Deriving Heat Capacities using the Debye Model

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Previously we have used the Einstein Model

- Solid crystal model with atoms treated as independent harmonic oscillators vibrating with the same frequency
- Allowed calculation of the vibrational energy U & heat capacity $C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V}$
- The continuous calculation of the general heat capacity can be found as follows:

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{1}{\epsilon}\frac{\partial S}{\partial q} = \frac{k}{\epsilon}\frac{\partial}{\partial q}[qln(q+N) - qln(q) + Nln(q+N) - Nln(N)] = \frac{k}{\epsilon}\ln\left(1+\frac{N}{q}\right) = \frac{1}{\mathrm{T}}$$

$$T = \epsilon/kln\left(1+\frac{N\epsilon}{U}\right) \qquad U = \frac{N\epsilon}{e^{\epsilon/kT}-1} \qquad C_V = \frac{\partial}{\partial T}\frac{N\epsilon}{e^{\epsilon/kT}-1}$$

$$C_V = \frac{N\epsilon^2}{kT^2}\frac{e^{\epsilon/kT}}{(e^{\epsilon/kT}-1)^2}$$

-predicts $C_V = Nk$ in the high temperature limit

-predicts exponential decay in the $T \rightarrow 0$ limit

Debye's theoretical solid model

- Proposes that we must account for both low-frequency modes of oscillation in which large groups of atoms are all moving together, and high-frequency modes, in which atoms are moving opposite to their neighbors.
- These modes of oscillation are reminiscent of the modes of the electromagnetic field from blackbody radiation.
- These mechanical oscillations are referred to as 'sound waves' by Schroeder, they behave quite similarly to light waves, but with key differences; sound waves travel at relatively low speeds c_s, they have 3 polarizations, & their wavelengths are dependent on the atomic spacing of the solid.

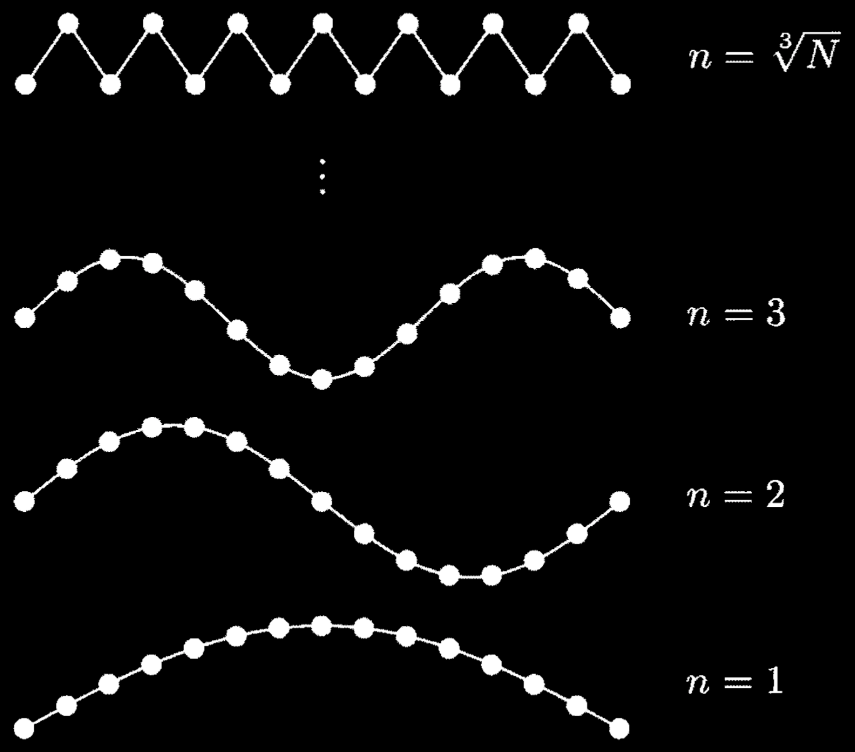
‘Sound Waves’ & U

- $\epsilon = hf = \frac{hc_s}{\lambda} = \frac{hc_s n}{2L}$
  - Thought of as **“Phonons”**

- Average number of energy units contained in the solid is given by the Planck distribution:

$$\bar{n}_{Pl} = \frac{1}{e^{\epsilon/kT} - 1}$$

- $U = 3\sum_{n_x}\sum_{n_y}\sum_{n_z} \epsilon\,\bar{n}_{Pl}(\epsilon)$



Transitioning U into an integral in spherical coordinates

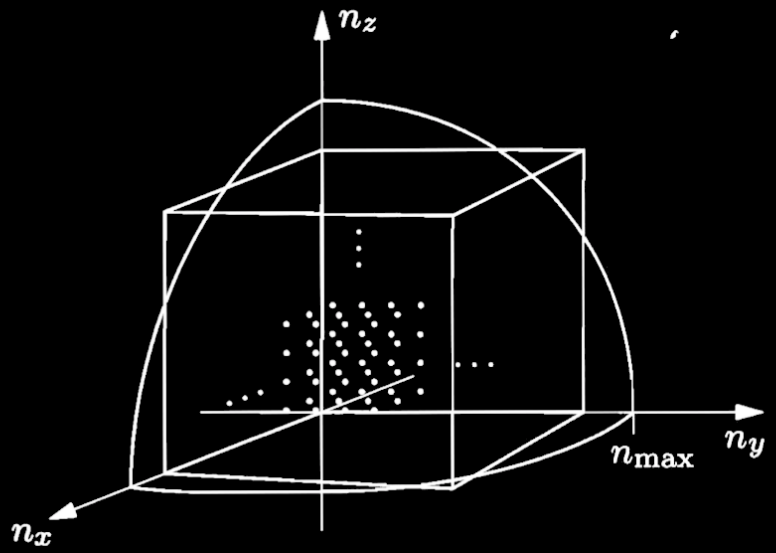
$$U = 3 \sum_{n_x} \sum_{n_y} \sum_{n_z} \epsilon\, \bar{n}_{Pl}(\epsilon)$$

$$N = \frac{1}{8}\frac{4}{3}\pi n_{max}^3$$

$$n_{max} = \left(\frac{6N}{\pi}\right)^{1/3}$$

$$U = 3\int_0^{\pi/2} d\phi \int_0^{\pi/2} sin\theta d\theta \int_0^{n_{max}} n^2 \frac{\epsilon}{e^{\epsilon/kT} - 1} dn$$

$$U = \frac{3\pi}{2}\int_0^{n_{max}} \left(\frac{hc_s}{2L}\right)\left(\frac{n^3}{e^{\frac{hc_s n}{2LkT}} - 1}\right) dn$$



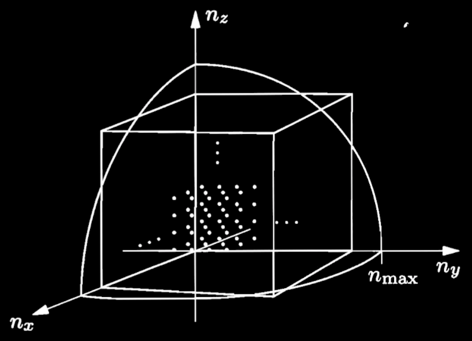
$$n = \frac{2LkT}{hc_s}(x)$$

$$T_D = \frac{hc_s}{2Lk}\left(\frac{6N}{\pi}\right)^{1/3}$$

Derivation of vibrational energy using Debye Theory

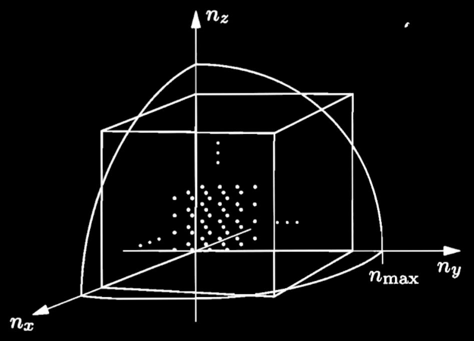
$$U = \frac{3\pi}{2}\int_0^{n_{max}} \left(\frac{hc_s}{2L}\right)\left(\frac{n^3}{e^{\frac{hc_s n}{2LkT}} - 1}\right) dn = \frac{3\pi}{2}\int_0^{x_{max}} \left(\frac{hc_s}{2L}\right)\left(\frac{2LkT}{hc_s}\right)^4 \left(\frac{x^3}{e^x - 1}\right) dx$$

$$= \frac{3\pi}{2}\left(\frac{2L}{hc_s}\right)^3 (kT)^4 \int_0^{x_{max}} \left(\frac{x^3}{e^x - 1}\right) dx = \frac{9NkT^4}{T_D^3}\int_0^{x_{max}} \left(\frac{x^3}{e^x - 1}\right) dx$$



$$x = \frac{hc_s n}{2LkT} \qquad x_{max} = \frac{hc_s}{2kT}\left(\frac{6N}{\pi V}\right)^{1/3} \equiv \frac{T_D}{T} \qquad T_D = \frac{hc_s}{2Lk}\left(\frac{6N}{\pi}\right)^{1/3}$$

$$n = \frac{2LkT}{hc_s}(x) \qquad \left(\frac{2L}{hc_s}\right)^3 = \frac{6N}{\pi}\frac{1}{k^3 T_D^3}$$



C_V in the extreme temperature limits of the Debye Model

$$U = \frac{9NkT^4}{T_D^3}\int_0^{T_D/T}\left(\frac{x^3}{e^x - 1}\right)dx$$

- When $T \gg T_D$, $U = 3NkT$ $C_V = 3Nk$
  - $x \ll 1$: $e^x \approx 1 + x$

- When $T \ll T_D$, $U = \frac{3\pi^4}{5}\frac{NkT^4}{T_D^3}$ $C_V = \frac{12NK\pi^4}{5}\left(\frac{T}{T_D}\right)^3$

(integral calculated by Schroeder, see appendix B.5)

Derivation of the general formula for heat capacity under Debye Theory

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{3\pi}{2}\int_0^{n_{max}} \left(\frac{hc_s}{2L}\right)\frac{\partial}{\partial T}\left(\frac{n^3}{e^{\frac{hc_s n}{2LkT}} - 1}\right)dn$$

$$C_V = \frac{3\pi}{2}\int_0^{n_{max}} \left(\frac{hc_s}{2L}\right)\left(\frac{\left(\frac{hc_s n}{2LkT^2}\right)e^{\frac{hc_s n}{2LkT}}(n)^3}{\left(e^{\frac{hc_s n}{2LkT}} - 1\right)^2}\right)dn$$

$$C_V = \frac{3\pi}{2}\left(\frac{hc_s}{2L}\right)^2 \frac{1}{kT^2}\int_0^{n_{max}} \frac{n^4 e^{\frac{hc_s n}{2LkT}}}{\left(e^{\frac{hc_s n}{2LkT}} - 1\right)^2}dn$$

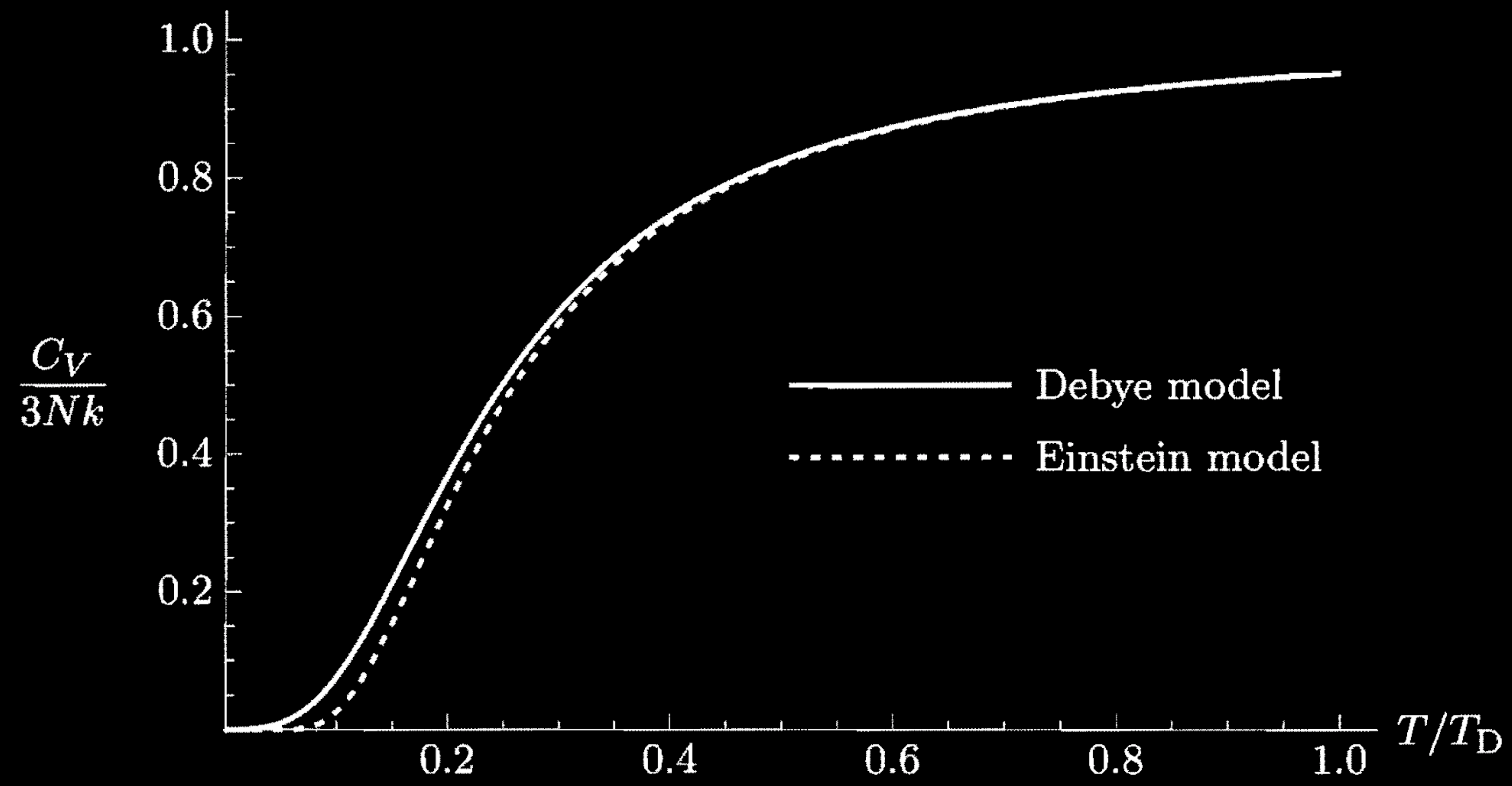
Derivation of the general formula for heat capacity under Debye Theory

$$C_V = \frac{3\pi}{2}\left(\frac{hc_s}{2L}\right)^2 \frac{1}{kT^2}\int_0^{n_{max}} \frac{n^4 e^{\frac{hc_s n}{2LkT}}}{\left(e^{\frac{hc_s n}{2LkT}}-1\right)^2}\, dn \qquad [n = \frac{2LkT}{hc_s}(x)]$$

$$C_V = \frac{3\pi}{2}\left(\frac{2L}{hc_s}\right)^3 k^4 T^3 \int_0^{x_{max}} \frac{x^4 e^x}{(e^x - 1)^2}\, dx \qquad [\left(\frac{2L}{hc_s}\right)^3 = \frac{6N}{\pi}\frac{1}{k^3 T_D^3}]$$

$$C_V = 9NK\left(\frac{T}{T_D}\right)^3 \int_0^{T_D/T} \frac{x^4 e^x}{(e^x - 1)^2}\, dx$$

Finally, we can plot our newly defined C_V and compare against our previous model



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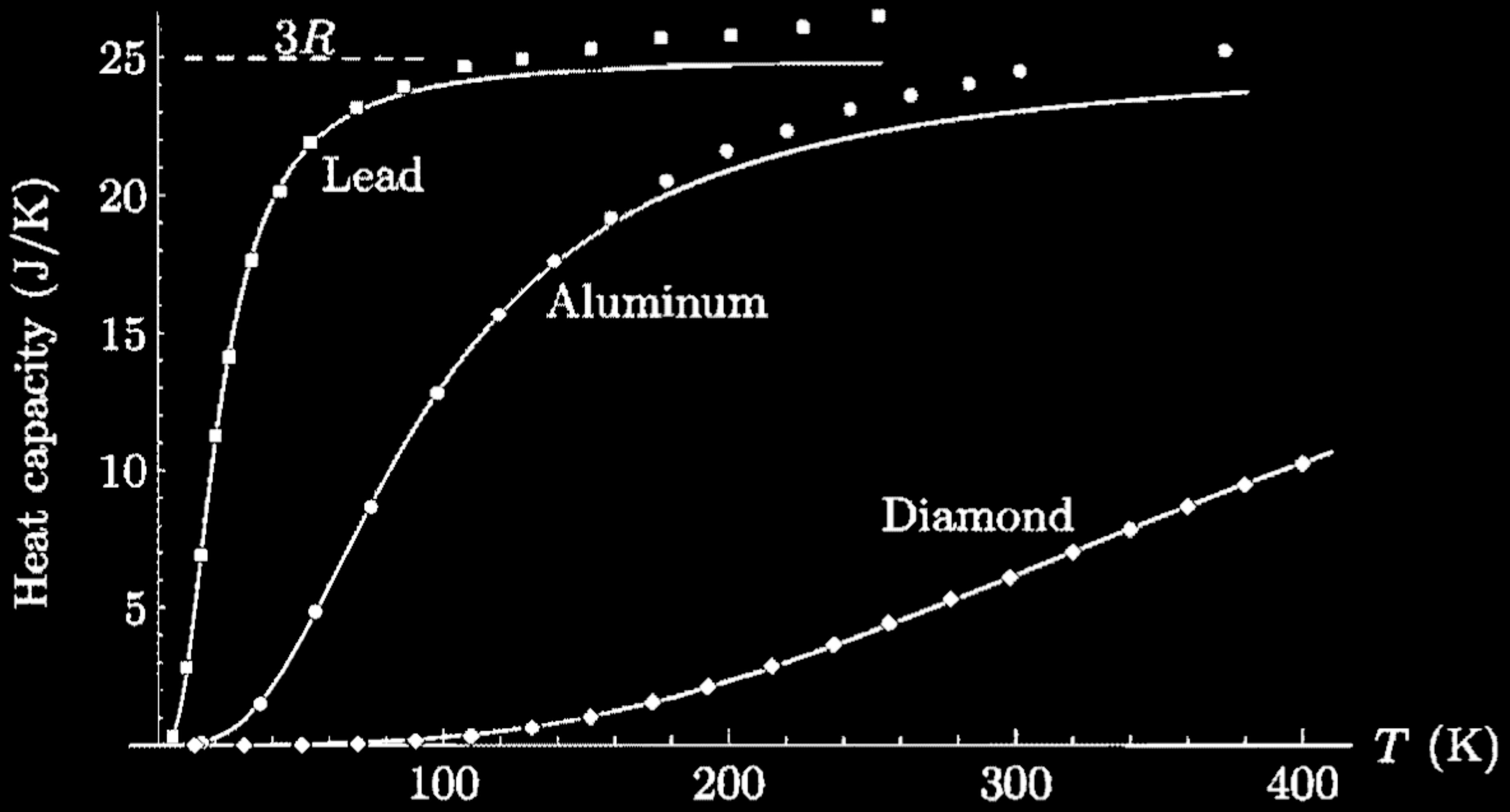

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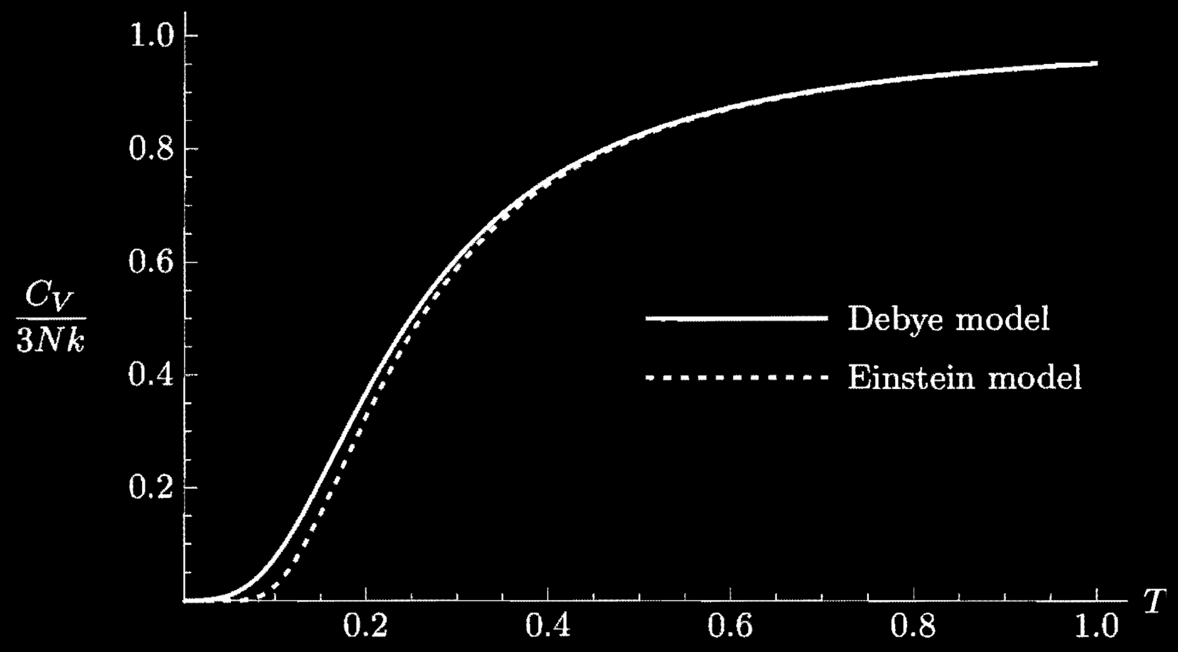

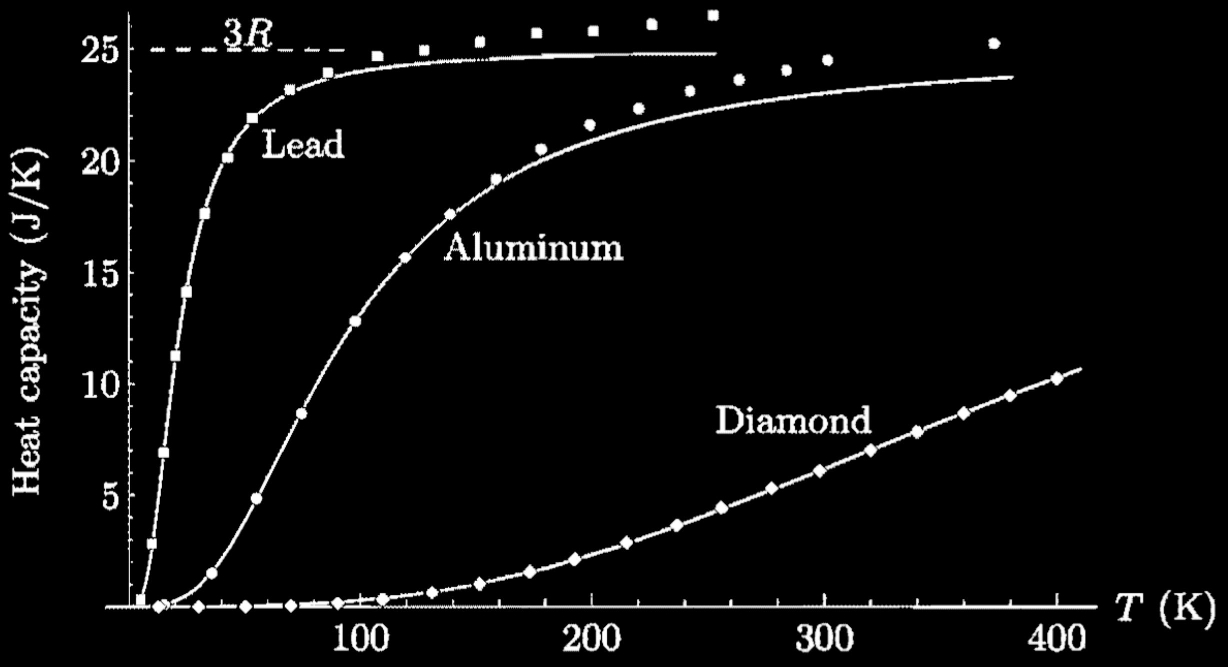

In Summary

- Both models give the same result in the high temperature limit, demonstrating that at high temperatures all the oscillators essentially have the same energy
- The Debye model gives correct results at the low temperature limit because it accounts for both low and high frequency modes of oscillation
- The Debye model is used across solid state physics as it gives accurate predictions while being ridiculously simple to work with once you know the c_s for the material you are working with.

- $C_V = 9NK\left(\frac{T}{T_D}\right)^3 \int_0^{T_D/T} \frac{x^4 e^x}{(e^x-1)^2} dx$ w/ $x = \frac{hc_s n}{2LkT}$ & $T_D = \frac{hc_s}{2Lk}\left(\frac{6N}{\pi}\right)^{1/3}$