

VII. Thermal Properties of Solids I

Mostly Phonons

A. The Heat Capacity of Solids

Experimentally, $C = \frac{\Delta Q}{\Delta T}$ (JK⁻¹)
 An input of heat energy

Heat capacity of an object
 temperature rise

To discuss heat capacity of a material,

use JK⁻¹kg⁻¹ (specific heat capacity)

JK⁻¹mol⁻¹ (molar heat capacity)

heat capacity of N_A = 6.023 x 10²³ atoms or molecules

Depending on method of measurement:

C_p or C_v

For solids, usually measure C_p.

Fortunately, since the expansivity of solids is small (α ~ 10⁻⁵ K⁻¹), C_p is typically only a few percent greater than C_v.

C_p of elements at 25°C

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.

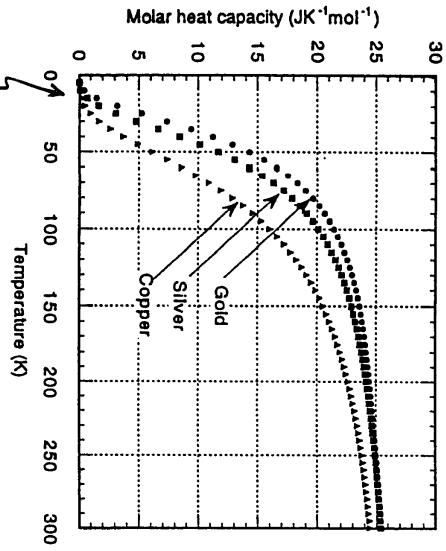
Z	Element	A	ρ	C _p	Z	Element	A	ρ	C _p
		(kg m ⁻³)	(J K mol ⁻¹)				(kg m ⁻³)	(J K mol ⁻¹)	
1	Hydrogen, H	1008	89	28.82	49	Indium, In	114.8	7290	26.74
2	Helium, He	4.003	230	20.786	50	Tin, Sn	118.7	7285	26.59
3	Lithium, Li	6.941	533	24.770	51	Antimony, Sb	121.7	6892	25.23
4	Beryllium, Be	9.012	1846	16.44	52	Tellurium, Te	127.6	6247	25.73
5	Boron, B	10.81	2466	11.09	53	Iodine, I	127.3	4933	54.78
6	Carbon (graphite), C	12.01	2266	8.53	54	Xenon, Xe	135.3	5501	20.786
7	Carbon (diamond), C	12.01	3513	6.11	55	Cesium, Cs	132.9	1900	32.17
8	Nitrogen, N	14.01	1033	29.125	56	Barium, Ba	137.3	3594	28.07
9	Oxygen, O	16.00	1450	29.355	57	Lanthanum, La	138.9	6174	27.11
10	Fluorine, F	19.00	1140	31.300	58	Cerium, Ce	140.1	6711	26.94
11	Neon, Ne	20.18	1442	20.786	59	Praseodymium, Pr	140.9	6779	27.20
12	Sodium, Na	22.99	966	28.24	60	Neodymium, Nd	144.2	7000	27.45
13	Magnesium, Mg	24.31	1738	24.89	61	Promethium, Pm	145.0	7220	26.81
14	Aluminium, Al	26.98	2698	24.35	62	Samarium, Sm	150.4	7536	29.54
15	Silicon, Si	28.09	2329	20.0	63	Europium, Eu	152.0	5248	27.66
16	Phosphorus, P	30.97	1820	23.84	64	Gadolinium, Gd	157.2	7870	37.03
17	Sulphur, S	32.06	2086	22.64	65	Terbium, Tb	158.9	8267	28.91
18	Chlorine, Cl	35.45	2030	33.907	66	Dysprosium, Dy	162.5	8531	28.16
19	Argon, Ar	39.95	1636	20.786	67	Holmium, Ho	164.9	8797	27.15
20	Potassium, K	39.10	862	29.58	68	Erbium, Er	167.3	9044	167.3
21	Calcium, Ca	40.08	1530	25.31	69	Thulium, Th	168.9	9325	27.03
22	Scandium, Sc	44.96	2992	25.52	70	Ytterbium, Yb	173.0	6966	26.74
23	Titanium, Ti	47.90	4508	25.02	71	Lutetium, Lu	175.0	9842	26.86
24	Vanadium, V	50.94	6090	24.89	72	Hafnium, Hf	178.5	13276	25.73
25	Chromium, Cr	52.00	7194	23.35	73	Tantalum, Ta	180.9	16670	25.36
26	Manganese, Mn	54.94	7473	26.32	74	Tungsten, W	183.9	19254	24.27
27	Iron, Fe	55.85	7873	25.10	75	Rhenium, Re	186.2	21023	25.48
28	Cobalt, Co	58.93	8900	24.81	76	Osmium, Os	190.2	22580	24.70
29	Nickel, Ni	58.70	8907	26.07	77	Iridium, Ir	192.2	22550	25.10
30	Copper, Cu	63.55	8933	24.44	78	Platinum, Pt	195.1	21450	25.86
31	Zinc, Zn	65.38	7135	25.40	79	Gold, Au	197.0	19261	25.42
32	Gallium, Ga	69.72	5905	25.86	80	Mercury, Hg	200.6	3546	27.98
33	Germanium, Ge	72.59	5323	23.35	81	Thallium, Tl	204.4	11871	26.32
34	Arsenic, As	74.92	5776	24.64	82	Lead, Pb	207.2	11343	26.44
35	Selenium, Se	78.96	4808	25.36	83	Bismuth, Bi	209.0	9803	25.52
36	Bromine, Br	79.90	3120	75.69	84	Polonium, Po	209	9400	25.75
37	Krypton, Kr	83.80	3000	20.79	85	Astatine, At	210	—	—
38	Ruddium, Rb	85.47	1533	31.06	86	Radon, Rn	222	—	—
39	Strontium, Sr	87.62	2583	26.40	87	Francium, Fr	223	2410	31.70
40	Yttrium, Y	88.91	4475	26.53	88	Radium, Ra	226	5000	25.76
41	Zirconium, Zr	91.22	6507	25.36	89	Actinium, Ac	227	10060	27.20
42	Niobium, Nb	92.91	8578	24.60	90	Thorium, Th	232	11725	27.32
43	Molybdenum, Mo	95.94	10222	24.06	91	Protactinium, Pa	231	15370	27.20
44	Technetium, Tc	97	11496	25.86	92	Uranium, U	238	19050	27.66
45	Ruthenium, Ru	101.1	12360	24.06	93	Neptunium, Np	237	20250	29.62
46	Rhodium, Rh	102.9	12420	24.98	94	Plutonium, Pu	244	19840	32.80
47	Palladium, Pd	106.4	11995	25.98	95	Americium, Am	243	13670	25.86
48	Silver, Ag	107.9	10500	25.35	96	Curium, Cm	247	1350	27.70
49	Cadmium, Cd	112.4	8647	25.98					

• More than 50% have C_p ~ 25 JK⁻¹mol⁻¹ (range: 22-32 JK⁻¹mol⁻¹)
 From "Understanding the Properties of Matter" by de Padesta.

• If we compare some other properties, e.g. conductivity, of solids, there can be some 10^{20} difference!

∴ There must be some simple explanation.

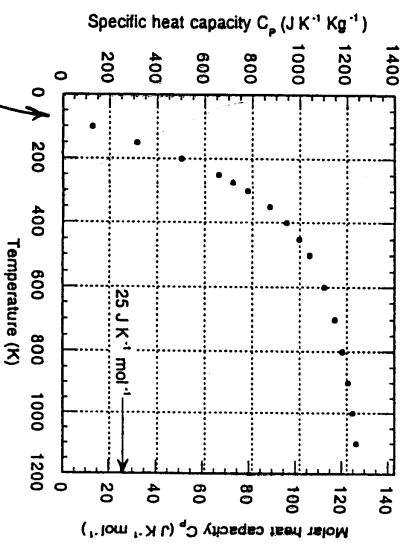
$C_p \propto T$



← $25 \text{ JK}^{-1} \text{ mol}^{-1}$

elements: Al, Ag, Cu

drops to zero as temperature decreases



← $25 = 5 \times 25 \text{ JK}^{-1} \text{ mol}^{-1}$

C_p of sapphire (Al_2O_3)

tends to drop to zero as temperature decreases

• Why the elements take on $\sim 25 \text{ JK}^{-1} \text{ mol}^{-1}$ at room temperature
 • Why does C_p drop with temperature and tend to zero?

B. Knowing harmonic approximation, but not quantum mechanics

Elements: 1 atom per primitive cell

⇒ $3N$ degrees of freedom in one mole ($N = \#$ primitive cells)

Harmonic approximations

⇒ after finding normal modes,

$3N$ independent oscillators

recall: the eigenfrequencies form

3 acoustic branches

For a classical harmonic oscillator:

$$h = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2$$

at temperature T

contributes $\frac{1}{2} kT$ to average energy $\bar{\epsilon}$

also contributes $\frac{1}{2} kT$ to average energy $\bar{\epsilon}$ "equipartition of energy"

For 3N oscillators treated classically (they could have different ω 's!): $U = \sum_{\text{all oscillators}} (2 \times \frac{1}{2} kT) + U_0$ a constant

internal energy $U = 3N \times (2 \times \frac{1}{2} kT) + U_0$

3 degrees of freedom per atom
atoms
each oscillator

$C_V = \frac{dU}{dT}$ (note: this is C_V , not C_p)

$= 3Nk$

Molar $C_V \Rightarrow N = N_A$

$\therefore C_V (\text{molar}) = 3N_A k = 3R$

$= 3 \times 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$
 $= 24.93 \text{ J K}^{-1} \text{ mol}^{-1}$

[Note: Solids' expansivity is small ($\sim 10^{-5} \text{ K}^{-1}$), and thus the volume change in a change in temperature is small \Rightarrow work done term in 1st law of thermodynamics is tiny.]

Thus, $C_p \approx C_V$.

If the assumption does not hold, then we expect $C_p > C_V$.]

$C_V (\text{molar}) = 3R \approx C_p (\text{molar})$ for more than 50% of the elements

- comes from classical treatment of harmonic oscillations
- lattice vibrations dominate the contributions to C_p at room temperature

(true even for metallic elements! Why? should the electrons also contribute?)

- harmonic approximation

\Rightarrow rely only on existence of equilibrium positions

and bonding mechanisms don't matter!

thus nearly same behavior for all elements!

This $C = 3R$ result is called the law of Dulong and Petit.

How about Al_2O_3 ?

- $\rho = 5$ atoms in a primitive cell
- $\Rightarrow 3\rho N$ degrees of freedom
- $\Rightarrow 3\rho N$ normal modes
- $\Rightarrow 3\rho N$ independent oscillators

$$U = \sum_{\text{all oscillators}} \bar{u}_{\text{each oscillator}} + U_0$$

$$= \sum_{\substack{3p \text{ branches} \\ \vec{q} \in \text{BZ}}}^S (kT) + U_0$$

$$= 3p N kT + U_0$$

$$C_V = 3p N k$$

$$C_V (\text{molar}) = p 3R$$

$$\text{Al}_2\text{O}_3: p=5 \Rightarrow C (\text{molar}) = 15R$$

agrees with measurement at high temperature

But, for classical oscillators

- No temperature dependence

$\Rightarrow C$ will not drop as T drops!

Need quantum treatment or phonons to explain $C(T)$

C. Treating oscillators quantum mechanically

After solving normal modes, we have

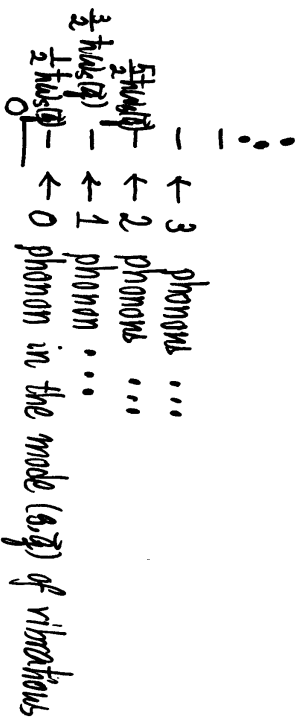
$$\omega_s(\vec{q}) \quad (3pN \text{ of them})$$

Labels $3p$ branches

These are independent oscillators.

- For one oscillator of angular frequency $\omega_s(\vec{q})$ QM says the energy spectrum for this mode is

$$(N_s, \vec{q} + \frac{1}{2}) \hbar \omega_s(\vec{q}); \quad N_s, \vec{q} = 0, 1, 2, \dots$$



[Classical treatment neglects the discreteness, or $\hbar T \gg \hbar \omega_s(\vec{q})$]

$T=0$; oscillator in GS $\Rightarrow 0$ phonon

$T \neq 0$, how many phonons are there?

Let's write down an expression for U

Using the phonon picture, the "mode of vibration" (s, \vec{q}) can be occupied by 0, or 1, or 2, or 3, ... phonons and each phonon carries an energy $\hbar\omega_s(\vec{q})$

\Rightarrow Bosons

At temp. T, the thermal average or mean number of phonons in the mode $\omega_s(\vec{q})$ is $(\beta = \frac{1}{kT})$

$$\frac{1}{e^{\beta\hbar\omega_s(\vec{q})} - 1}$$

Bose-Einstein distribution with chemical potential $\mu=0$

Thus,

$$U(\omega_s(\vec{q})) = \frac{1}{2}\hbar\omega_s(\vec{q}) + \frac{\hbar\omega_s(\vec{q})}{e^{\beta\hbar\omega_s(\vec{q})} - 1}$$

= internal energy at temp. T contributed by the mode $\omega_s(\vec{q})$

since phonon number is not fixed, but changes with temp.

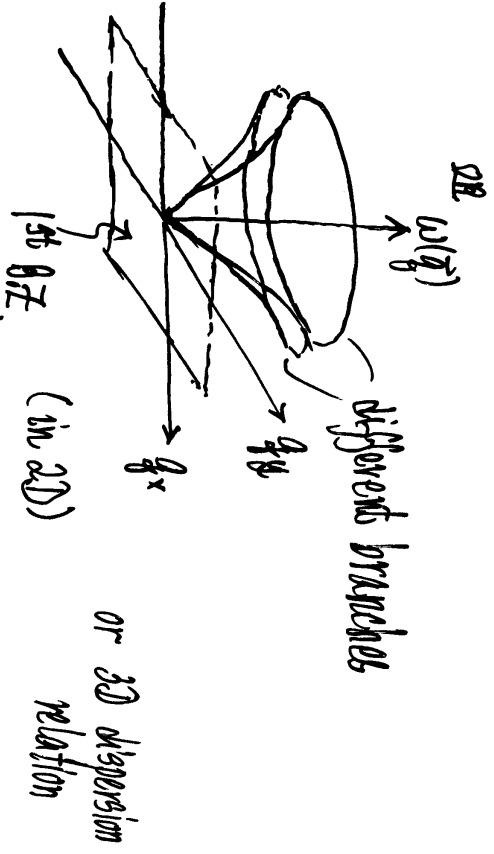
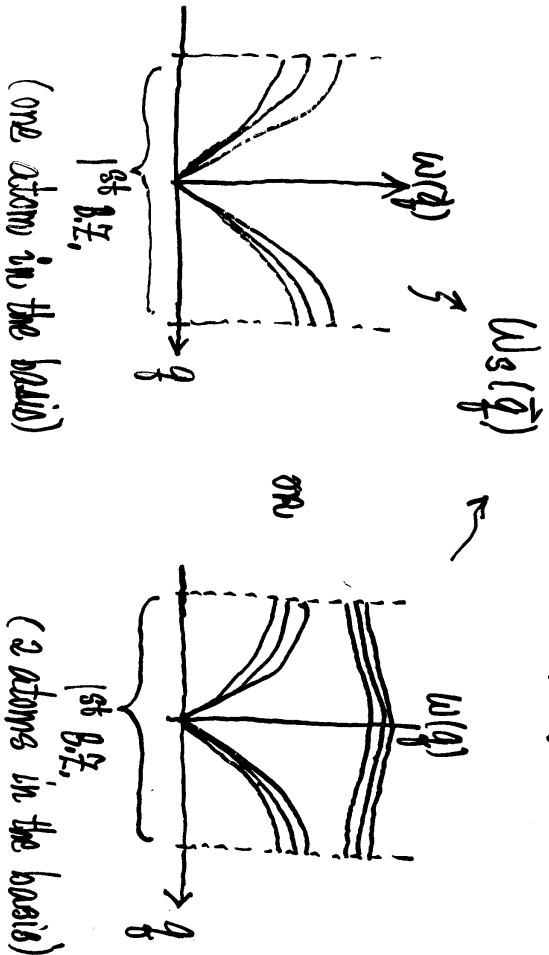
$$U = U_0 + \sum_s \sum_{\vec{q}} \frac{\hbar\omega_s(\vec{q})}{e^{\beta\hbar\omega_s(\vec{q})} - 1}$$

U_0 is ground state energy, $\sum_s \sum_{\vec{q}}$ adds up all modes

The problem is thus to evaluate:

$$\sum_s \sum_{\vec{q}} \frac{\hbar\omega_s(\vec{q})}{e^{\beta\hbar\omega_s(\vec{q})} - 1}$$

given that ω is related to \vec{q} by



Recovering the classical limit:

if $kT \gg \hbar \omega_s(\vec{q})$ for all $\omega_s(\vec{q})$ (and $T < \text{melting point}$)

$$\frac{\hbar \omega_s(\vec{q})}{e^{\hbar \omega_s(\vec{q})/kT} - 1} \approx \frac{\hbar \omega_s(\vec{q})}{\hbar \omega_s(\vec{q})} = kT$$

$$\therefore U = U_0 + \sum_s \sum_{\vec{q}} kT = U_0 + 3pNkT$$

$$C_V = 3pNk$$

$$\text{or } C_V(\text{molar}) = 3pR$$

Physics is clear now!

At some T , $kT \gg \hbar \omega_s(\vec{q})$ for some modes (contributes k)

$kT < \hbar \omega_s(\vec{q})$ for some modes \Rightarrow contributes less to C_V

$\Rightarrow C_V$ drops with temperature!

D. Phonons: Statistical Mechanical Approach[†]

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

$$\vec{q} \in 1^{\text{st}} \text{ B.Z.}$$

3p branches with 3 acoustic branches
 \nearrow p atoms/primitive cell

N allowed \vec{q} 's

[†] Treated in standard undergraduate statistical mechanics courses.

• The normal modes behave as

3pN independent harmonic oscillators

• Upon quantization, for each mode labelled by (s, \vec{q}) the oscillator can take on energies of the form:

$$\left(n_{s, \vec{q}} + \frac{1}{2} \right) \hbar \omega_s(\vec{q}) \text{ with } n_{s, \vec{q}} = 0, 1, 2, \dots$$

Internal Energy and Partition Function

• Ground state energy

$$n_{s, \vec{q}} = 0 \text{ for all } s \text{ and } \vec{q} \text{ (all modes)}$$

Each oscillator contributes its zero-point energy

$$\therefore \text{GS energy } U_0 = \sum_s \sum_{\vec{q}} \frac{1}{2} \hbar \omega_s(\vec{q})$$

sum over all modes

U_0 does not depend on temperature T

$\Rightarrow U_0$ plays no role in calculating C_V

Key results in statistical mechanics:

$$Z = \sum_{\vec{n}} e^{-\beta E_{\vec{n}}} \quad \beta = \frac{1}{kT}$$

partition function \rightarrow a possible energy of the system

over all possible eigen-energies of the system

3pN oscillators

$$U = -\frac{\partial}{\partial \beta} \ln Z = \langle H \rangle$$

Hamiltonian

The system of 3pN oscillators has possible energy of the form:

$$\sum_s \sum_{\vec{q}} \left(n_{s,\vec{q}} \hbar \omega_s(\vec{q}) + \frac{1}{2} \hbar \omega_s(\vec{q}) \right)$$

with each $n_{s,\vec{q}} = 0, 1, \dots$

$$\therefore Z = \sum_{\dots} \sum_{\dots} e^{-\beta \sum_s \sum_{\vec{q}} \left(n_{s,\vec{q}} + \frac{1}{2} \right) \hbar \omega_s(\vec{q})}$$

each $n_{s,\vec{q}} = 0$

$$= \prod_s \prod_{\vec{q}} \sum_{n=0}^{\infty} e^{-\beta n \hbar \omega_s(\vec{q})} e^{-\frac{1}{2} \beta \hbar \omega_s(\vec{q})}$$

product

partition function of an oscillator with freq. $\omega_s(\vec{q})$

$$\frac{1}{1 - e^{-\beta \hbar \omega_s(\vec{q})}}$$

$$Z = \prod_s \prod_{\vec{q}} \frac{e^{-\frac{1}{2} \beta \hbar \omega_s(\vec{q})}}{1 - e^{-\beta \hbar \omega_s(\vec{q})}}$$

$$-\ln Z = \sum_s \sum_{\vec{q}} \left[\frac{1}{2} \beta \hbar \omega_s(\vec{q}) + \ln \left(\frac{1}{1 - e^{-\beta \hbar \omega_s(\vec{q})}} \right) \right]$$

$$U = -\frac{\partial}{\partial \beta} \ln Z = \sum_s \sum_{\vec{q}} \frac{1}{2} \hbar \omega_s(\vec{q}) + \sum_s \sum_{\vec{q}} \frac{\hbar \omega_s(\vec{q})}{e^{\beta \hbar \omega_s(\vec{q})} - 1}$$

$$U = U_0 + \sum_s \sum_{\vec{q}} \frac{\hbar \omega_s(\vec{q})}{e^{\beta \hbar \omega_s(\vec{q})} - 1}$$

GRS energy

over all modes

interpretations:

- At a temp, T, each oscillator has an average occupation number of $\langle n_{s,\vec{q}} \rangle = \frac{1}{e^{\beta \hbar \omega_s(\vec{q})} - 1}$
- Phonon gas: bosons with chemical potential $\mu=0$

Then $C_V = \frac{\partial U}{\partial T}$

\therefore The problem is to evaluate U.

E. The Einstein Model

- A simple approximation: ignore dispersion relation!
- Assumes all normal modes carry the same frequency.

ie., $\omega_s(\vec{q}) = \omega_E$ (non-dispersive)

[Note: This is obviously a very crude approximation to the rather complicated $\omega_s(\vec{q})$]

System becomes a collection of identical oscillators.

Consider N unit cells with 1 atom in the basis, there are 3N normal modes

$$\therefore U = U_0 + 3N \frac{\hbar \omega_E}{e^{\beta \hbar \omega_E} - 1}$$

Heat Capacity, due to lattice vibrations within Einstein model is

$$C_{Vib} = \left(\frac{\partial U}{\partial T} \right)_{VN} = 3Nk_B \left(\beta \hbar \omega_E \right)^2 \frac{e^{\beta \hbar \omega_E}}{\left(e^{\beta \hbar \omega_E} - 1 \right)^2}$$

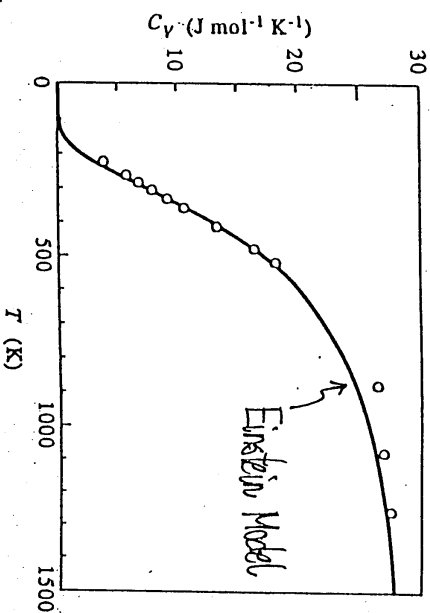
$\frac{x^2 e^x}{(e^x - 1)^2} \equiv E(x)$ ← Einstein function

Generalising to p atoms in the chemical formula:

$$C_V (\text{molar}) = 3pR \left(\frac{\hbar \omega_E}{kT} \right)^2 \frac{e^{\hbar \omega_E / kT}}{\left(e^{\hbar \omega_E / kT} - 1 \right)^2} = 3pR \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E / T}}{\left(e^{\theta_E / T} - 1 \right)^2}$$

ω_E or $\theta_E \equiv \frac{\hbar \omega_E}{k}$ is used as a fitting parameter to experimental data

Does it work?



1875 Data Very Old data

The heat capacity of diamond compared to Einstein's theory (1907). The experimental values shown are those of Weber (1875) which were used by Einstein when he compared his theory to experiment.

C becomes T-dependent
First theory that gives $C \rightarrow 0$ as $T \rightarrow 0$!

• High T behaviour $hT \gg h\nu$

$C_V \rightarrow 3R$ (same as classical result)

(Dulong and Petit law)

• Low T behaviour $hT \ll h\nu$

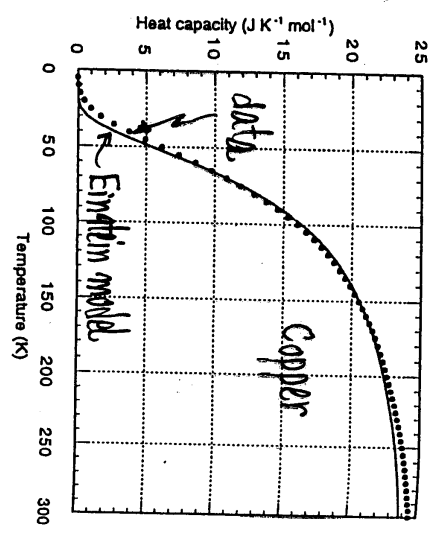
$C_V \rightarrow 3R \left(\frac{h\nu}{kT}\right)^2 e^{-h\nu/kT}$

$\rightarrow 0$ as $T \rightarrow 0$ with $e^{-h\nu/kT}$ behaviour

(same physics as in Planck's black body radiation formula)

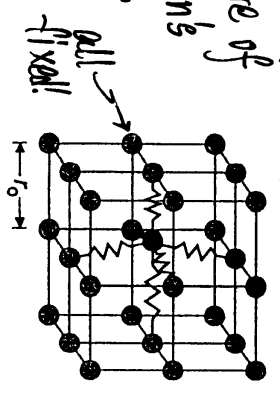
Problem!

C_V Einstein drops too fast at low T, when compared with data!



Why? Neglected lattice vibrational waves (i.e. dispersion)

Picture of Einstein's model



Only one atom vibrates upon disturbance!