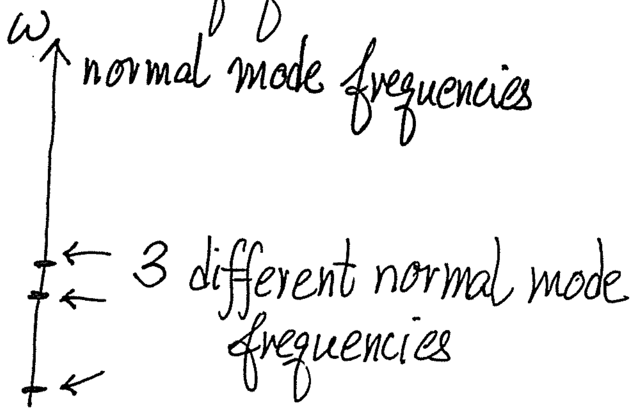
- 3N oscillators
- But $\omega_i$ $(i=1,\dots,3N)$ should not be the same
- Why?
  Atom vibrations are coupled by chemical bonds
  (c.f. balls (atoms) connected by springs (bonds))

$\underbrace{\omega = 0}_{\text{CM motion}}$ and $\underbrace{\omega = \sqrt{\frac{k}{\mu}}}_{\text{relative motion}}$



(e.g. linear motions only)

⇒ Normal modes and normal mode frequencies



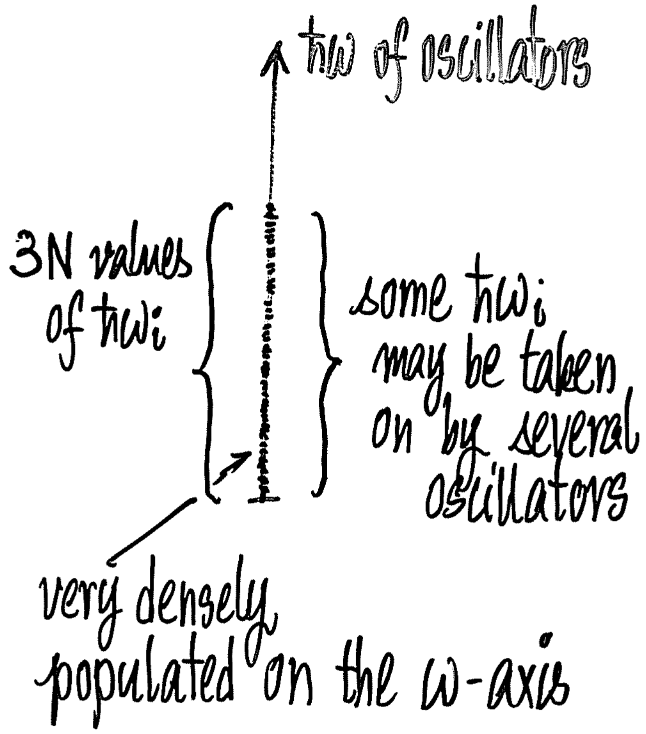
Recall: (Classical Mechanics)

- Each normal mode refers to an independent oscillation of the normal mode frequency
- A normal mode involves all atoms
- System can be treated as independent oscillators, but the frequencies are the normal mode frequencies.

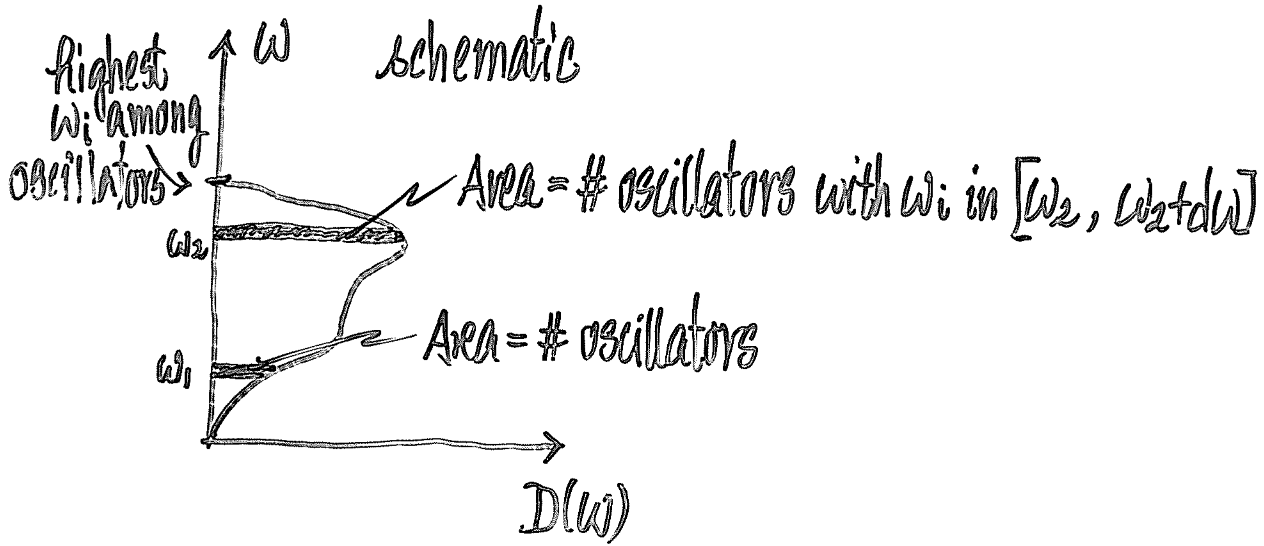
---

- Often N is hugh, $N \sim 10^{22}$ in a volume $V \sim cm^3$ (3D)

Let's say these 3N oscillators have $\omega_i$'s that are distributed between $\hbar\omega \sim 0$ to $\hbar\omega \sim 0.5\,eV$

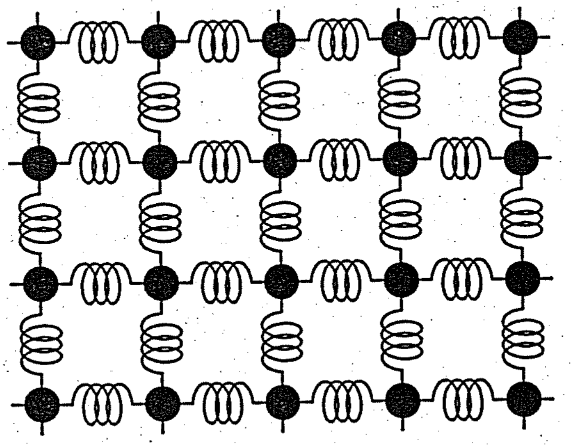


$D(\omega)\,d\omega$ = # oscillators with $\omega_i$ in the interval $\omega$ to $\omega + d\omega$



By construction, $\int_{\text{lowest value}}^{\text{highest value}} D(\omega)\,d\omega = 3N = \overbrace{\text{total number of oscillators (of normal mode frequencies)}}$

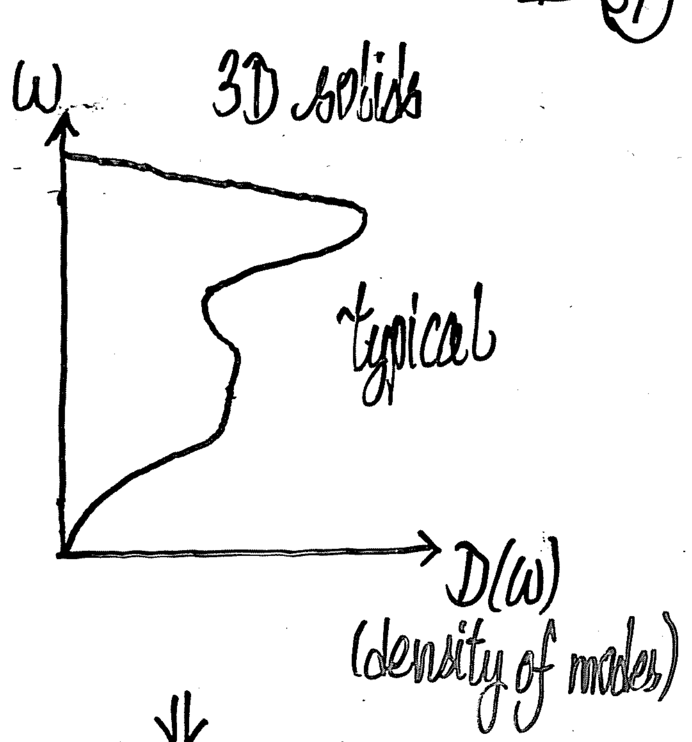
In a solid,



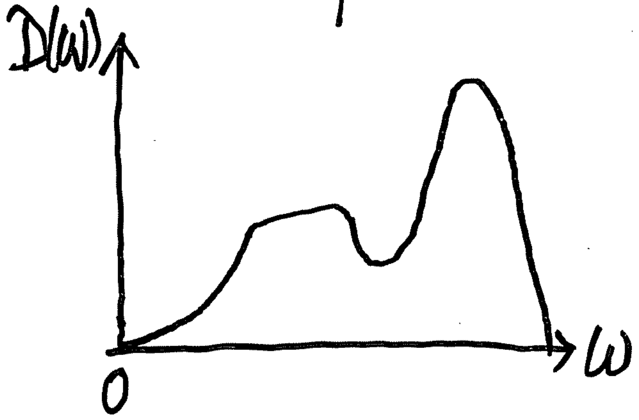
↑ schematic, should be a 3D structure (coupled oscillators)

But, we still have

$$\int D(\omega)d\omega = 3N$$

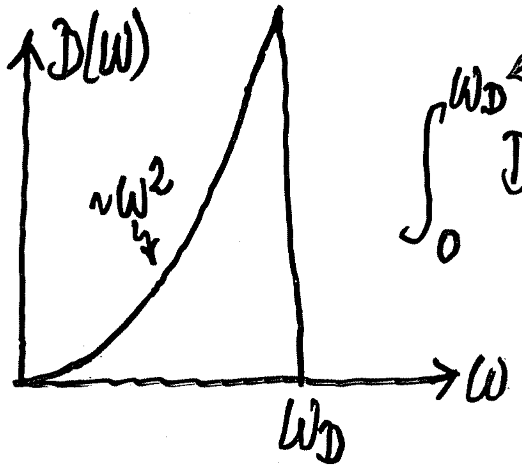


⇓ rotate the picture



**Debye:** (1912)

- should take into account of different ω's of the 3N independent oscillators (normal modes)
- Approximate:



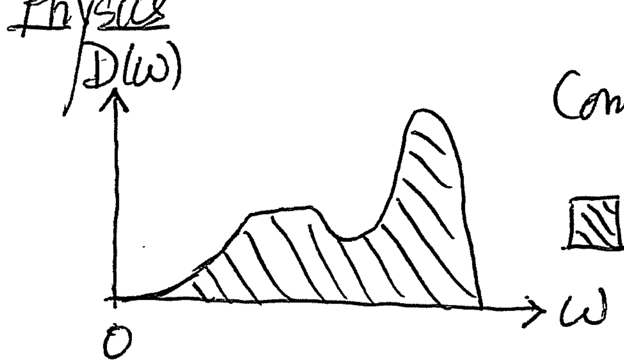
$$\int_0^{\omega_D} D(\omega)\,d\omega = 3N$$

$\omega_D$ ← a parameter

low-T behavior governs by low-ω modes

## Debye Model: Physics

- Actual D(ω) (3D solids)



Complicated!

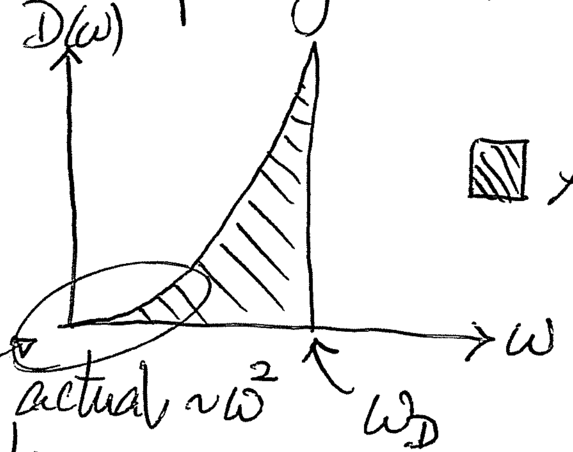
▨ Area under curve = 3N

- Einstein's Model: Discrepancies only at low temperatures

⇒ Should be more careful in dealing with normal modes (oscillators) of small ω's

deal with this part more carefully!
(this part goes like ω²)

- Debye: Approximated



▨ Area under curve = 3N (by adjusting $\omega_D$)

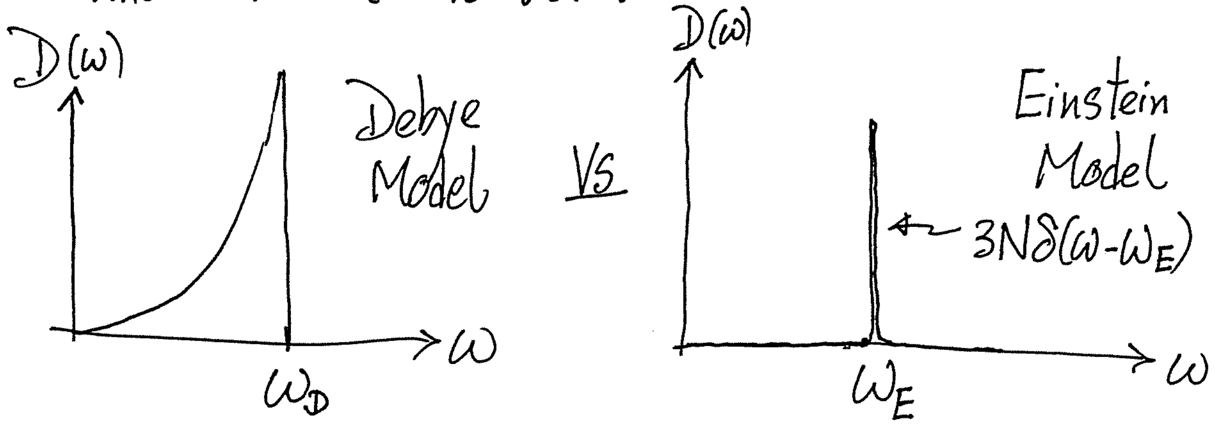
same as actual ~$\omega^2$ up to $\omega_D$

Debye frequency $\omega_D$

depending on material
[a material's parameter]

Thus, the points are ...

- Atoms are coupled by chemical bonds (springs), i.e. there are interactions
- Small oscillations - coupling is harmonic
- Normal modes & normal mode frequencies
- Each normal mode (say, with frequency ω) behaves as an independent oscillator
- But there is a distribution of frequencies among the normal modes
- Therefore, the idea of a collection of independent oscillators remains valid.
- Then we need the statistical mechanics of oscillators with different ω's. We know how to do that!



$C \sim T^3$ at low temperature [insulators]

Flow of ideas: $\langle E\rangle \rightarrow \frac{\partial\langle E\rangle}{\partial T}$ gives $C$

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

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

(using $D(\omega)d\omega$)

Debye:

$D(\omega) \propto \omega^2$ and cutoff at $\omega_D$

$$\therefore \int_0^{\omega_D} D(\omega)d\omega = A\int_0^{\omega_D}\omega^2 d\omega = 3N$$

$$\Rightarrow A\frac{\omega_D^3}{3} = 3N \Rightarrow A = \frac{9N}{\omega_D^3}$$

$$\therefore \boxed{D(\omega) = \frac{9N}{\omega_D^3}\cdot\omega^2}$$

$$\langle E\rangle = \underbrace{\frac{9N}{8}\hbar\omega_D}_{\text{just a constant for ground state energy}} + \underbrace{\frac{9N\hbar}{\omega_D^3}\int_0^{\omega_D}\frac{\omega^3 d\omega}{e^{\frac{\hbar\omega}{kT}}-1}}_{\text{gives T dependence of }\langle E\rangle}$$

$$\langle E\rangle = \underset{\text{energy}}{\text{G.S.}} + \frac{9N\hbar}{\omega_D^3}\underbrace{\int_0^{\omega_D}\frac{\omega^3\,d\omega}{e^{\frac{\hbar\omega}{kT}}-1}}$$

$$x \equiv \frac{\hbar\omega}{kT}\ ; \quad \omega = \left(\frac{kT}{\hbar}\right)x$$

$$\omega^3 d\omega = \left(\frac{kT}{\hbar}\right)^4 x^3 dx$$

$$\sim T^4 \int_0^{\frac{\hbar\omega_D}{kT}} \frac{x^3 dx}{e^x - 1}$$

low T ($kT \ll \hbar\omega_D$)

$$\sim T^4 \underbrace{\int_0^{\infty}\frac{x^3 dx}{e^x-1}}_{\text{just a number}}$$

$$\therefore \langle E\rangle = \underset{\text{energy}}{\text{G.S.}} + A T^4$$

$$\Rightarrow C = \frac{\partial\langle E\rangle}{\partial T} \sim T^3 \text{ at low temperature}$$

Done!

Ex: Work out the pre-factor.
See Solid State Physics under Lattice Vibrations and phonons.

# Debye Model Works!

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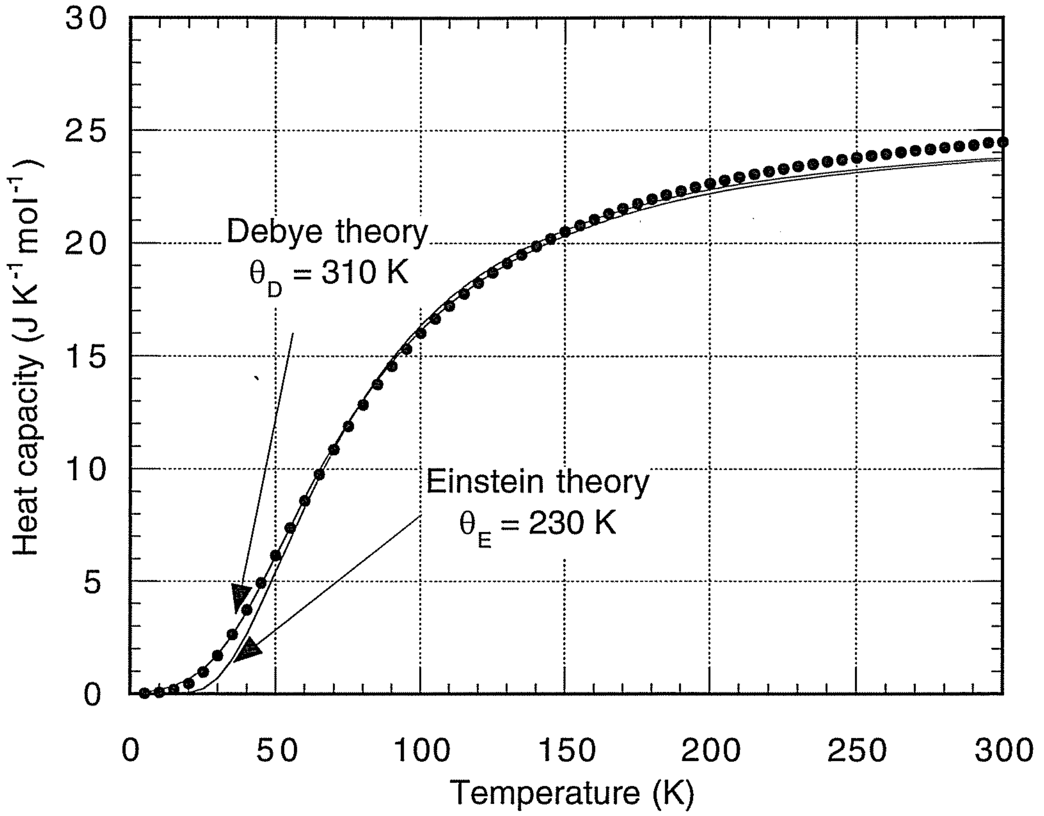
**Figure 7.29** The Debye prediction for the heat capacity of copper compared with the Einstein prediction shown in Figure 7.25.



- $\omega_D$ is a material parameter
- $\frac{\hbar\omega_D}{k} \equiv \theta_D$ = Debye temperature is also a material parameter
- In Debye Model, the contributions of oscillators to C do <u>not</u> drop rapidly at the same temperature as in Einstein model.
- <u>Given T</u>, those with $\hbar\omega \gg kT$ contribute little, but those oscillators (normal modes) with $\hbar\omega \lesssim kT$ still contribute to C.