

The Debye Crystal

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Debye Crystal

The Einstein solid works pretty well except that interparticle interactions are ignored. Every oscillator is the same. In fact, at significant temperatures, a solid acts more like a multibody system with $3N$ degrees of freedom.

In such a multibody problem, all vibrations can be expressed in terms of the so called “normal coordinates” which correspond to the “normal modes” of vibration, each of which oscillates like a harmonic oscillator.



In consequence there is a wide distribution, $g(\nu)$, of natural frequencies in a real solid, although the total number of modes that can exist at one time must be $3N$. So the normalization criteria must be

$$\int_0^{\nu_m} g(\nu) d\nu = 3N$$

We will discuss the meaning of ν_m in a later slide. We can thus write the partition function as

$$-\ln Q = N \frac{U(0)}{2kT} + \int_0^\infty \left[\ln(1 - e^{-\theta/T}) + \frac{\theta}{2T} \right] g(\nu) d\nu$$

The question is, what to use for the distribution function of frequencies? Einstein used

$$g(\nu) = 3N\delta(\nu - \nu_E)$$

Debye assumed that he could determine the distribution using elastic wave analysis and ignoring quantum effects.

The wave analysis results in a wave velocity distribution that is essentially the same as the translational energy distribution from the particle in a box problem.

The bottom line is that

$$g(v)dv = \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) 4\pi V v^2 dv$$

where v_t and v_l are the transverse and longitudinal wave speeds in the solid. Defining an effective wave speed as

$$\frac{3}{v_0^3} = \frac{2}{v_t^3} + \frac{1}{v_l^3}$$

we can write

$$g(v)dv = \frac{12\pi V}{v_0^3} v^2 dv$$

Using the normalization criteria

$$\int_0^{v_m} g(v) dv = 3N$$

we obtain

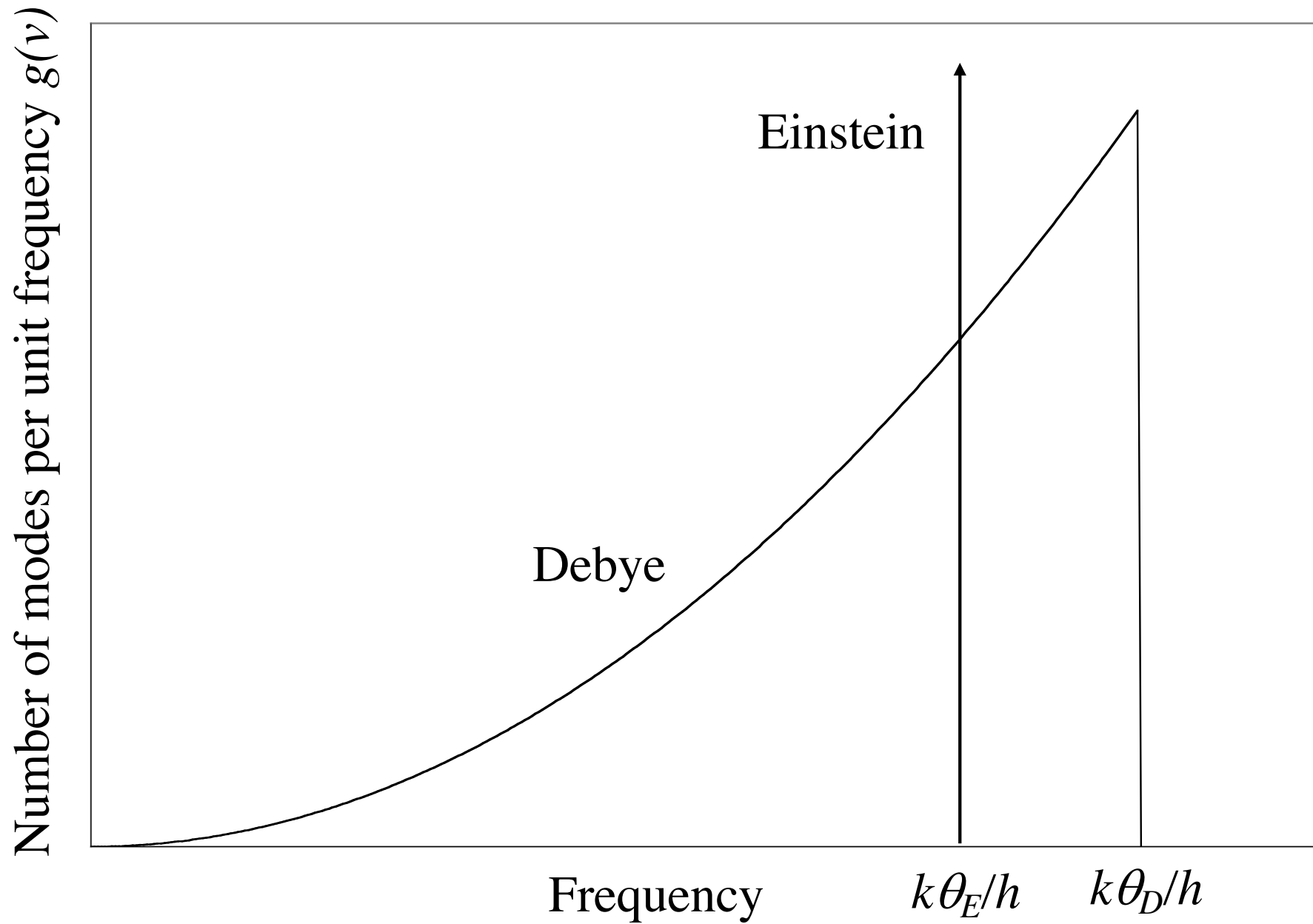
$$v_m = \left(\frac{3N}{4\pi V} \right)^{1/3} v_0$$

so

$$\begin{aligned} g(v)dv &= \left(\frac{9N}{v_m^3} \right) v^2 dv, & 0 \leq v \leq v_m \\ &= 0, & v > v_m \end{aligned}$$

v_m is called the cutoff frequency





Plugging all this into the Fundamental Relation

$$\frac{F}{kT} = -N \left\{ \frac{U(0)}{2kT} + \frac{9}{8} \frac{\theta_D}{T} + 3 \ln(1 - e^{-\theta_D/T}) - 3 \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^3 dx}{e^x - 1} \right\}$$

where

$$\theta_D \equiv \frac{h\nu_m}{k}$$

is called the Debye temperature.



Then

$$\frac{U}{kT} = -N \left\{ \frac{U(0)}{2kT} + \frac{9}{8} \frac{\theta_D}{T} + 9 \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^3 dx}{e^x - 1} \right\}$$

$$\frac{S}{k} = 9N \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \left[\frac{x^3}{e^x - 1} - x^2 \ln(1 - e^{-x}) \right] dx$$

$$\frac{C_v}{k} = 3ND \left(\frac{T}{\theta_D} \right)$$

where the “Debye Function” is defined as

$$D \left(\frac{T}{\theta_D} \right) \equiv 3 \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

Limits:

Einstein

Debye

$$T \rightarrow 0$$

$$\frac{C_v}{Nk} \rightarrow 3 \left(\frac{\theta_E / T}{e^{\theta_E / 2T}} \right)^2$$

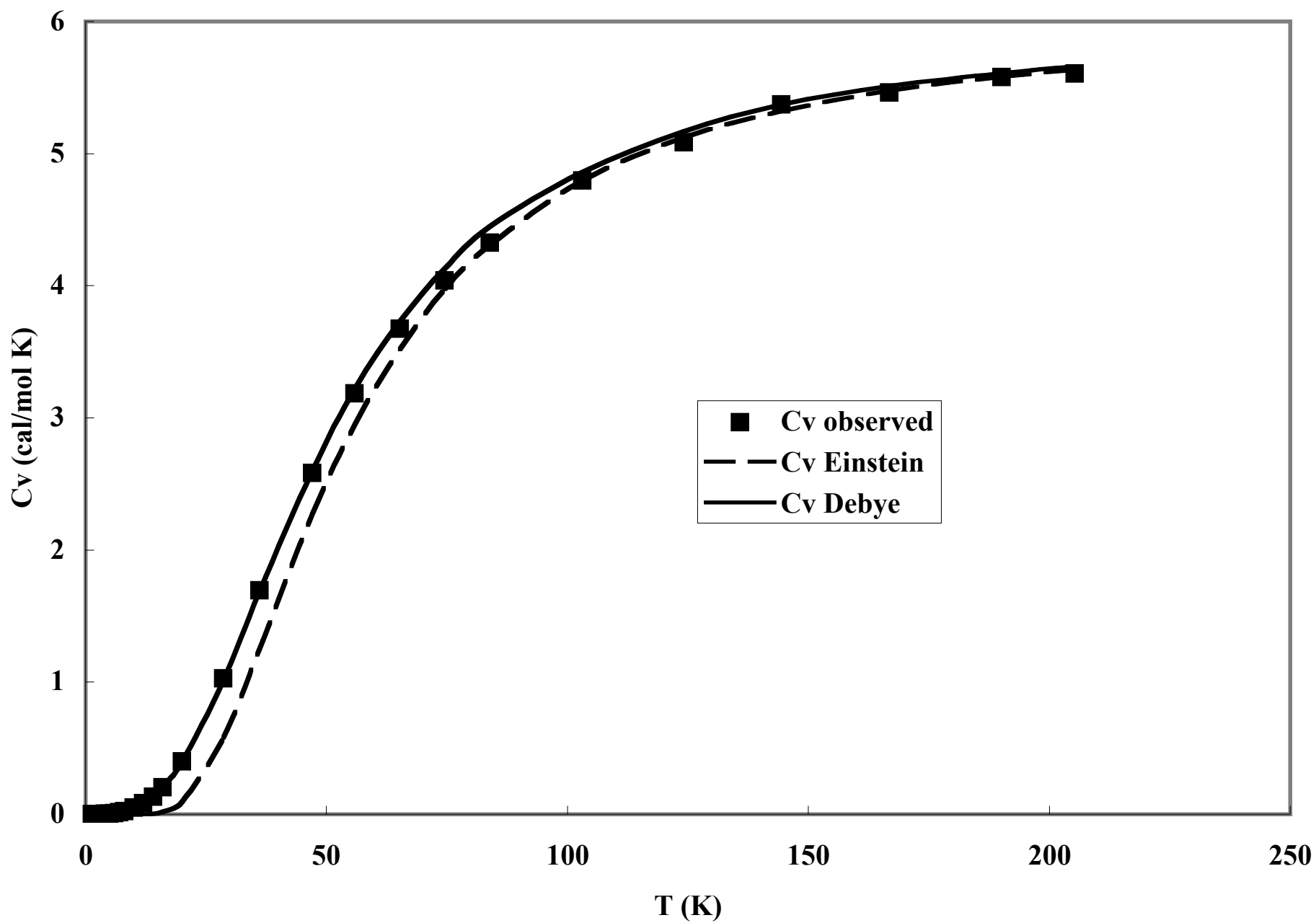
$$\frac{C_v}{Nk} \rightarrow \frac{12\pi^4}{5} \left(\frac{T}{\theta_D} \right)^3$$

$$T \rightarrow \infty$$

$$\frac{C_v}{Nk} \rightarrow 3$$

$$\frac{C_v}{Nk} \rightarrow 3$$

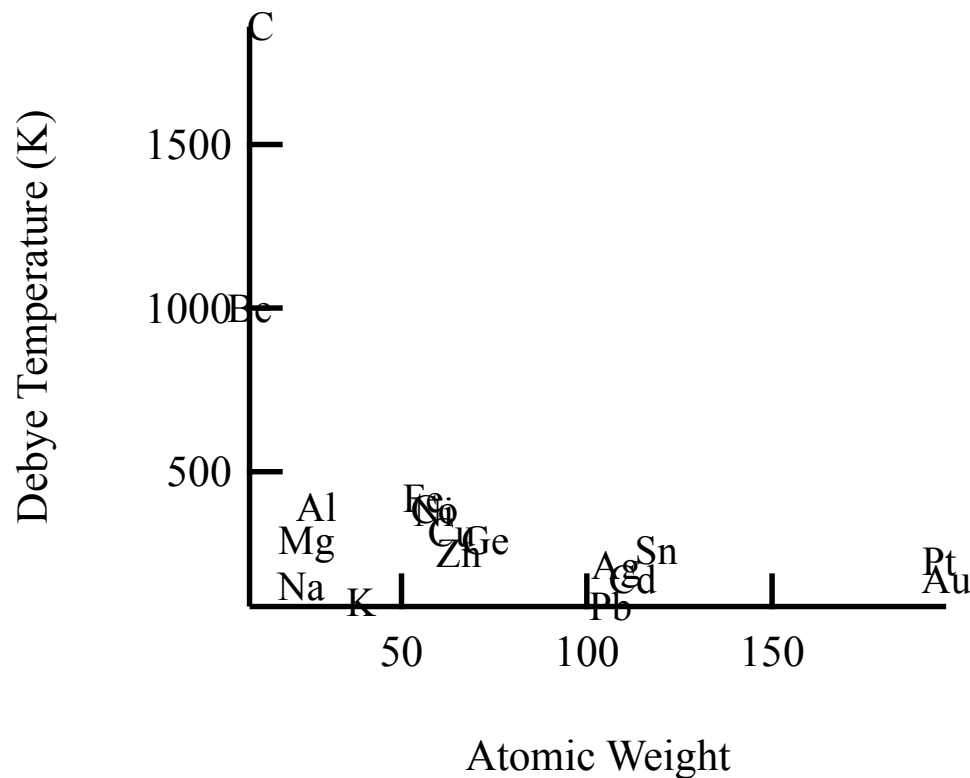




The Debye temperature can be inferred from specific heat data or from elastic constants.

Solid	θ_D(K)	Solid	θ_D(K)
Na	150	Fe	420
K	100	Co	385
Cu	315	Ni	375
Ag	215	Al	390
Au	170	Ge	290
Be	1000	Sn	260
Mg	290	Pb	88
Zn	250	Pt	225
Cd	172	C (Diam)	1860

The Debye temperature tends to decrease with increasing atomic mass. This is because the frequency of a harmonic oscillator is proportional to the spring constant over the mass.



Typical values of Θ_D are fairly low, usually of the order of room temperature or less. This is due to relatively low force constants and large masses in monatomic crystals.

In general, Debye theory fits fairly well for monatomic crystal solids. It does not work for non-crystal solids.