Thermodynamics of materials
17. Chemical potentials of Einstein and Debye Crystals

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Helmholtz energy from partition function

- The ensemble has ν_i microstates, the number of ways arranging these is

$$\Omega_\nu = \frac{\nu!}{\nu_1! \nu_2! \nu_3! \cdots}$$

- Using Sterling's approximation, when N is large,

$$\ln N! \simeq N \ln N - N$$

we have

$$\ln \Omega_\nu = \nu \ln \nu - \nu - \sum_i \left(\nu_i \ln \nu_i - \nu_i \right)$$

$$= \sum_i \nu_i \left(\ln \nu_i / \nu \right) = -\nu \sum_i p_i \ln p_i$$

where

$$p_i = \frac{\nu_i}{\nu} = \frac{\exp\left(-\varepsilon_i \beta \right)}{Z}$$

Helmholtz energy from partition function

- Since the ensemble entropy is

$$S_\nu = k_\mathsf{B} \ln \Omega_\nu = -k_\mathsf{B} \nu \sum_i p_i \ln p_i$$

- Normalize total number of microstates ν, we have the average entropy of the state,

$$\overline{S} = -k_\mathsf{B} \sum_i p_i \ln p_i = -k_\mathsf{B} \sum_i p_i \big(-\varepsilon_i \beta - \ln Z \big)$$

$$= k_\mathsf{B} \big(\overline{E} \beta + \ln Z \big) = \frac{\overline{E}}{T} + k_\mathsf{B} \ln Z$$

Rearrange to

$$k_\mathsf{B} T \ln Z = -\overline{E} + T\overline{S} = -F$$

therefore,

$$F = -k_\mathsf{B} T \ln Z$$

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Einstein Solid

- The crystalline solid with $3N$ harmonic oscillators, which emulate the lattice vibrations, at same frequency ω. The energy of each oscillator is

$$E_n = \frac{\hbar\omega}{k_{\mathrm{B}}T}\left(n + \frac{1}{2}\right)$$

At sufficiently high temperature T, when the energy of the oscillator is much higher than $k_{\mathrm{B}}T$, the partition function for the single oscillator is

$$z = \sum_{n=0}^{\infty} \exp\left[\frac{\hbar\omega}{k_{\mathrm{B}}T}\left(n + \frac{1}{2}\right)\right] = \exp\left(\frac{-\hbar\omega}{2k_{\mathrm{B}}T}\right)\sum_{n=0}^{\infty}\exp\left(\frac{-n\hbar\omega}{k_{\mathrm{B}}T}\right)$$

$$= \exp\left(\frac{-\hbar\omega}{2k_{\mathrm{B}}T}\right)\sum_{n=0}^{\infty}\left[\exp\left(\frac{-\hbar\omega}{k_{\mathrm{B}}T}\right)\right]^n = \frac{\exp\left(-\hbar\omega/2k_{\mathrm{B}}T\right)}{1 - \exp\left(-\hbar\omega/k_{\mathrm{B}}T\right)}$$

Einstein Solid

- In 3-D, there have to be $3N$ harmonic oscillator, then

$$z_{3D} = \left[\frac{\exp\left(-\hbar\omega/2k_BT\right)}{1 - \exp\left(-\hbar\omega/k_BT\right)} \right]^{3N}$$

- At $0\,\text{K}$, when the system energy at given molar volume v is $u(0,v)$, then the partition function is

$$Z = \left[\frac{\exp\left(-\hbar\omega/2k_BT\right)}{1 - \exp\left(-\hbar\omega/k_BT\right)} \right]^{3N} \exp\left(-\frac{Nu(0,v)}{k_BT}\right)$$

Einstein Solid

- The Helmholtz energy of Einstein solid is

$$F(T, V, N) = -3N k_{\mathsf{B}} T \ln \left[\frac{\exp\left(-\hbar\omega/2k_{\mathsf{B}}T\right)}{1 - \exp\left(-\hbar\omega/k_{\mathsf{B}}T\right)} \right] + N u(0, v)$$

then can be rewritten by

$$F(T, V, N) = N u(0, v) + 3N k_{\mathsf{B}} T \ln \left[2 \sinh \left(\frac{\hbar\omega}{2k_{\mathsf{B}}T} \right) \right]$$

- The chemical potential of Einstein solid is

$$\mu(T, v) = \left(\frac{\partial F}{\partial N} \right)_{T,V} = u(0, v) + 3 k_{\mathsf{B}} T \ln \left[2 \sinh \left(\frac{\hbar\omega}{2k_{\mathsf{B}}T} \right) \right]$$

Einstein Solid

- The entropy is

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = -3Nk_{\mathrm{B}} \ln\left(1 - \exp\left(-\beta\hbar\omega\right)\right)$$

$$+ \frac{3N\hbar\omega}{T} \frac{\exp\left(-\beta\hbar\omega\right)}{1 - \exp\left(-\beta\hbar\omega\right)}$$

- The internal energy is

$$U = F + TS = Nu(0,v) + \frac{3}{2}N\hbar\omega + \frac{3N\hbar\omega}{\exp\left(\beta\hbar\omega\right) - 1}$$

Einstein Solid

- The heat capacity of the Einstein solid us

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = 3Nk_{\mathsf{B}}\left(\beta\hbar\omega\right)^2 \frac{\exp\left(\beta\hbar\omega\right)}{\left(\exp\left(\beta\hbar\omega\right) - 1\right)^2}$$

- At low temperature,

$$\exp\left(\beta\hbar\omega\right) - 1 \simeq \exp\left(\beta\hbar\omega\right)$$

therefore,

$$C_V = 3Nk_{\mathsf{B}}\left(\beta\hbar\omega\right)^2 \exp\left(-\beta\hbar\omega\right)$$

Einstein Solid

- At high temperature,

$$\exp\left(\beta\hbar\omega\right) - 1 \simeq \beta\hbar\omega \qquad \exp\left(\beta\hbar\omega\right) \simeq 1$$

therefore,

$$C_V = 3Nk_{\mathsf{B}}$$

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- For Debye solid, one can obtain the Helmholtz free energy is

$$F(T, V, N) = Nu(0, v) + \int_0^{\omega_{\mathsf{D}}} \left[\ln \left(\frac{\exp \left(-\frac{\beta \hbar \omega}{2} \right)}{1 - \exp \left(-\beta \hbar \omega \right)} \right) \right] \frac{9N}{\omega_{\mathsf{D}}^3} \omega^2 d\omega$$

where ω_{D} is the Debye frequency.

- Performing integration by parts,

$$F(T, V, N) = Nu(0, v) + \frac{9N\hbar\omega_D}{8} + 3Nk_BT \ln\left(1 - \exp\left(-x\right)\right)$$
$$- \frac{3N\hbar}{\omega_D^3}\left(\frac{k_BT}{\hbar}\right)^4 \int_0^{x_D} \frac{x^3}{\exp\left(x\right) - 1} dx$$

where

$$x = \frac{\hbar\omega}{k_BT} \qquad x_D = \frac{\hbar\omega_D}{k_BT}$$

- At low temperatures,

$$\ln\left(1 - \exp\left(-x\right)\right) \to 0 \qquad x_{\mathsf{D}} \to \infty$$

from Riemann integral, we have

$$\int_0^\infty \frac{x^3}{\exp\left(x\right) - 1} = \frac{\pi^4}{15}$$

then the Helmholtz free energy at low temperature is

$$F = Nu(0, v) + \frac{9N\hbar\omega_{\mathsf{D}}}{8} - \frac{N\hbar}{5\omega_{\mathsf{D}}^3}\left(\frac{\pi k_{\mathsf{B}}T}{\hbar}\right)^4$$

- The entropy is

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = \frac{4\pi^4 N k_{\mathsf{B}}}{5}\left(\frac{k_{\mathsf{B}}T}{\hbar\omega_{\mathsf{D}}}\right)^3$$

- The constant volume heat capacity is

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{N,V} = \frac{12\pi^4 N k_{\mathsf{B}}}{5}\left(\frac{T}{T_{\mathsf{D}}}\right)^3$$

where the Debye temperature

$$T_{\mathsf{D}} = \frac{\hbar\omega_{\mathsf{D}}}{k_{\mathsf{B}}}$$

Debye Solid

- At high temperature,

$$F \simeq N u(0, v) + \frac{9 N \hbar \omega_\mathsf{D}}{8} + 3 N k_\mathsf{B} T \ln \left(\frac{\hbar \omega_\mathsf{D}}{k_\mathsf{B} T} \right) - N k_\mathsf{B} T$$

and

$$S = -\left(\frac{\partial F}{\partial T} \right)_{N,V} = -3 N k_\mathsf{B} \ln \left(\frac{\hbar \omega_\mathsf{D}}{k_\mathsf{B} T} \right) + 4 N k_\mathsf{B}$$

the heat capacity is

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_{N,V} = 3 N k_\mathsf{B}$$