

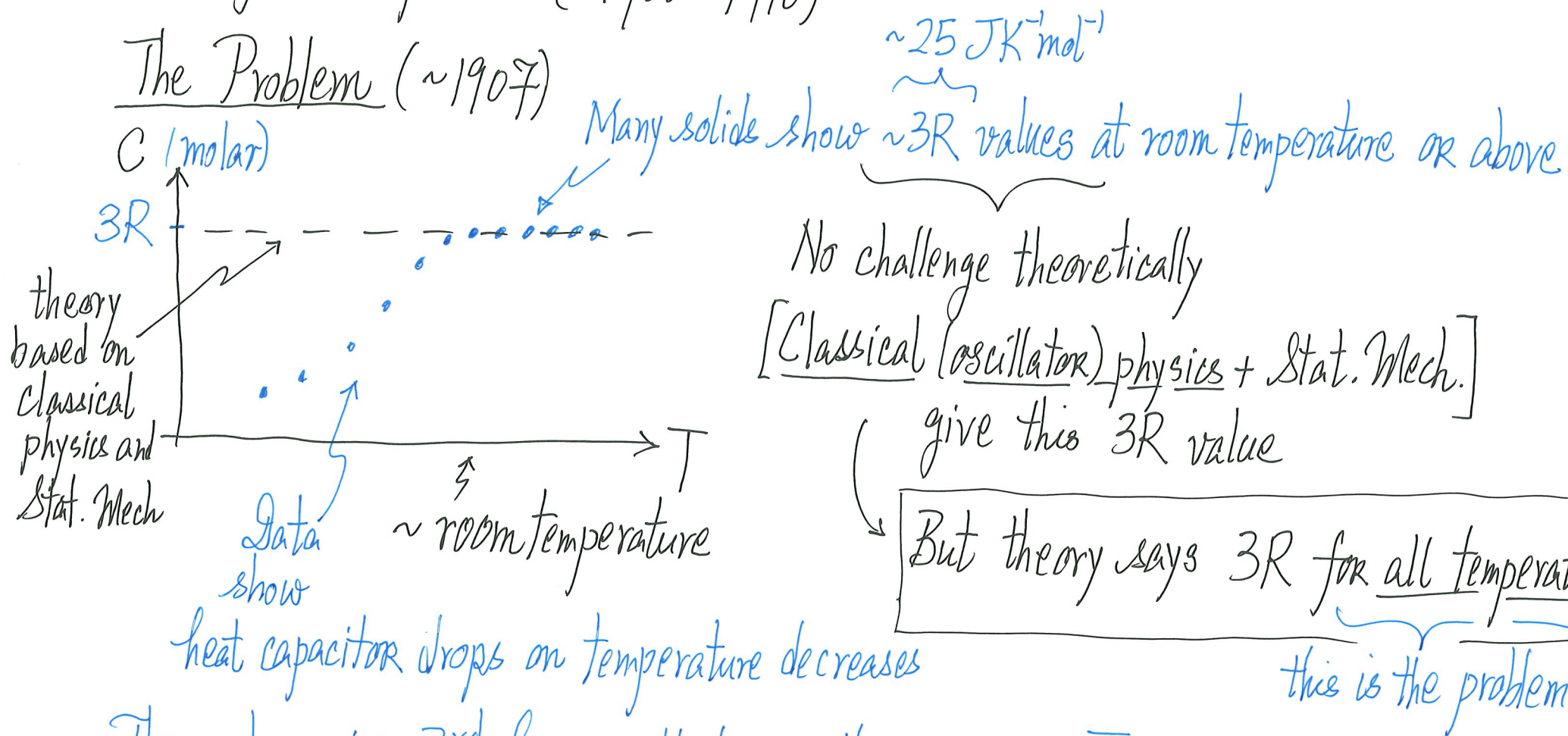
Application A

Heat Capacity of Solids & Einstein's model

Heat Capacity of Solids (insulators) at Low Temperature

- A famous problem (~1900-1910)

The Problem (~1907)



- Thermodynamics 3rd law: Heat capacity $\rightarrow 0$ as $T \rightarrow 0$

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

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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	ρ (kg m ⁻³)	C_p (J K mol ⁻¹)	Z	Element	A	ρ (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, Nd	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	Protactinium, 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					

Data of C_p (molar) of Elements at 25°C
[some elements are not solids at 25°C]

Many (more than 50%) show

$$C_p \sim 25 \text{ J K}^{-1} \text{ mol}^{-1}$$

(range: 22-32 J K⁻¹ mol⁻¹)

This can be explained by classical oscillator physics and Statistical mechanics

Remark

Thermal and Statistical Physics
is about real stuff!

The Physics Problem (~ 1907) was ... to look for a theory of heat capacity of Solids that gives the behavior at low temperatures, especially $C \rightarrow 0$ as $T \rightarrow 0$ so as to be in line with the 3rd law and (limited) experimental data at that time.

What were there ~ 1907 ?

- Planck (~ 1900) thermal radiation formula

- Oscillator has discrete allowed energies

some $\omega \rightarrow \sqrt{\frac{K}{m}}$

can be: $0 \cdot \hbar\omega$, $1 \cdot \hbar\omega$, $2 \cdot \hbar\omega$, $3 \cdot \hbar\omega$, ..., $n \cdot \hbar\omega$, ...

[zero-point $\frac{1}{2} \hbar\omega$ needed to wait until QM was established]

• Einstein (~1905) photoelectric effect ($h\nu$) energy packets for light

[Einstein also did his special relativity and $E=mc^2$ papers in 1905]

So, naturally Einstein (~1907-1908) worked on this Heat capacity of Solids problem

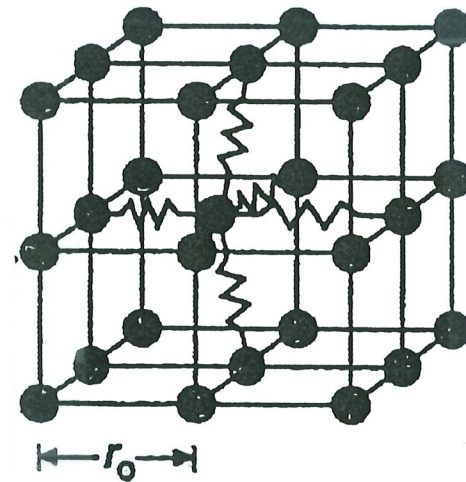
Oscillator Physics Enters

Solid: An array of atoms (lattice)

$T=0$, all atoms sit quietly
(still) at equilibrium positions

$T \neq 0$, must do something to
"entertain" the fact that $T \neq 0$

[atoms Vibrate: Oscillator Physics]



Schematically showing vibration
of an atom at $T \neq 0$

Einstein's Model

- Every atom oscillates about equilibrium position independently
- Every atom fills the same potential energy trap about equilibrium position

$$U(x, y, z) = \frac{1}{2} m \omega^2 (x^2 + y^2 + z^2)$$

(about equilibrium position taken to be $(0, 0, 0)$)

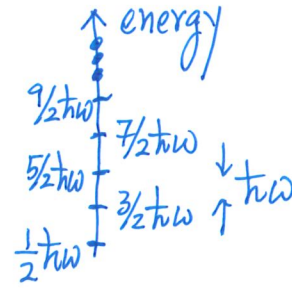
- Each atom : 3 oscillators of angular frequency ω (x, y, z directions)
- N atoms in solid : $3N$ oscillators, all with same ω
- Accounting for discrete allowed energies of an oscillator [new element!]

This set up the stage for using Microcanonical Ensemble Approach to the problem

Einstein's Model of Heat Capacity of Solids: Microcanonical Ensemble

- $3N$ harmonic oscillators, ALL with same characteristic frequency ω
[in solid state physics, ω_E (Einstein angular frequency) is used]
- Despite identical oscillators (same ω), they can be distinguished by their equilibrium positions in a solid
- Microcanonical Ensemble Approach
[fix E , count W , obtain S , derivatives of S give other variables]
Energy E to be divided among the $3N$ oscillators of N atoms
Let
$$E = \underbrace{3M \cdot \hbar\omega}_{\text{to divide among oscillators}} + \underbrace{3N \frac{\hbar\omega}{2}}_{\text{this is } \hbar\omega/2 \text{ ground state energy for } 3N \text{ oscillators}}$$

QM of one oscillator:



$\frac{1}{2}\hbar\omega + n\hbar\omega$, $n = 0, 1, 2, \dots$
 G.S. energy some units of $(\hbar\omega)$ energy

Counting Problem is: $3M$ units of energy to divide among $3N$ oscillators

[c.f. $3M$ balls + $(3N-1)$ sticks $\Rightarrow$ ways to divide $3M$ energy]
 into $3N$ groups

$$\therefore W(E = \underbrace{3M\hbar\omega}_{\text{(units of } \hbar\omega\text{)}}, \underbrace{3N}_{\substack{\text{\# oscillators} \\ \text{\Û (or N atoms)}}}) = \frac{(3M + 3N - 1)!}{(3M)! (3N - 1)!} \quad (A1)$$

or write this in terms of E ,

$$W(E, 3N) = \frac{\left(\frac{E}{\hbar\omega} + \frac{3N}{2} - 1\right)!}{\left(\frac{E}{\hbar\omega} - \frac{3N}{2}\right)! (3N - 1)!}$$

$$(A2) \left(\because 3M = \frac{E}{\hbar\omega} - \frac{3N}{2} \right) \text{ (Ex.)}$$

$$S(E, 3N) = k \ln W(E, 3N)$$

Boltzmann's Formula

$$= k \ln \left(\frac{E}{\hbar\omega} + \frac{3N}{2} - 1 \right)! - k \ln \left(\frac{E}{\hbar\omega} - \frac{3N}{2} \right)! - k \ln (3N-1)!$$

[Stirling approximation: $\ln n! \approx n \ln n - n$] (here, $\underbrace{N \approx 10^{23}}_{1 \text{ cm}^3 \text{ of solid}} \gg 1$)

$$= k \left(\frac{E}{\hbar\omega} + \frac{3N}{2} - 1 \right) \ln \left(\frac{E}{\hbar\omega} + \frac{3N}{2} - 1 \right) - k \left(\frac{E}{\hbar\omega} - \frac{3N}{2} \right) \ln \left(\frac{E}{\hbar\omega} - \frac{3N}{2} \right) - k (3N-1) \ln (3N-1)$$

+ 3 more terms that cancel out each other
(really? try it out! Must try!)

$$\Rightarrow \boxed{S(E, 3N) \approx k \left(\frac{E}{\hbar\omega} + \frac{3N}{2} \right) \ln \left(\frac{E}{\hbar\omega} + \frac{3N}{2} \right) - k \left(\frac{E}{\hbar\omega} - \frac{3N}{2} \right) \ln \left(\frac{E}{\hbar\omega} - \frac{3N}{2} \right) - k 3N \ln 3N} \quad (A3)$$

Done! We get the entropy! Unit is right as each term $\sim k$
But the physics problem is about $C_v(T)$ behaviour.

Central Equation (1st + 2nd laws)

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N} = \frac{k}{\hbar\omega} \ln \left(\frac{E}{\hbar\omega} + \frac{3N}{2} \right) + \cancel{\frac{k}{\hbar\omega}} - \frac{k}{\hbar\omega} \ln \left(\frac{E}{\hbar\omega} - \frac{3N}{2} \right) - \cancel{\frac{k}{\hbar\omega}}$$

$$\Rightarrow \left[\underbrace{\frac{1}{T}}_{\text{temperature}} = \underbrace{\frac{k}{\hbar\omega}}_{\text{No unit}} \ln \left(\frac{\frac{E}{\hbar\omega} + \frac{3N}{2}}{\frac{E}{\hbar\omega} - \frac{3N}{2}} \right) \right] \quad (A4)$$

In this approach, T (or $1/T$) is derived! (E is given, S is calculated)

Write E as the subject of equation (Ex), (start extracting the physics)

$$E = 3N \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} + 3N \frac{\hbar\omega}{2} \quad (A5)$$

this gives $E(T)$ (or $U(T, V, N)$)
in thermodynamics)

then $C_v(T) = \frac{\partial E}{\partial T}$ follows

Look at the Physics (from the Math results)

- What is low temperature, what is high temperature?

see $\frac{\hbar\omega}{kT}$ ratio in result

i.e. comparison of two energies in the problem

$\hbar\omega$ vs kT
 ↑ energy scale of oscillators ← "thermal energy"

(A6)

[This is what thermal and Statistical Physics all about!]

Given a system: some energy scale [$\hbar\omega$, μB (magnetic dipole moment times B -field)]
 then explores how kT competes with intrinsic scale in system

$$E(T) = 3N \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} + 3N \frac{\hbar\omega}{2}$$

Think physics!

It is internal energy as a function of temperature.

(i) $kT \gg \hbar\omega$ (high temperature regime)

$$E(T) \approx 3N \frac{\hbar\omega}{\left(1 + \frac{\hbar\omega}{kT}\right) - 1} + 3N \frac{\hbar\omega}{2} = 3NkT + 3N \frac{\hbar\omega}{2} \approx 3NkT \quad (A7)$$

$$\therefore C_v = \frac{\partial E}{\partial T} = 3Nk \text{ (high temp)} \quad \text{thus } C_v^{(\text{molar})} = 3N_A k = 3R$$

(ii) $kT \ll \hbar\omega$ (low temperature regime)

just classical physics result

$$E(T) \approx \frac{3N\hbar\omega}{e^{\hbar\omega/kT}} + 3N \frac{\hbar\omega}{2} = \underbrace{3N \frac{\hbar\omega}{2}}_{\substack{\text{just a} \\ \text{constant} \\ \text{(zero-pt energies)}}} + \underbrace{3N\hbar\omega e^{-\hbar\omega/kT}}_{\substack{e^{-(\text{big number})} \\ \text{vanishing contribution}}} \quad (A7)$$

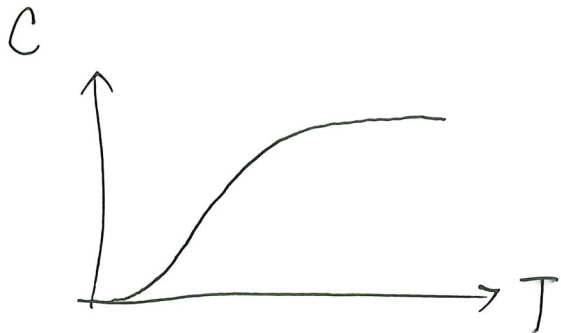
Heat Capacity $C_v = \frac{\partial E}{\partial T} = 3Nk \underbrace{\left(\frac{\hbar\omega}{kT}\right)^2}_{\text{no unit}} \frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT} - 1)^2} \quad (\text{AB}) \quad (\text{Ex.})$

(extensive) *right unit*

(i) $kT \gg \hbar\omega$, $C_v \sim 3Nk$ ($3R$ for molar C_v) (A9)

(ii) $kT \ll \hbar\omega$, $C_v \approx 3Nk \underbrace{\left(\frac{\hbar\omega}{kT}\right)^2}_{\text{goes to zero as } T \rightarrow 0} e^{-\hbar\omega/kT}$ (A9)

goes to zero as $T \rightarrow 0$ ($e^{-\hbar\omega/kT}$ drops faster than increase of $1/T^2$)



First theory that has $C \rightarrow 0$ as $T \rightarrow 0$!

Physics behind the success



- Classical oscillator physics

all energies are possible!

[depending on how you kick off the motion]

energy



any value is allowed

- Quantum Oscillator physics (two sets an energy inside oscillator problems)

Given ω
(two)

energy

$kT \gg \hbar\omega$

$\hbar\omega \uparrow$

0-pt $\rightarrow$



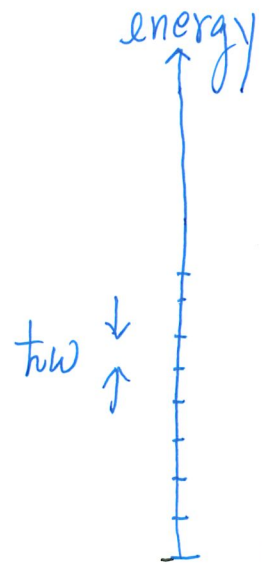
this is thermal energy
 kT

[discreteness of allowed energies is not noticable]
when $kT \gg \hbar\omega$

$\approx$ classical physics

(or kT can excite oscillator to high excited states)

closer and closer to classical physics

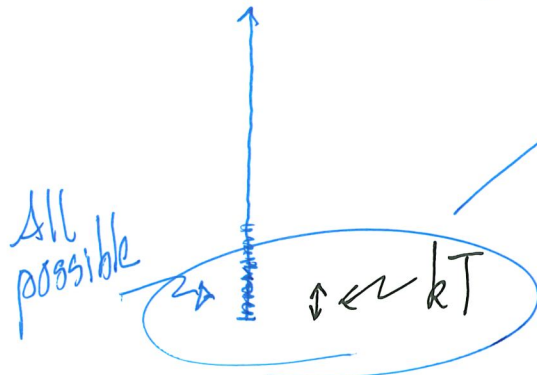


kT can hardly excite an oscillator

this is related to discrete energies of oscillator, i.e. QM

$\therefore$ Oscillators can't contribute to C_v ,
so $C_v \rightarrow 0$ as $T \rightarrow 0$

Classical Physics



Blow this up



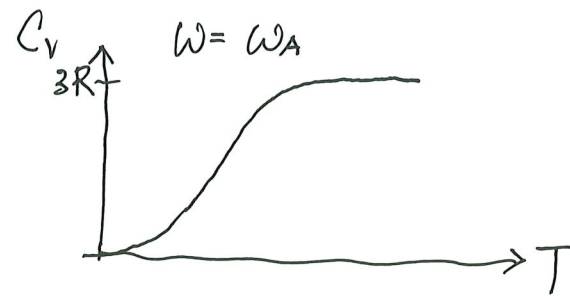
many oscillator states
can be excited

$C_v = 3R$ always (any temperature)

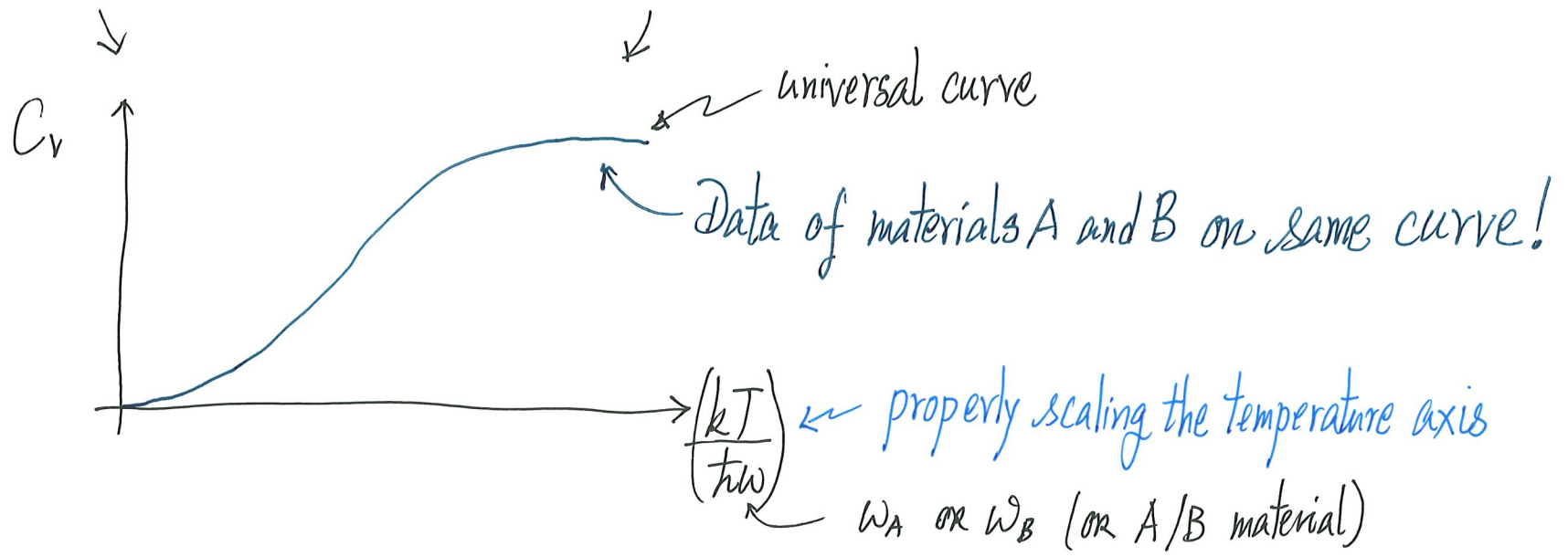
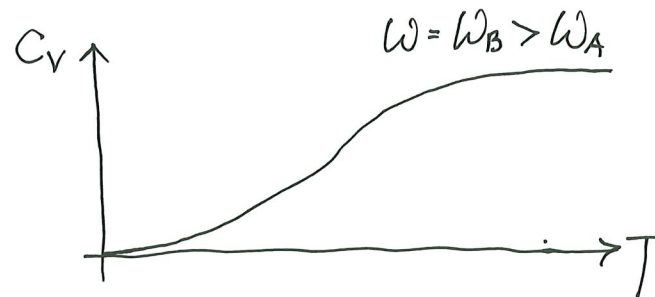
Universal Feature of Einstein's Result

$$C_v = 3Nk \left(\frac{\hbar\omega}{kT} \right)^2 \frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT} - 1)^2} \quad \left[\frac{\hbar\omega}{kT} \text{ enters as a ratio} \right]$$

Material A: ω_A



Material B: ω_B



Was Einstein 100% right?

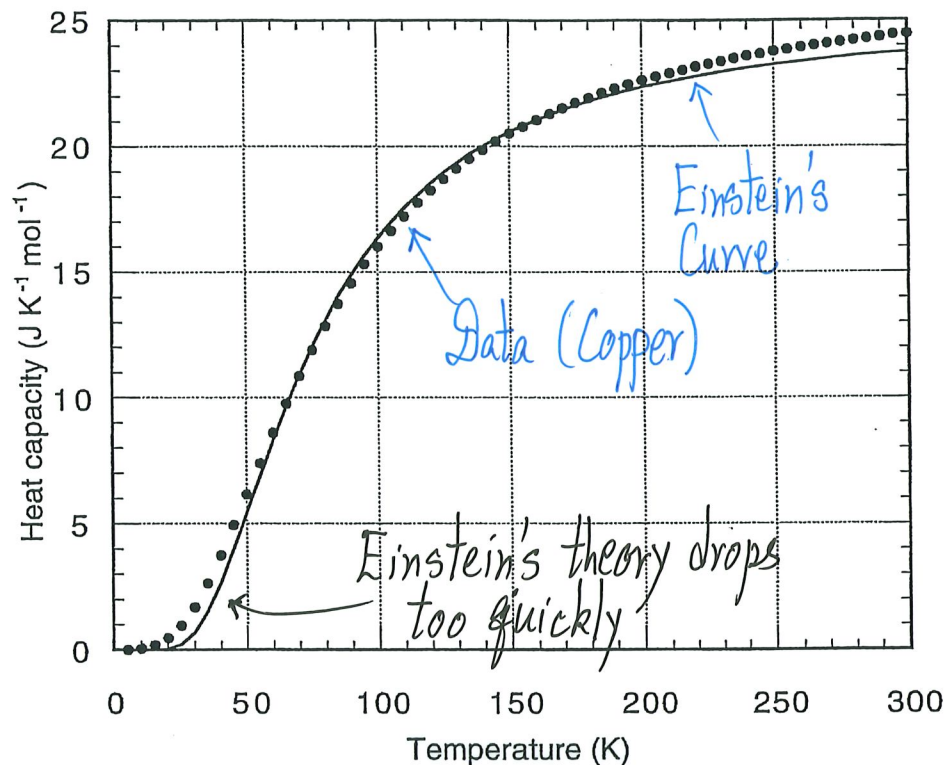
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The heat capacity of copper plotted together with the Einstein prediction for the heat capacity based on $\Theta_E = 230$ K. The predicted Einstein temperature corresponds to a spring constant of $K = 2.423 \text{ J m}^{-2}$, and a frequency of vibration of $f_0 = 4.79 \times 10^{12} \text{ Hz}$. 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 .



Basically Correct!

But at low temperatures, Einstein's theory predicts C_V to drop too quickly when compared with data

Debye (1912) gave a more accurate model with $C_V \sim T^3$ at low temperatures in agreement with data

Remarks

- Can do the same problem using other Stat. Mech. approaches (e.g. canonical ensemble)
- This is about insulators
- How about C_v of metals?

$$C_v \sim \underbrace{aT}_{\substack{\uparrow \\ \text{due to}}} + \underbrace{bT^3}_{\text{Debye (atoms vibrate or lattice vibrations)}}$$

or "phonons" in solid state physics

conduction (freely moving) electrons in metal

fermions
[physics of ideal Fermi gas]
non-interacting

takes into account of requirement of fermions

The form $E = 3N \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} + (\text{a constant})$

is NOT new! This appeared in Planck's thermal radiation⁺ formula (1900)!
 [Not wonder - also about oscillator physics]

$\frac{1}{e^{\hbar\omega/kT} - 1}$ is a special form of the Bose-Einstein distribution

["phonons" behave as bosons]

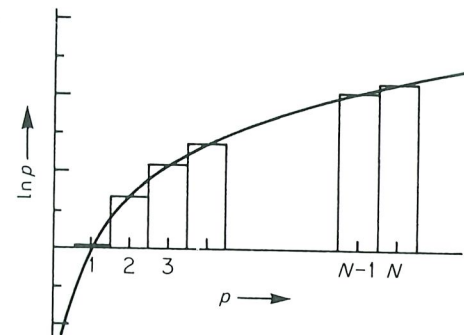
⁺ Planck's formula $B(\omega, T) = \frac{\omega^2}{4\pi^3 c^2} \cdot \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}$ oscillator Physics

The Stirling's Formula for $\ln N!$ ($N \gg 1$)

- Practically, $\ln N! \approx N \ln N - N$ is sufficient for our purposes
use your calculator to "prove" it

Poorman's Approach

$$\ln N! = \ln[N \cdot (N-1) \cdot (N-2) \cdots 1] = \sum_{p=1}^N \ln p$$



Approximation of $\ln(N!)$ by the area under the curve of $\ln p$.

Approximate it as area under curve $\ln p$

$$\int_1^N \ln p \, dp = x \ln x \Big|_1^N - \int_1^N x \frac{1}{x} \, dx$$

$$= N \ln N - N + 1 \approx N \ln N - 1 \quad (\text{Done})$$

$$\left[\int u \, dv = uv - \int v \, du \right]$$

by parts

Stirling's Formula[†]

$$\ln N! \approx \underbrace{N \ln N - N}_{\text{useful form}} = N \ln N - N \ln e = \underbrace{N \ln \left(\frac{N}{e} \right)}_{\text{another useful form}}$$

[†]A proper proof of Stirling's Formula needs the background of the Gamma Functions $\Gamma(n)$.

Stirling Formula works well even when N is not so big

e.g. $N=100$, $\ln N! = 363.7$ (exact), $N \ln N - N = 360.5$

In Statistical Mechanics, systems are macroscopic, e.g. 1 m^3 of ^{ideal gas} air at STP

$$n \approx 40 \text{ moles} \quad \left[n = \frac{pV}{RT} \right]$$

$$n \cdot N_A = N \sim 2.4 \times 10^{25} \text{ molecules [in m}^3] \therefore \text{Stirling's Formula works very well}$$