

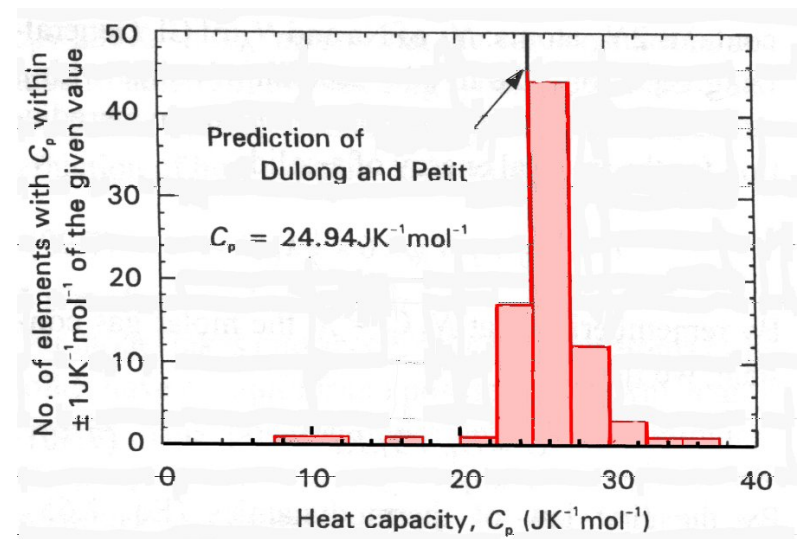
PHONON HEAT CAPACITY

Lecture 11

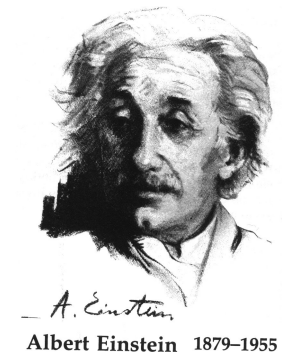
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4.5 Experimental Specific Heats

Element	Z	A	C_p J K ⁻¹ mol ⁻¹	Element	Z	A	C_p J K ⁻¹ mol ⁻¹
Lithium	3	6.94	24.77	Rhenium	75	186.2	25.48
Beryllium	4	9.01	16.44	Osmium	76	190.2	24.70
Boron	5	10.81	11.06	Iridium	77	192.2	25.10
Carbon	6	12.01	8.53	Platinum	78	195.1	25.86
Sodium	11	22.99	28.24	Gold	79	197.0	25.42
Magnesium	12	24.31	24.89	Mercury	80	200.6	27.98
Aluminium	13	26.98	24.35	Thallium	81	204.4	26.32
Silicon	14	28.09	20.00	Lead	82	207.2	26.44
Phosphorus	15	30.97	23.84	Bismuth	83	209.0	25.52
Sulphur	16	32.06	22.64	Polonium	84	209.0	25.75



Classical equipartition of energy gives specific heat of $3pR$ per mole, where p is the number of atoms in the chemical formula unit. For elements, $3R = 24.94 \text{ J K}^{-1} \text{ mol}^{-1}$. Experiments by James Dewar showed that specific heat tended to decrease with temperature.



Einstein (1907): “If Planck’s theory of radiation has hit upon the heart of the matter, then we must also expect to find contradictions between the present kinetic molecular theory and practical experience in other areas of heat theory, contradictions which can be removed in the same way.”

Einstein's model If there are N atoms in the solid, assume that each vibrates with frequency ω in a potential well. Then

$$E = N \langle n \rangle \hbar \omega = \frac{N \hbar \omega}{e^{\frac{\hbar \omega}{k_B T}} - 1},$$

and

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V$$

Now

$$\left(\frac{\partial}{\partial T} \right) \frac{\hbar \omega}{k_B T} = -\frac{\hbar \omega}{k_B T^2},$$

so

$$\left(\frac{\partial}{\partial T} \right) e^{\frac{\hbar \omega}{k_B T}} = -\frac{\hbar \omega}{k_B T^2} e^{\frac{\hbar \omega}{k_B T}},$$

and

$$C_V = N k_B \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{\frac{\hbar \omega}{k_B T}}}{\left(e^{\frac{\hbar \omega}{k_B T}} - 1 \right)^2}.$$

Limits

$$C_V = N k_B \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{\frac{\hbar \omega}{k_B T}}}{\left(e^{\frac{\hbar \omega}{k_B T}} - 1 \right)^2}.$$

$T \rightarrow \infty$. Then $\frac{\hbar \omega}{k_B T} \rightarrow 0$, so $e^{\frac{\hbar \omega}{k_B T}} \rightarrow 1$ and $e^{\frac{\hbar \omega}{k_B T}} - 1 \rightarrow \frac{\hbar \omega}{k_B T}$, and

$$C_V \rightarrow N k_B \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{1}{\left(\frac{\hbar \omega}{k_B T} \right)^2} = N k_B.$$

This is the expected classical limit.

Limits

$$C_V = N k_B \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{\frac{\hbar \omega}{k_B T}}}{\left(e^{\frac{\hbar \omega}{k_B T}} - 1 \right)^2}.$$

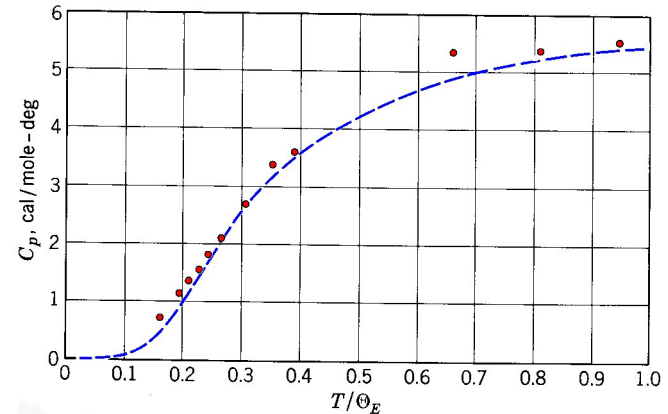
$T \rightarrow 0$. Then $e^{\frac{\hbar \omega}{k_B T}} \gg 1$ and

$$C_V \rightarrow N k_B \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{\frac{\hbar \omega}{k_B T}}}{\left(e^{\frac{\hbar \omega}{k_B T}} \right)^2} \rightarrow T^{-2} e^{-\frac{\hbar \omega}{k_B T}}.$$

Convenient to define Einstein temperature, $\Theta_E = \hbar \omega / k_B$.

5

7

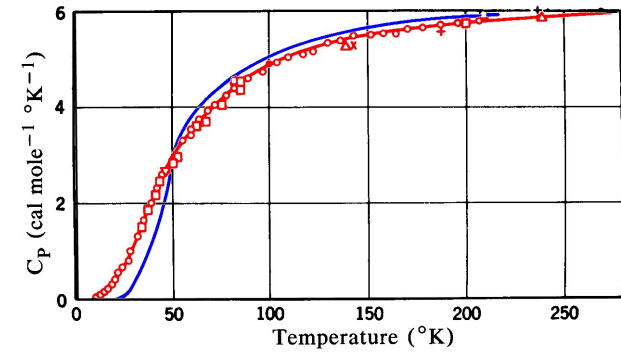


Comparison of experimental values of the heat capacity of diamond with values calculated on the Einstein model, using the characteristic temperature $\Theta_E = \hbar \omega / k_B = 1320^\circ \text{K}$. [After A. Einstein, Ann. Physik 22, 180 (1907).]

6

8

- Einstein theory shows correct trends with temperature.
- For simple harmonic oscillator, spring constant α , mass m , $\omega = \sqrt{\alpha/m}$.
- So light, tightly-bonded materials (e.g. diamond) have high frequencies.
- But higher $\omega \rightarrow$ lower specific heat.
- Hence Einstein theory explains low specific heats of some elements.



Specific heat data (points) for silver. The lines are the fits from the Einstein and Debye results. The Debye curve goes through the data points.

Systematic deviations from Einstein model at low T. Nernst and Lindemann fitted data with two Einstein-like terms. Einstein realised that the oscillations of a solid were complex, far from single-frequency. Key point is that however low the temperature there are always some modes with low enough frequencies to be excited.

9

11



Walther Nernst (1864–1941)

Walther Nernst, working towards the Third Law of Thermodynamics (As we approach absolute zero the entropy change in any process tends to zero), measured specific heats at very low temperature.

10

4.6 Debye Theory



Peter Debye, 1884–1966.

Based on classical elasticity theory (pre-dated the detailed theory of lattice dynamics).

12

The assumptions of Debye theory are

- the crystal is harmonic
- elastic waves in the crystal are non-dispersive
- the crystal is isotropic (no directional dependence)
- there is a high-frequency cut-off ω_D determined by the number of degrees of freedom

Taking, as in Lecture 10, an average sound speed v we have for each mode

$$g(\omega) = \frac{V}{2\pi^2} \frac{\omega^2}{v^3},$$

so

$$\begin{aligned} N &= \int_0^{\omega_D} \frac{V}{2\pi^2} \frac{\omega^2}{v^3} d\omega \\ &= \frac{V}{6\pi^2} \frac{\omega_D^3}{v^3} \\ \omega_D^3 &= \frac{6N\pi^2}{V} v^3 \end{aligned}$$

Equivalent to Debye frequency ω_D is $\Theta_D = \hbar\omega_D/k_B$, the Debye temperature.

13

4.6.1 The Debye Frequency

The cut-off ω_D is, frankly, a fudge factor.

If we use the correct dispersion relation, we get $g(\omega)$ by integrating over the Brillouin zone, and we know the number of allowed values of k in the Brillouin zone is the number of unit cells in the crystal, so we automatically have the right number of degrees of freedom.

In the Debye model, define a cutoff ω_D by

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

where N is the number of unit cells in the crystal, and $g(\omega)$ is the density of states in one phonon branch.

14

15

4.6.2 Debye specific heat

Combine the Debye density of states with the Bose-Einstein distribution, and account for the number of branches S of the phonon spectrum, to obtain

$$C_V = S \int_0^{\omega_D} \frac{V}{2\pi^2} \frac{\omega^2}{v^3} k_B \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{\frac{\hbar\omega}{k_B T}}}{\left(e^{\frac{\hbar\omega}{k_B T}} - 1 \right)^2} d\omega.$$

Simplify this by writing

$$x = \frac{\hbar\omega}{k_B T}, \quad \text{so} \quad \omega = \frac{k_B T x}{\hbar}, \quad x_D = \frac{\hbar\omega_D}{k_B T},$$

and

$$\begin{aligned} C_V &= S \int_0^{x_D} \frac{V}{2\pi^2} \frac{k_B^2 T^2 x^2}{\hbar^2 v^3} k_B x^2 \frac{e^x}{(e^x - 1)^2} \frac{k_B T}{\hbar} dx \\ &= S k_B \frac{V}{2\pi^2} \frac{k_B^3 T^3}{\hbar^3 v^3} \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx \end{aligned}$$

16

$$C_V = S k_B \frac{V k_B^3 T^3}{2\pi^2 \hbar^3 v^3} \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx.$$

Remember that

$$\omega_D^3 = \frac{6N\pi^2}{V} v^3,$$

so

$$\frac{V}{2\pi^2 v^3} = \frac{3N}{\omega_D^3} = \frac{3N\hbar^3}{k_B^3 \Theta_D^3}$$

and

$$\begin{aligned} C_V &= S k_B \frac{3N\hbar^3 k_B^3 T^3}{k_B^3 \Theta_D^3 \hbar^3} \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx, \\ &= 3N S k_B \frac{T^3}{\Theta_D^3} \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx. \end{aligned}$$

As with the Einstein model, there is only one parameter – in this case Θ_D .

4.6.3 Debye model: high T

$$C_V = 3N S k_B \frac{T^3}{\Theta_D^3} \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx.$$

At high T, $x_D = \hbar\omega_D/k_B T$ is small. Thus we can expand the integrand for small x :

$$e^x \approx 1,$$

and

$$(e^x - 1) \approx x$$

so

$$\int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx \approx \int_0^{x_D} x^2 dx = \frac{x_D^3}{3}.$$

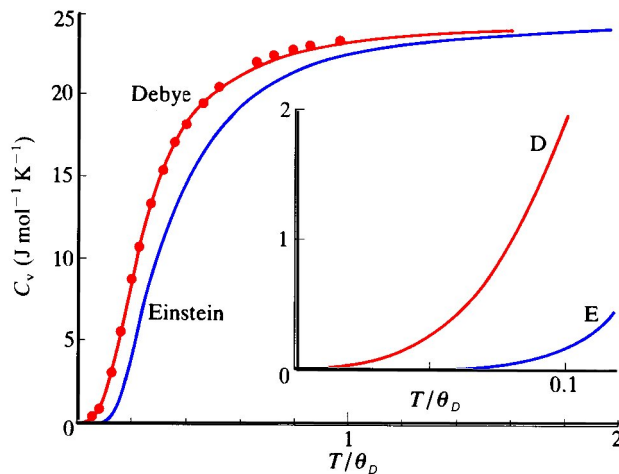
The specific heat, then, is

$$C_V \approx 3N S k_B \frac{T^3}{\Theta_D^3} \frac{x_D^3}{3},$$

17

19

Improvement over Einstein model.



Debye and Einstein models compared with experimental data for Silver. Inset shows details of behaviour at low temperature.

$$C_V \approx 3N S k_B \frac{T^3}{\Theta_D^3} \frac{x_D^3}{3},$$

but

$$x_D = \frac{\hbar\omega_D}{k_B T} = \frac{\Theta_D}{T}$$

so

$$C_V \approx N S k_B.$$

This is just the classical limit, $3R = 3N_A k_B$ per mole. We should have expected this: as $T \rightarrow \infty$, $C_V \rightarrow k_B$ for each mode, and the Debye frequency was chosen to give the right total number of oscillators.

18

20

4.6.4 Debye model: low T

$$C_V = 3NSk_B \frac{T^3}{\Theta_D^3} \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx.$$

At low, $x_D = \hbar\omega_D/k_B T$ is large. Thus we may let the upper limit of the integral tend to infinity.

$$\int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} dx = \frac{4\pi^4}{15}$$

so

$$C_V \approx 3NSk_B \frac{T^3}{\Theta_D^3} \frac{4\pi^4}{15}$$

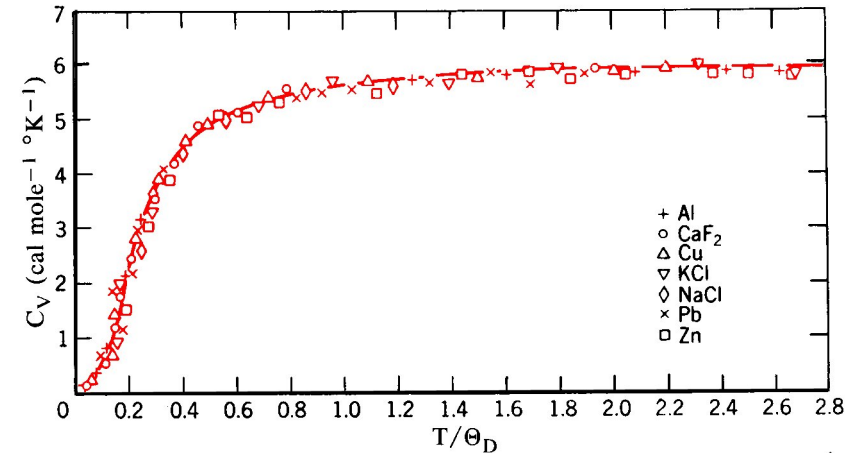
For a monatomic crystal in three dimensions $S = 3$, and N , the number of unit cells, is equal to the number of atoms. We can rewrite this as

$$C_V \approx 1944 \left(\frac{T}{\Theta_D} \right)^3$$

which is accurate for $T < \Theta_D/10$.

4.6.5 Successes and shortcomings

Debye theory works well for a wide range of materials.

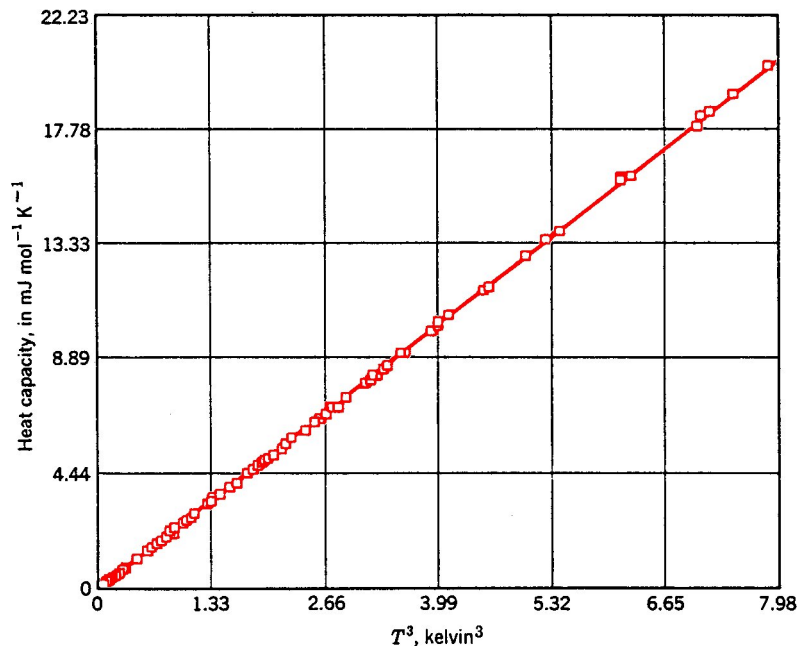


Heat capacity vs. reduced temperature for a number of materials.

But we know it can't be perfect.

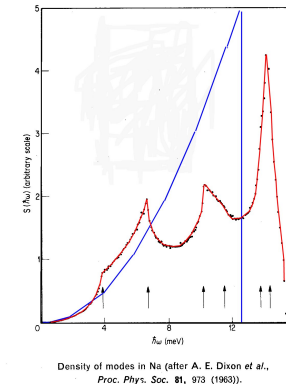
21

23



The low-temperature heat capacity of solid argon compared with the Debye T^3 prediction with $\Theta_D = 92$ K (solid line).

22



Density of modes in Na (after A. E. Dixon et al., Proc. Phys. Soc. 81, 973 (1963)).

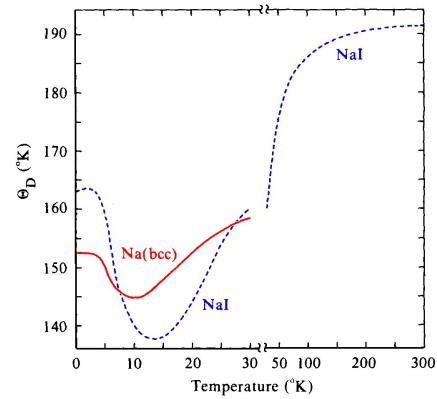
Roughly: only excite oscillators at T for which $\omega \leq k_B T/\hbar$. So we expect:

- Very low T: OK
- Low T: real DOS has more low-frequency oscillators than Debye, so C_V higher than Debye approximation.
- High T: real DOS extends to higher ω than Debye, so reaches classical limit more slowly.

24

Use Debye temperature Θ_D as a fitting parameter: expect:

- Very low T: good result with Θ_D from classical sound speed;
- Low T: rather lower Θ_D ;
- High T: need higher Θ_D .



The temperature dependence of Θ_D metallic sodium [J. D. Filby and D. L. Martin, Proc. Roy. Soc. (London) **276A**, 187 (1963).]
NaI [W. T. Berg and J. A. Morrison, Proc. Roy. Soc. (London) **242A**, 467 (1957)].