H. The Debye Model

- A good approximation for acoustic modes (1912)

Consider one branch: Assume $\omega = v q$ $\quad (q = |\vec{q}|)$

Remark: Constant-ω-"surface" $\begin{cases} \text{1D (two points)} \\ \text{2D (a circle in } (q_x, q_y)\text{-space)} \\ \text{3D (a spherical surface in } (q_x, q_y, q_z)\text{-space)} \end{cases}$

3D:

$$D(\omega) = \frac{V}{(2\pi)^3} \frac{4\pi q^2}{v}$$

q = radius of sphere so that the $\vec{q}$'s on surface correspond to ω

$$= \frac{V}{2\pi^2} \frac{1}{v^3} \underbrace{\omega^2}$$

describe DOS well at low ω $\rightsquigarrow$ ω^2 (standard ω-dependence in 3D within Debye approximation)

This result is obtained readily by:

$$D(\omega)\,d\omega = \frac{V}{(2\pi)^3} \cdot (\text{Volume between two constant-}\omega\text{-surfaces})$$

$$= \frac{V}{(2\pi)^3} \cdot 4\pi q^2 dq \qquad \text{(Debye)}$$

$$\Rightarrow D(\omega) = \frac{V}{(2\pi)^3} \frac{1}{\frac{d\omega}{dq}} 4\pi q^2 = \frac{V}{(2\pi)^3} \frac{1}{v} \cdot 4\pi q^2$$

$$= \frac{V}{2\pi^2} \frac{1}{v^3} \omega^2$$

In general, $v_\ell \neq v_t$

v_ℓ ← longitudinal (LA); v_t ← transverse (TA)

$$D_\ell(\omega) = \frac{V}{2\pi^2} \frac{1}{v_\ell^3} \omega^2 \qquad \text{(longitudinal branch)}$$

$$D_t(\omega) = 2 \cdot \frac{V}{2\pi^2} \frac{1}{v_t^3} \omega^2 \qquad \text{(transverse branches)}$$

2 ← two transverse branches

Of course, we can't let $D(\omega) \sim \omega^2$ for all ω

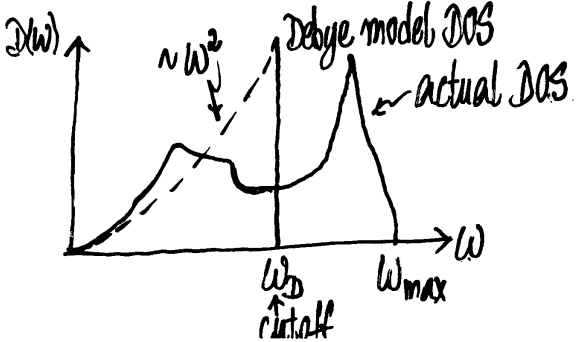
⇒ need to cut it off by conserving number of modes

[Can do it branch by branch or on the total DOS]

For the 3 acoustic branches, the total DOS is

$$D(\omega) = \frac{V}{2\pi^2}\left(\frac{1}{v_\ell^3} + \frac{2}{v_t^3}\right)\omega^2 \quad \text{for } 0 < \omega < \omega_D$$

$$= \frac{V}{2\pi^2} \frac{3}{v_D^3} \omega^2 \qquad \text{(Debye model)}$$



ω_D is fixed by:

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

Fixing ω_D:

$$\int_0^{\omega_D} D(\omega)\,d\omega = 3N \quad \leftarrow \text{equation to fix } \omega_D$$

$$\Rightarrow \frac{V}{2\pi^2}\frac{3}{v_0^3}\int_0^{\omega_D}\omega^2 d\omega = 3N$$

$$\Rightarrow \frac{V}{2\pi^2}\frac{3}{v_0^3}\frac{\omega_D^3}{3} = 3N \Rightarrow \boxed{\omega_D = \underbrace{\left(6\pi^2\frac{N}{V}\right)^{1/3}}_{\substack{q_D \\ \uparrow \\ \text{cutoff in wave number}}} v_0 = q_D \cdot v_0}$$

$$\Rightarrow \frac{V}{2\pi^2}\frac{3}{v_0^3} = \frac{9N}{\omega_D^3}$$

$$\frac{N}{V} = \frac{1}{\left(\frac{V}{N}\right)} = \frac{1}{\underset{\uparrow\ \text{volume of unit cell}}{\Omega_c}}$$

∴ D(ω) can also be written as

$$\boxed{D(\omega) = \frac{9N}{\omega_D^3}\cdot\omega^2, \quad 0<\omega<\omega_D \quad \text{in Debye Approximation.}}$$

Alternatively, one can fix q_D first and ω_D (by $\omega_D = v_0 q_D$).

Since the dispersion relation is $\underbrace{\text{isotropic}}_{\omega\sim q\ (q=|\vec{q}|)}$ in Debye Approximation, the constant-ω-surface is a spherical surface and it encloses a volume $\frac{4\pi}{3}q^3$ in q-space for a sphere of radius q.

q_D = radius of sphere in q-space that enclosed $\underbrace{N \text{ modes}}$

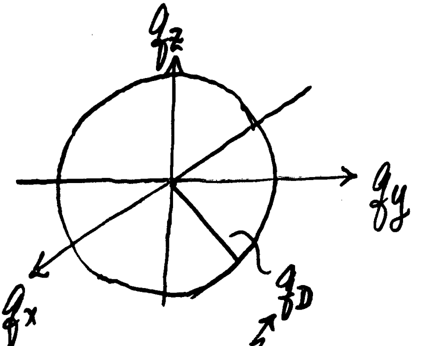
Note: In defining v_0, we assume three identical branches each with $\omega = v_0 q$.

$$\therefore \left(\frac{4\pi}{3}q_D^3\right)\cdot\frac{V}{(2\pi)^3} = N$$

$$\Rightarrow \boxed{q_D = \left(6\pi^2\frac{N}{V}\right)^{1/3}}$$

and

$$\boxed{\underset{\substack{\uparrow \\ \text{Debye frequency}^{\dagger}}}{\omega_D} = v_0\left(6\pi^2\frac{N}{V}\right)^{1/3}}$$



q_D is fixed by requiring a total of N allowed $\vec{q}$'s inside the sphere.

Within Debye Approximation,

$$U(T) = U_0 + \int_0^{\omega_D}\frac{\hbar\omega}{e^{\beta\hbar\omega}-1}D_{\text{Debye}}(\omega)\,d\omega$$

$$= \underset{\substack{\uparrow \\ \text{No T-dependence}}}{U_0} + \frac{9N}{\omega_D^3}\int_0^{\omega_D}\frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\cdot\omega^2 d\omega$$

$\hbar\omega_D$ = some energy $\equiv k\theta_D$

where $\theta_D = \frac{\hbar\omega_D}{k}$ = Debye temperature

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† ω_D is a representative vibrational frequency and θ_D is the frequency expressed as temperature. They are material properties.

$$C = \frac{\partial U}{\partial T} = k\frac{9N}{\omega_D^3}\int_0^{\omega_D}\left(\frac{\beta\hbar\omega}{e^{\beta\hbar\omega}-1}\right)^2 e^{\beta\hbar\omega}\,\omega^2 d\omega$$

Put $x = \beta\hbar\omega$,

$$\boxed{C = 9Nk\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^4 e^{+x}}{(e^x-1)^2}\,dx} \leftarrow \text{useful in numerical calculations}$$

Since $\dfrac{x^4 e^{+x}}{(e^x-1)^2} = -\dfrac{d}{dx}\left(\dfrac{x^4}{e^x-1}\right) + \dfrac{4x^3}{e^x-1}$,

$$\boxed{C = 3Nk\left[-\frac{3\theta_D}{T}\frac{1}{e^{\theta_D/T}-1} + 12\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^3}{e^x-1}dx\right]} \quad (*)$$

RHS is a function of T/θ_D

$\Rightarrow$ Different solids with the same $\frac{T}{\theta_D}$ have the same $\frac{C}{Nk}$.

<u>At high temperatures</u> ($T \gg \theta_D$):

From(*): $[\cdots] \cong -3 + 12\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T} x^2 dx = -3+4 = 1$

$\therefore$ $C = 3Nk$ as expected from the equipartition theorem.

[The physics is:

$kT \gg \hbar\theta_D \Rightarrow$ quantum (discrete) nature of oscillator becomes unimportant]

<u>At low temperatures</u> ($T \ll \theta_D$):

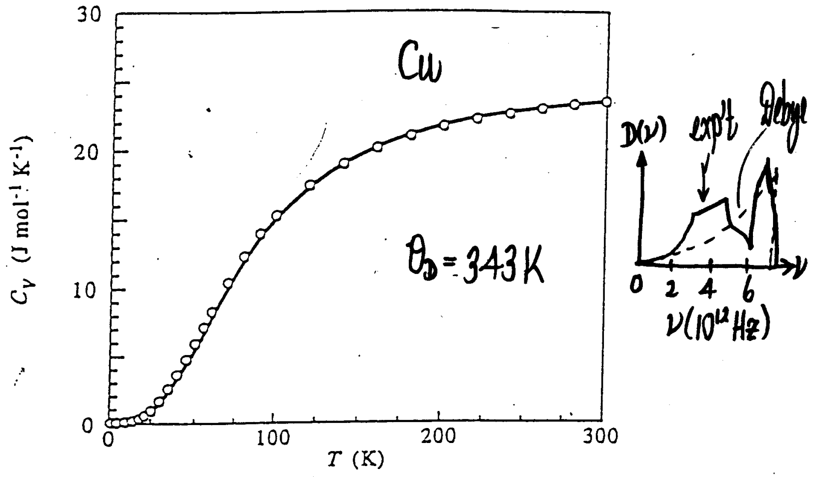
$$\text{From}(*):\ [\cdots] \approx \underbrace{-3\frac{\theta_D}{T}e^{-\theta_D/T}}_{\downarrow\ 0} + 12\left(\frac{T}{\theta_D}\right)^3\underbrace{\int_0^{\overset{\text{note}}{\downarrow}\ \infty}\frac{x^3 dx}{e^x-1}}_{=\frac{\pi^4}{15}}$$

$\frac{\pi^4}{15}$ ↖ a number related to Γ and ζ functions

$$= \frac{12\pi^4}{15}\left(\frac{T}{\theta_D}\right)^3$$

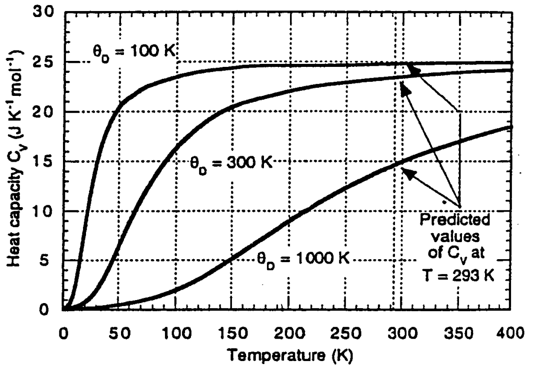
$$\boxed{\underset{\uparrow\ \text{low temp.}}{C} = \frac{12\pi^4}{5}Nk\left(\frac{T}{\theta_D}\right)^3 \propto T^3} \leftarrow \text{c.f. Einstein's model}$$

- gives $\sim T^3$ behaviour as observed experimentally at low temperatures
- This is called the <u>Debye T^3 law</u>
- The physics is: As temperature drops, fewer and fewer oscillators contribute to C. The number of oscillators that can contribute is related to $D(\omega)$ and the ω^2-dependence captures the correct DOS at low frequencies. The low-ω oscillators govern $C(T)$ at low temperatures.



The molar heat capacity of copper plotted as a function of temperature compared to the Debye theory.

[Remark: There is another story at the lowest temperatures (e.g. T < 10 K) that is related to the electrons.]



Element	Z	Θ_D (K)	Element	Z	Θ_D (K)
Beryllium	4	1440	Zirconium	40	291
C(Diamond)	6	2230	Molybdenum	42	450
Magnesium	12	400	Silver	47	225
Aluminium	13	428	Cadmium	48	209
Titanium	22	420	Tin	50	200
Vanadium	23	380	Tantalum	73	240
Chromium	24	630	Tungsten	74	400
Manganese	25	410	Platinum	78	240
Iron	26	470	Gold	79	165
Nickel	28	450	Lead	82	105
Copper	29	343	Uranium	92	207

For materials with $\theta_D \gg$ room temperature, C(molar) at room temperature tends to be smaller.

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 (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, 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% have $C_p \sim 25$ JK^{-1}mol^{-1} (range: 22-32 JK^{-1}mol^{-1})

From "Understanding the Properties of Matter" by de Podesta.

"Scaling behaviour":

Debye: $C = 9Nk\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x-1)^2}\,dx$

Given a value of $\frac{T}{\theta_D}$, the expression gives a value of C.

Debye

The predicted value of the heat capacity of monatomic solids according to the Debye theory. Also tabulated is the fraction of the high temperature limiting value ($3R$) expected at the temperature indicated.

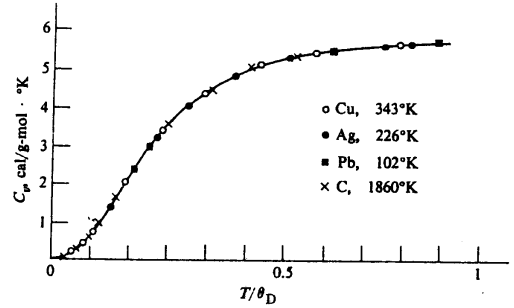
T/Θ_D	$C(T)$ J K^{-1} mol^{-1}	$C(T)/R$
0	0	0
0.01	1.944×10^{-3}	7.7927×10^{-5}
0.02	1.555×10^{-2}	6.2342×10^{-4}
0.03	5.248×10^{-2}	2.1040×10^{-3}
0.04	0.1244	4.9873×10^{-3}
0.05	0.2430	9.7408×10^{-3}
0.06	0.4198	1.6829×10^{-2}
0.07	0.6658	2.6693×10^{-2}
0.08	0.9903	3.9702×10^{-2}
0.09	1.399	5.6074×10^{-2}
0.1	1.891	7.5821×10^{-2}
0.2	9.195	0.36863
0.3	15.158	0.60770
0.4	18.604	0.74585
0.5	20.588	0.82541
0.6	21.795	0.87380
0.7	22.572	0.90495
0.8	23.098	0.92603
0.9	23.469	0.94089
1.0	23.739	0.95173
1.1	23.942	0.95987
1.2	24.098	0.96612
1.3	24.221	0.97103
1.4	24.318	0.97495
1.5	24.398	0.97813
1.6	24.463	0.98074
1.7	24.517	0.98291
1.8	24.562	0.98474
1.9	24.601	0.98629
2.0	24.634	0.98761

Does it work experimentally?

C(T) different from different materials.

How about

C Vs $\left(\frac{T}{\theta_D}\right)$?



Data of different materials collapse onto the same curve!

Further evidence that the theory is valid

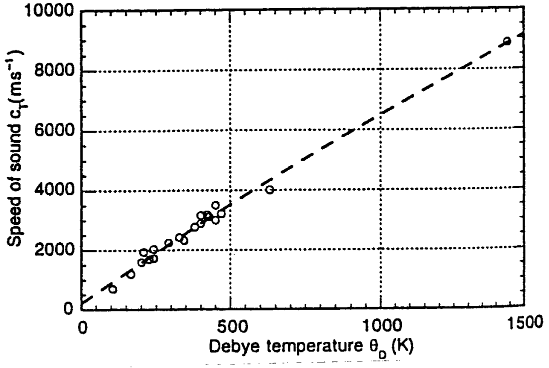
$\theta_D = \frac{\hbar\omega_D}{k}$ and $\omega_D = v_0\left(6\pi^2 \frac{N}{V}\right)^{1/3}$

thus, we expect $\theta_D \sim v_0$

values fitted from heat capacity measurements

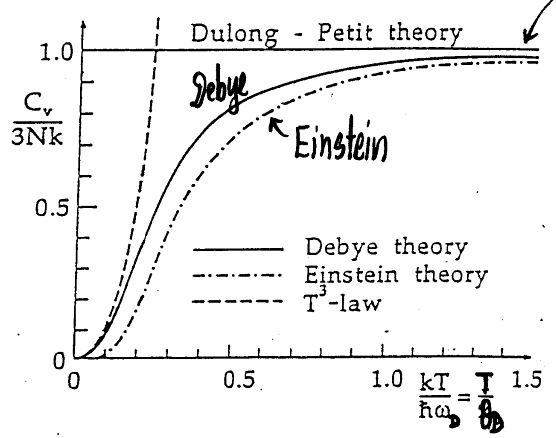
speed of sound from acoustic measurements

Does it work?



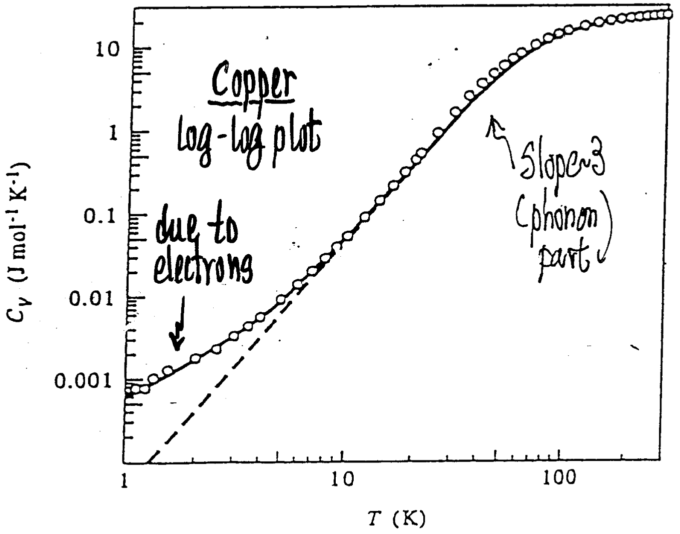
for elements

Comparing different models



classical stat. mech. (no T-dependence)

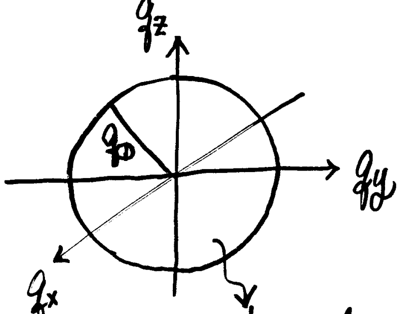
Warning: Metals at very low temperatures



At low temp.

$$C_V = \underbrace{\gamma T}_{\substack{\text{contribution}\\\text{due to}\\\text{electrons}}} + \underbrace{aT^3}_{\substack{\text{phonon}\\\text{contribution}\\\text{(Debye)}}}$$

I. A Physical ("hand-waving" argument) argument for $C \sim T^3$



sphere of radius q_D contains N modes

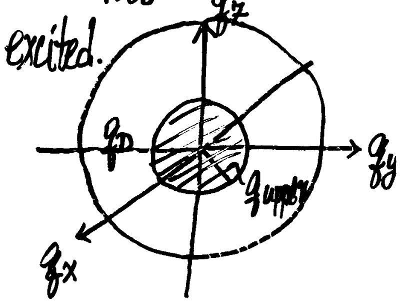
Key point: Modes are oscillators. At low temp., not all the modes are excited. Only a fraction are excited!

How many modes are excited at a low temp. T?

- Modes up to some q_{upper} and ω_{upper} are excited

$$kT \sim \hbar\omega_{upper} \sim \hbar v_0 q_{upper} \Rightarrow q_{upper} \sim \frac{kT}{\hbar v_0} \ (\sim T)$$

Modes upto a radius $q_{upper} \sim \frac{kT}{\hbar v_0}$ are excited.



Number of modes per branch excited $= \frac{V}{(2\pi)^3}\cdot\frac{4\pi}{3}\left(\frac{kT}{\hbar v_0}\right)^3 \sim T^3$

Recall: $N = \frac{V}{(2\pi)^3}\frac{4\pi}{3}q_D^3 = \frac{V}{(2\pi)^3}\frac{4\pi}{3}\left(\frac{k\Theta_D}{\hbar v_0}\right)^3$

$\therefore$ Number of modes excited per branch $= N\overbrace{\left(\frac{T}{\Theta_D}\right)^3}^{\text{fraction of volume of shaded region to whole sphere}}$

$\therefore$ Number of modes excited in 3 branches $= 3N\left(\frac{T}{\Theta_D}\right)^3$

Each excited mode is assumed to carry the classical thermal energy kT

Then,
$$U \sim \underbrace{kT}_{\substack{\text{an excited}\\ \text{mode carries}\\ \text{energy } kT}} \cdot \underbrace{3N}_{\substack{\text{total}\\ \text{number}\\ \text{of modes}}} \underbrace{\left(\frac{T}{\theta_D}\right)^3}_{\substack{\text{fraction of modes in the sphere}\\ \text{containing all modes that are excited}}} \sim T^4$$

$$\therefore\ C = \frac{\partial U}{\partial T} \cong 12\, Nk \left(\frac{T}{\theta_D}\right)^3 \qquad \text{low } T$$

[c.f. $C = \frac{12\pi^4}{5} Nk \left(\frac{T}{\theta_D}\right)^3$, not bad!]

Refs: Kittel: Ch 5, Christman: Sec. 8.1

Class notes/textbook of statistical mechanics course

- An interesting phenomena is that $C(T)$ in glasses and amorphous solids does not follow T^3. Why? A plausible explanation can be found in the famous paper by Anderson, Halperin, Varma, Phil. Mag. 25, 1 (1972). Each of the authors is a big star in condensed matter physics. [This is a good application of two-level systems discussed in statistical mechanics courses.]

Remarks:

- Our discussion is based on the Harmonic Approximation,

i.e.
$$V(x_1, x_2, \cdots, x_N) = \text{potential energy of system}$$
$$= V(\{x_i\}) = V(\{\overset{\text{equilibrium positions}}{x_i^0} + u_i\})$$
$$\approx V(\{x_i^0\}) + \cancelto{0}{\sum_j \left(\frac{\partial V}{\partial u_j}\right)_{\{x_i^0\}}} u_j + \underbrace{\frac{1}{2!}\sum_{j,k} \left(\frac{\partial^2 V}{\partial u_j \partial u_j}\right)_{\{x_i^0\}} u_j \cdot u_j}_{\substack{\text{harmonic term}\\ \text{(quadratic)}\\ \sim u\cdot u}} \underbrace{+ \cdots}_{\substack{\text{anharmonic terms}\\ (\text{e.g.} \sim u\cdot u\cdot u\\ \sim u\cdot u\cdot u\cdot u)}}$$

Harmonic Approximation: Neglect anharmonic terms

- No thermal expansion!
- Normal modes → independent oscillators → phonons (non-interacting
$$\underbrace{\sum_{\vec{q},s} \hat{a}^{\dagger}_{\vec{q},s} \hat{a}_{\vec{q},s} \hbar\omega_s(\vec{q})}_{\substack{\text{does not have phonon-phonon}\\ \text{interaction term!}}} + \text{zero pt. term}$$
- Can't explain thermal conductivity