

Solids

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Einstein



Debye



Flory

Solids

- Solids are materials in which the constituent atoms and molecules are so closely packed together that under a sustained shear load they may initially deform, but not continuously like a fluid.
- Examples of solid materials are:
 - metals, minerals, ceramics, polymers, semiconductors, composites, biomaterials (wood, tissue, etc.)

Classification

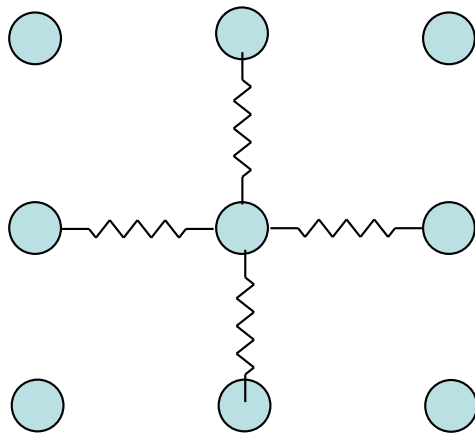
- Solids are classified according to whether they are
 - Crystalline – Base atoms/molecules locked in ordered array
 - Amorphous - Base atoms/molecules or macromolecules arranged in randomized patterns.

Solid State Physics

- The study of solids falls under the purview of solid state physics, sometimes called material science.
- This is beyond the scope of our course.
- However, simple crystalline substances can be analyzed using tools we have developed.
- Two examples we will explore are
 - Einstein monatomic solid
 - Debye monatomic solid

Einstein Monatomic Crystal

Suppose we construct a crystal out of atoms so that every atom sees the same environment:



Number of atoms is
fixed: Canonical
ensemble

If we also assume each atom only moves a little bit, and the motion is harmonic, then we have a system of distinguishable, independent harmonic oscillators.



For a harmonic oscillator, the potential energy is:

$$U(x,y,z) = U(0) + \frac{1}{2}a(x^2 + y^2 + z^2)$$

$U(0)$ is the equilibrium (zero point) potential energy and a is the force constant. $U(0)$ and a will be a function of V/N . This gives the volume dependency.

The energy of the system can be written

$$U_j = \frac{NU(0)}{2} + \sum_{n=1}^{3N} \varepsilon_{nj}$$

(The $1/2$ is to avoid counting each interparticle interaction twice.)

ε_{nj} is the vibrational energy of the n th oscillator when the system is in the j th quantum state. The sum is over all oscillators, of which there are $3N$, not particles.

The canonical partition function is

$$Q = \sum_j e^{-\beta U_j}$$

Subbing in U_j

$$Q = e^{-\frac{N\beta U(0)}{2}} \sum_j e^{-\beta \sum_{n=1}^{3N} \varepsilon_{nj}}$$

$$Q = e^{-\frac{N\beta U(0)}{2}} \sum_j \prod_{n=1}^{3N} e^{-\beta \varepsilon_{nj}}$$



The sum of the products may be factored into a product of sums such that

$$Q = \exp \left[-N \frac{\beta U(0)}{2} \right] \prod_{n=1}^{3N} q_n$$

where

$$q_n = \sum_j e^{-\beta \epsilon_{nj}}$$

is a partition function and ϵ_{nj} is the energy of oscillator n in its j quantum state.

q_n is just the vibrational partition function that we developed for ideal gases:

$$q_n = \frac{e^{-\theta_E/2T}}{1 - e^{-\theta_E/T}} = \frac{1}{2\text{Sinh}(\theta_E / 2T)}$$

where $\theta_E = \frac{h\nu_{vib}}{k}$ is a characteristic vibrational temperature.

Typically

$$\theta_E \sim 300K$$

$$\nu_{vib} \sim 6 \times 10^{12} \text{ sec}^{-1}$$

The partition function then becomes:

$$Q = e^{-N \frac{U(0)}{2kT}} \left(2 \sinh \frac{\theta_E}{2T} \right)^{-3N}$$

So the Fundamental Relation is

$$\frac{F}{kT} = - \left\{ \frac{NU(0)}{2kT} + 3N \ln \left(2 \sinh \frac{\theta_E}{2T} \right) \right\}$$

Internal Energy

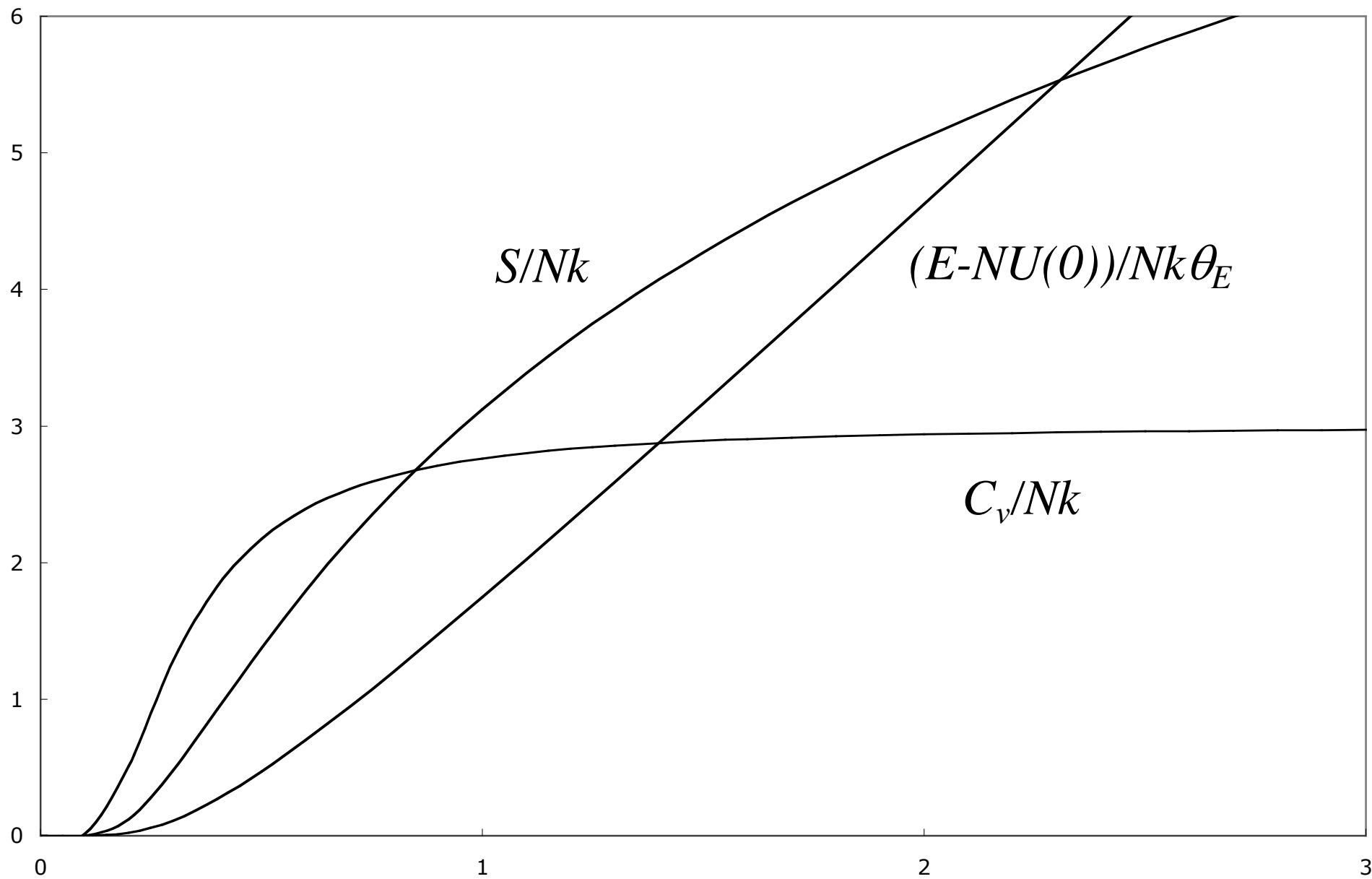
$$U = \frac{NU(0)}{2} + \frac{3}{2}Nk\theta_E \coth \frac{\theta_E}{2T}$$

Specific Heat

$$C_v = 3Nk \left[\frac{\theta_E / 2T}{\sinh(\theta_E / 2T)} \right]^2$$

Entropy

$$S = 3Nk \left[\frac{\theta_E}{2T} \coth \frac{\theta_E}{2T} - \ln \left(2 \sinh \frac{\theta_E}{2T} \right) \right]$$



Dimensionless Temperature T/θ_E



Note that for:

$$T \rightarrow 0 \qquad \frac{C_v}{Nk} \rightarrow 3 \left(\frac{\theta_E / T}{e^{\theta_E / 2T}} \right)^2$$

$$T \rightarrow \infty \qquad \frac{C_v}{Nk} \rightarrow 3$$

