Mineral Physics I
Chapter 3. Lattice vibration
Section 4. Einstein model for heat capacity

Tomoo Katsura,

Bayerisches Geoinstitut, University of Bayreuth, Germany

This section

q Goal of this section: To obtain a heat capacity model of a crystal by assuming that the lattice vibrates with a single frequency

Ø Einstein model for heat capacity

q Flow of derivation

Ø The energy levels of one-dimensional quantum harmonic oscillator

Ø The average quantum number of the harmonic oscillators

ü Planck distribution

Ø Total vibrational energy

Ø Differentiation of the total vibrational energy by temperature to obtain a heat capacity

Total vibrational energy

q Sub-total vibrational energy at a given frequency = (the number of vibrational modes) * (average vibrational energy)

Ø $E_i = D(\omega_i)\langle\varepsilon(\omega_i)\rangle$ $\qquad\qquad\qquad\qquad$ (3.5.1)

q Total energy of the lattice vibration = sum of sub-total vibrational energy at each frequency

Ø $E_{total} = \Sigma_i E_i = \int E(\omega)\mathrm{d}\omega = \int D(\omega)\langle\varepsilon(\omega)\rangle\,\mathrm{d}\omega$ $\qquad\qquad$ (3.5.2)

Energy level of quantum mechanical harmonic oscillator
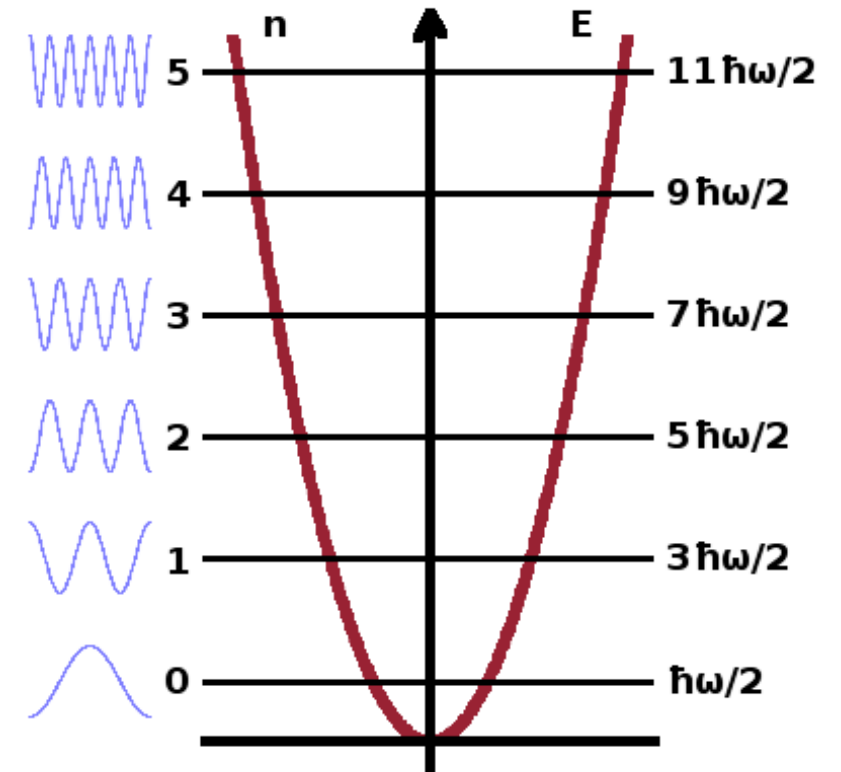
q Quantum-mechanical harmonic oscillator model

Ø The energy levels of a particular mode with the angular frequency ω and its harmonics:

ü $\varepsilon_n = \left(n + \dfrac{1}{2}\right)\hbar\omega$ (3.5.3)

§ n: quantum number

§ $n = 0$ term: zero-point energy $\varepsilon_0 = \dfrac{1}{2}\hbar\omega$

  ○ The fundamental mode

Relative population of each energy level

❑ The fraction $\frac{N_n}{N}$ of an oscillator with the *n*-th energy at an given frequency ω and a temperature, T

 Ø (probability to have the *n*-th level of energy) / (sum of probabilities for all levels)

 Ø Using Boltzmann distribution: $P_n \propto \exp\left(-\frac{\varepsilon_n}{k_B T}\right)$

 ü $\dfrac{N_n}{N} = \dfrac{\exp\left(\dfrac{-\left(n+\frac{1}{2}\right)\hbar\omega}{k_B T}\right)}{\sum_{S=1}^{\infty} \exp\left(\dfrac{-\left(s+\frac{1}{2}\right)\hbar\omega}{k_B T}\right)} = \dfrac{\exp\left(-\dfrac{n\hbar\omega}{k_B T}\right)}{\sum_S \exp\left(-\dfrac{s\hbar\omega}{k_B T}\right)}$ (3.5.4)

 ü The ½ disappeared by cancelation

Planck distribution

q The average quantum number $\langle n \rangle$

$$\langle n \rangle = \sum_s s \frac{N_s}{N} = \sum_s \frac{s \exp\left(-\frac{s\hbar\omega}{k_B T}\right)}{\sum_p \exp\left(-\frac{p\hbar\omega}{k_B T}\right)} = \frac{\sum_s s\left\{\exp\left(-\frac{\hbar\omega}{k_B T}\right)\right\}^s}{\sum_p \left\{\exp\left(-\frac{\hbar\omega}{k_B T}\right)\right\}^p} = \frac{\sum_s s x^s}{\sum_p x^p} = \left(\frac{x}{(1-x)^2}\right) \Big/ \left(\frac{1}{1-x}\right) = \frac{x}{1-x}$$

$$(3.5.5) \qquad\qquad x = \exp\left(-\frac{\hbar\omega}{k_B T}\right)$$

$$\langle n \rangle = \frac{\exp\left(-\frac{\hbar\omega}{k_B T}\right)}{1-\exp\left(-\frac{\hbar\omega}{k_B T}\right)} = \frac{\exp\left(-\frac{\hbar\omega}{k_B T}\right)\exp\left(+\frac{\hbar\omega}{k_B T}\right)}{\left\{1-\exp\left(-\frac{\hbar\omega}{k_B T}\right)\right\}\exp\left(+\frac{\hbar\omega}{k_B T}\right)} = \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right)-1} \qquad (3.5.6)$$

ü Planck distribution

q Average energy of an oscillator with an angular frequency ω at a temperature T

$$\langle \varepsilon(\omega) \rangle = \left(\langle n \rangle + \frac{1}{2}\right)\hbar\omega \approx \langle n \rangle \hbar\omega = \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right)-1} \qquad (3.5.7)$$

Total vibrational energy

q The total vibrational energy of the lattice

ø $E_{\text{total}} = \sum_i \langle \varepsilon(\omega_i) \rangle = \sum_i \dfrac{\hbar \omega_i}{\exp\left(\frac{\hbar \omega_i}{k_B T}\right) - 1}$ (3.5.8)

ü Each frequency can have more than one modes due to different $\vec{K}$ and polarization

q By approximating (3.5.5) by integration:

ø $E_{\text{total}} = \int D(\omega) \dfrac{\hbar \omega}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1} \mathrm{d}\omega$ (3.5.9)

ü $D(\omega)$: density of states as a function of ω

§ The Planck distribution takes care of the distribution at a given ω

Heat capacity

q Heat capacity C: T derivative of E_{total}

Ø $C = \dfrac{\mathrm{d}E_{\text{vib}}}{\mathrm{d}T} = \dfrac{\mathrm{d}}{\mathrm{d}T} \int D(\omega) \dfrac{\hbar\omega}{\exp(\hbar\omega/k_BT)-1} \mathrm{d}\omega$ (3.5.10)

ü $D(\omega)$: approximately independent from T

Ø $C = \int D(\omega) \dfrac{\mathrm{d}}{\mathrm{d}T} \left(\dfrac{\hbar\omega}{\exp(\hbar\omega/k_BT)-1} \right) \mathrm{d}\omega$

$= \int D(\omega) \left(-\dfrac{\hbar\omega}{(\exp(\hbar\omega/k_BT)-1)^2} \right) \dfrac{\mathrm{d}}{\mathrm{d}T} \left(\exp\left(\dfrac{\hbar\omega}{k_B}\dfrac{1}{T} \right) - 1 \right) \mathrm{d}\omega$

$= \int D(\omega) \left(-\dfrac{\hbar\omega}{(\exp(\hbar\omega/k_BT)-1)^2} \right) \exp\left(\dfrac{\hbar\omega}{k_BT} \right) \left(-\dfrac{\hbar\omega}{k_B}\dfrac{1}{T^2} \right) \mathrm{d}\omega$

$= \int D(\omega) \dfrac{\hbar^2\omega^2 \exp(\hbar\omega/k_BT)}{k_BT^2(\exp(\hbar\omega/k_BT)-1)^2} \mathrm{d}\omega$ (3.5.11)

$= \int D(\omega)k_B \dfrac{(\hbar\omega/k_BT)^2 \exp(\hbar\omega/k_BT)}{(\exp(\hbar\omega/k_BT)-1)^2} \mathrm{d}\omega = k_B \int D(\omega) \dfrac{x^2 e^x}{(e^x-1)^2} \mathrm{d}\omega$ (3.5.12)

ü $x = \hbar\omega/k_BT$ (3.5.13)

Einstein solid -1

q Einstein solid: the simplest model of heat capacity in which the results of statistical and quantum mechanics are considered.

  Ø Assumption

    ü All atoms oscillate with the same frequency

      § $\omega = \omega_\alpha$ only

        ○ $\nu_\alpha = \omega_\alpha / 2\pi$: Einstein frequency

      § $D(\omega) = D(\omega_\alpha) = const.$ (3.5.14)

  Ø The average energy of one-dimensional oscillation of an atom:

    ü $\langle \varepsilon_{\text{Es}} \rangle = \dfrac{\hbar\omega_\alpha}{\exp\left(\frac{\hbar\omega_\alpha}{k_B T}\right) - 1}$ (3.5.15)

Einstein solid -2

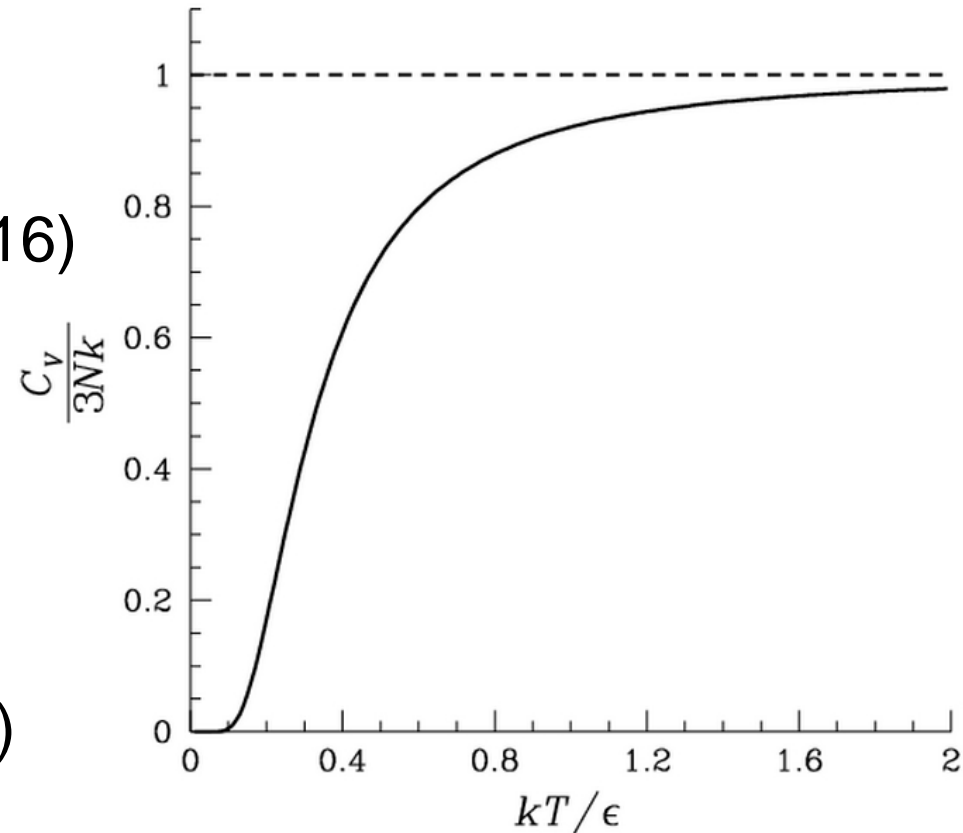❑ The total energy of the crystal consisting of 3-dimensional N atoms:

Ø $E_{\text{Es}} = 3N\langle\varepsilon_{\text{Es}}\rangle = \dfrac{3N\hbar\omega_\alpha}{\exp(\hbar\omega_\alpha/k_BT)-1}$ (3.5.16)

❑ The heat capacity of the crystal:

Ø $C_{V,\text{Es}} = \dfrac{3Nk_B\left(\dfrac{\hbar\omega_\alpha}{k_BT}\right)^2\exp\left(\dfrac{\hbar\omega_\alpha}{k_BT}\right)}{\left[\exp\left(\dfrac{\hbar\omega_\alpha}{k_BT}\right)-1\right]^2}$

$= 3Nk_B\left(\dfrac{T_\alpha}{T}\right)^2\dfrac{\exp\left(\dfrac{T_\alpha}{T}\right)}{\left[\exp\left(\dfrac{T_\alpha}{T}\right)-1\right]^2}$ (3.5.17)

ü $T_\alpha = \hbar\omega_\alpha/k_B$

§ Einstein temperature

https://en.wikipedia.org/wiki/Einstein_solid

High *T* limits of Einstein heat capacity

- **q** HT Limit: $T \to \infty$
  - **Ø** $T_\alpha / T \to 0$
  - **Ø** $\exp(T_\alpha / T) \to 1 + T_\alpha / T \to 1$
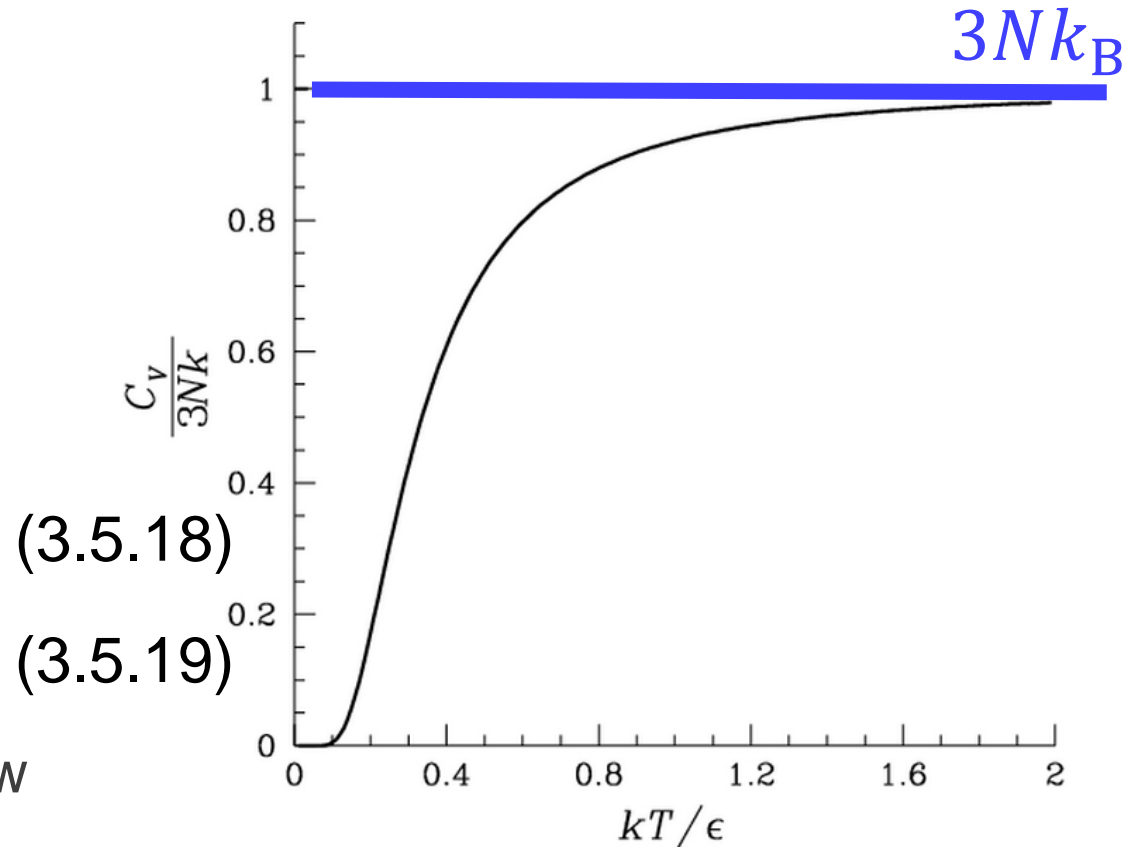 - **Ø** $C_{V,\mathrm{Es}} = \dfrac{3Nk_\mathrm{B}(T_\alpha/T)^2 \exp(T_\alpha/T)}{[\exp(T_\alpha/T)-1]^2}$

    $\to \dfrac{3Nk_\mathrm{B}(T_\alpha/T)^2(1+T_\alpha/T)}{(1+T_\alpha/T-1)^2} \to 3Nk_\mathrm{B}$

- **q** For one mole solid,
  - **Ø** $C_{V,\mathrm{Es}} \to 3R$
    - **ü** Approaches to Dulong-Pulit law
      - **§** $3R$: Dulong-Putit limit

$3Nk_\mathrm{B}$

(3.5.18)

(3.5.19)

https://en.wikipedia.org/wiki/Einstein_solid

Low *T* limits of Einstein heat capacity

❑ LT Limit: $T \to 0$

  Ø $T_\alpha/T \to \infty$

  Ø $\exp(T_\alpha/T) - 1 \to \exp(T_\alpha/T)$

  Ø $C_{V,\mathrm{Es}} = \dfrac{3Nk_\mathrm{B}(T_\alpha/T)^2 \exp(T_\alpha/T)}{[\exp(T_\alpha/T)-1]^2}$

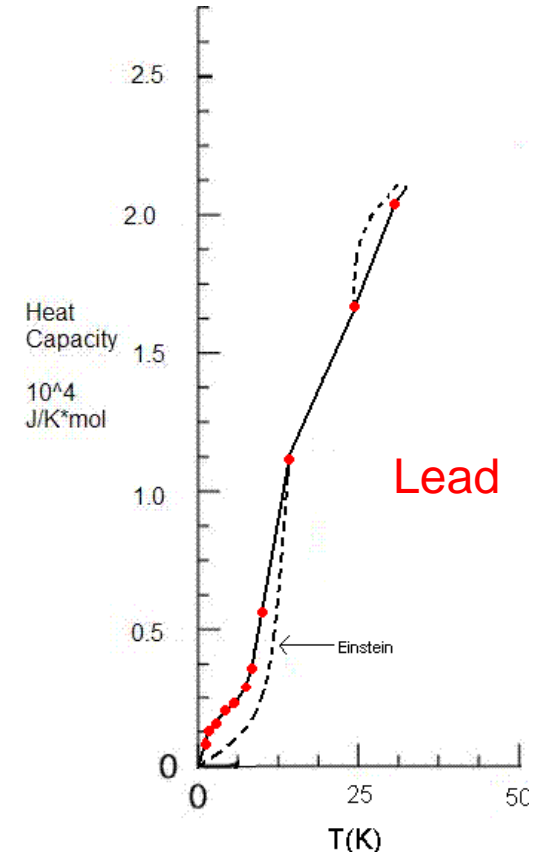 $\to \dfrac{3Nk_\mathrm{B}(T_\alpha/T)^2}{\exp(T_\alpha/T)} \to 0$ (3.5.20)

  Ø $\exp(T_\alpha/T) \gg (T_\alpha/T)^2$:

  ü $C_{V,\mathrm{Es}}$ rapidly geos to zero with $T \to 0$

https://en.wikipedia.org/wiki/Einstein_solid
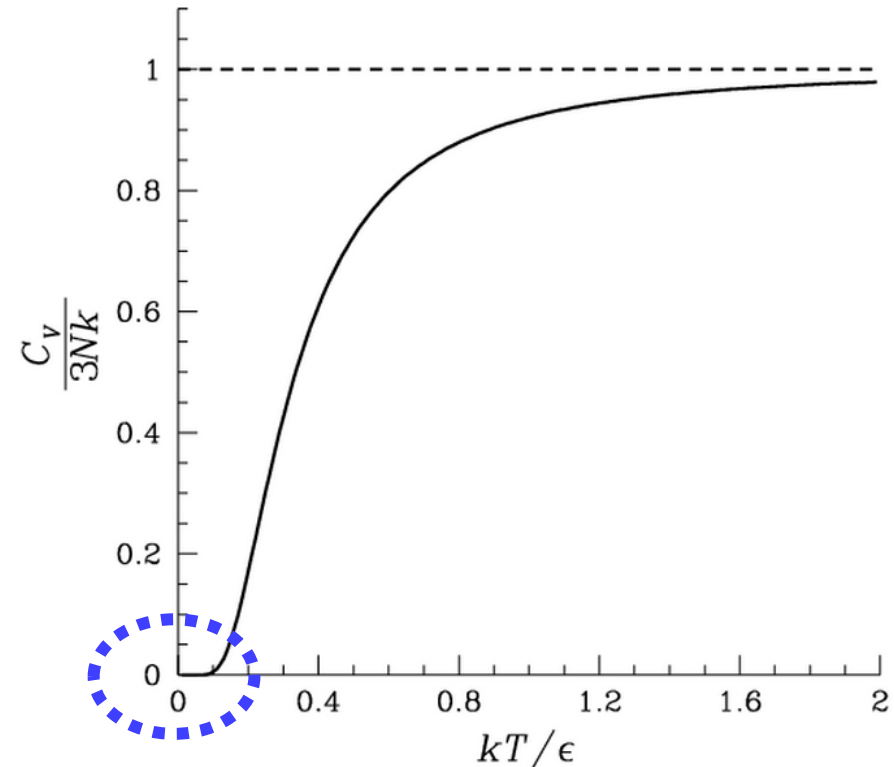
Underestimation of low-T heat capacity by Einstein model

q Einstein model vs real solids

  Ø Systematic deviation of heat capacity at low T

    ü The lattice vibration with a given ω cannot be excited at low T due to low thermal energy

  Ø The oscillation of solids: far from single- ω

    ü Maybe the ω of vibration excited at low T should be low

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End