

## Elastic Vibrations of a Solid

We can imagine the Hamiltonian for the periodic array of atoms in a solid to be

$$H = \sum_i \frac{\vec{p}_i^2}{2M} + \frac{1}{2} \sum_{i \neq j} U(\vec{r}_i - \vec{r}_j)$$

↑ pair wise interactions between the atoms.

The position of atom ~~can~~<sup>can</sup> be written as

$\vec{r}_i = \vec{R}_i + \vec{u}_i$  where  $\vec{R}_i$  is its position in the perfect periodic array, and  $\vec{u}_i$  is a small displacement from this position due to thermal fluctuations

then we can expand

$$\begin{aligned} U(\vec{r}_i - \vec{r}_j) &= U(\vec{R}_i - \vec{R}_j + \vec{u}_i - \vec{u}_j) \\ &= U(\vec{R}_i - \vec{R}_j) + \vec{\nabla} U \cdot (\vec{u}_i - \vec{u}_j) + \frac{1}{2} \sum_{\alpha, \beta} \frac{\partial^2 U}{\partial r_{i\alpha} \partial r_{j\beta}} (u_{i\alpha} - u_{j\alpha})(u_{i\beta} - u_{j\beta}) \end{aligned}$$

Now assuming the positions  $\vec{R}_i$  describe a stable equilibrium in the mechanical sense (i.e. the net force on each atom is zero), then

$$\sum_{i \neq j} \vec{\nabla} U \cdot (\vec{u}_i - \vec{u}_j) = 0$$

The Hamiltonian is then

$$H = \sum_i \frac{p_i^2}{2M} + \frac{1}{2} \sum_{i \neq j} \sum_{\alpha\beta} \frac{1}{2} \frac{\partial^2 U(\vec{r}_i, \vec{r}_j)}{\partial r_{i\alpha} \partial r_{j\beta}} (u_{i\alpha} - u_{j\alpha})(u_{j\beta} - u_{i\beta}) + \text{constant}$$

We see that  $H$  is quadratic in the displacements  $\vec{u}_i$ .  
We can rewrite the above as

$$H = \sum_i \frac{p_i^2}{2M} + \sum_{i \neq j} \sum_{\alpha\beta} D_{ij}^{\alpha\beta} u_{i\alpha} u_{j\beta}$$

where the "dynamical matrix"  $D$  is related to the  $\frac{\partial^2 U}{\partial r_{i\alpha} \partial r_{j\beta}}$ .  
One can show that it is always possible to choose "normal coordinates",  $\tilde{u}_{i\alpha} = \sum_{j\beta} C_{ij}^{\alpha\beta} u_{j\beta}$ , such that the above quadratic form is diagonalized.

(see Ashcroft & Mermin for details)

$$\sum_{i \neq j} \sum_{\alpha\beta} D_{ij}^{\alpha\beta} u_{i\alpha} u_{j\beta} = \sum_{i\alpha} \tilde{D}_i^{\alpha} \tilde{u}_{i\alpha}^2$$

Equipartition Theorem then says that each momentum  $p_{i\alpha}$  gives  $\frac{1}{2} k_B T$ , and each normal coord  $\tilde{u}_{i\alpha}$  also gives  $\frac{1}{2} k_B T$ .

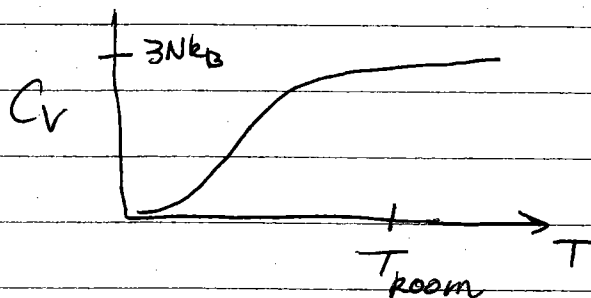
$\Rightarrow$  each of the  $6N$  degrees of freedom gives  $\frac{1}{2} k_B T$  towards the total average internal energy

$$\Rightarrow E = \langle H \rangle = (6N) \frac{1}{2} k_B T = \boxed{3N k_B T = E}$$

The contribution to the specific heat of a solid, due to atomic vibrations, is therefore

$$C_V = \frac{\partial E}{\partial T} = 3Nk_B \quad \text{Law of Dulong + Petit}$$

The classical result predicts a  $C_V$  that is independent of temperature. In real life however, one finds



at low  $T$ , see a clear decrease from Dulong-Petit prediction. Unexplainable classically

It was one of the early successes of quantum mechanics to explain why the Law of Dulong Petit fails at low  $T$ . This is an interesting example where the effects of quantum mechanics can be observed, not in atomic phenomena, but in the thermodynamics of macroscopic solids!

We will see the solution to this problem later when we discuss the statistics of bosons

## Paramagnetism - Classical spins

$N$  spins, ignore interactions between spins and only consider interaction of spin with external magnetic field  $\vec{H}$ .

$$\text{Hamiltonian } \mathcal{H} = -\sum_{i=1}^N \vec{\mu}_i \cdot \vec{H} = -\mu H \sum_{i=1}^N \cos \theta_i$$

where  $\vec{\mu}_i$  is magnetic moment of spin  $i$ ,  $|\vec{\mu}_i| = \mu$   
 $\theta_i$  is angle of  $\vec{\mu}_i$  with respect to  $\vec{H}$

Non interacting degrees of freedom

$\Rightarrow Q_N = (Q_1)^N$  no factor  $\frac{1}{N!}$  because the spins are distinguishable - we imagine each spin sits at a fixed position in space and so can be distinguished from any other spin.

where

$$Q_1 = \sum_{\theta} e^{\beta \mu H \cos \theta}$$

↑ sum is over all allowed orientations of the spin magnetic moment  $\vec{\mu}$ .

For spin in 3D space

$$Q_1 = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin \theta e^{\beta \mu H \cos \theta} = \frac{4\pi \sinh(\beta \mu H)}{\beta \mu H}$$

$$\text{as } \int_0^{\pi} d\theta \sin \theta e^{\beta \mu H \cos \theta} = \int_{-1}^1 dx e^{-\beta \mu H x} = \frac{e^{-\beta \mu H x}}{-\beta \mu H} \Big|_{-1}^1$$

average <sup>total</sup> magnetization  $\vec{M}$  is oriented along  $\vec{h}$ .  
 If we choose  $\vec{h} = h \hat{z}$  along  $\hat{z}$ , then

$$M_z = N \langle \mu \cos \theta \rangle = N \frac{\sum_{\theta} e^{\beta \mu h \cos \theta} \mu \cos \theta}{\sum_{\theta} e^{\beta \mu h \cos \theta}}$$

↑  
projection of  
 $\vec{\mu}$  along  $\vec{h}$

$$= N \frac{\frac{1}{\beta} \frac{\partial}{\partial h} \left( \sum_{\theta} e^{\beta \mu h \cos \theta} \right)}{\sum_{\theta} e^{\beta \mu h \cos \theta}}$$

$$= \frac{N}{\beta} \frac{\frac{\partial}{\partial h} (Q_1)}{Q_1} = \frac{N}{\beta} \frac{\partial}{\partial h} (\ln Q_1) = \frac{\partial}{\partial h} k_B T \ln Q_1^N$$

$$= \frac{N}{\beta} 4\pi \left[ \frac{\cosh(\beta \mu h)}{h} - \frac{\sinh(\beta \mu h)}{\beta \mu h^2} \right] \left. \begin{array}{l} = \frac{\partial}{\partial h} k_B T \ln Q_1 \\ = -\frac{\partial}{\partial h} A(T, h) \end{array} \right\}$$

$$\frac{4\pi \sinh(\beta \mu h)}{\beta \mu h}$$

$$= N \mu h \left[ \frac{\coth(\beta \mu h)}{h} - \frac{1}{\beta \mu h^2} \right]$$

$$\langle M_z \rangle = \frac{M_z}{N} = \mu \left[ \coth(\beta \mu h) - \frac{1}{\beta \mu h} \right]$$

$$L(x) = \coth x - \frac{1}{x} \quad \text{Langevin function}$$

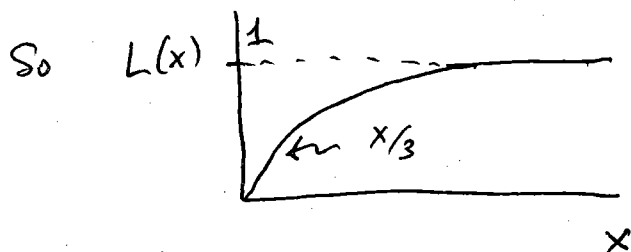
for large  $x$ ,  $L(x) \rightarrow 1$

$$\text{for small } x, \quad L(x) = \frac{\cosh x}{\sinh x} - \frac{1}{x}$$

$$\approx \frac{1 + \frac{x^2}{2}}{x + \frac{x^3}{6}} - \frac{1}{x} = \frac{1 + \frac{x^2}{2}}{x(1 + \frac{x^2}{6})} - \frac{1}{x}$$

$$\approx \frac{(1 + \frac{x^2}{2})(1 - \frac{x^2}{6})}{x} - \frac{1}{x} \approx \frac{1 + \frac{x^2}{2} - \frac{x^2}{6}}{x} - \frac{1}{x}$$

$$\approx \frac{x}{3}$$



$$x = \beta \mu h$$

$\Rightarrow$  at small  $h$  or at large  $T$  (small  $\beta$ )

$$\langle \mu_z \rangle = \frac{\mu^2 \beta h}{3} = \frac{\mu^2 h}{3 k_B T}$$

$$M_z = \frac{N \mu^2 h}{3 k_B T}$$

$$\text{magnetic susceptibility } \chi \equiv \lim_{h \rightarrow 0} \frac{\partial M_z}{\partial h} = \frac{N \mu^2}{3 k_B T} \propto \frac{1}{T}$$

Curie law of paramagnetism

$$\chi \propto \frac{1}{T}$$

## Entropy + Information

In canonical ensemble we had

$$\text{prob to be in energy } E \quad P(E) = \frac{\Omega(E) e^{-E/k_B T}}{\Delta Q_N}$$

or if we label microstates by an index  $i$  then the prob to be in state  $i$  is

$$P_i = \frac{e^{-E_i/k_B T}}{Q_N} \quad \text{where } Q_N = \sum_i e^{-E_i/k_B T}$$

Consider the average value of  $\ln P_i$

$$\langle \ln P_i \rangle = \sum_i P_i \ln P_i \quad \text{by definition of average}$$

$$\text{But also } \langle \ln P_i \rangle = \left\langle \ln \left[ \frac{e^{-E_i/k_B T}}{Q_N} \right] \right\rangle$$

$$= -\frac{\langle E \rangle}{k_B T} - \ln Q_N$$

$$\Rightarrow k_B T \langle \ln P_i \rangle = -\langle E \rangle + A = -T \langle S \rangle$$

$$\text{as } A = E - TS$$

Entropy as computed in canonical ensemble

$$\Rightarrow \boxed{\langle S \rangle = -k_B \sum_i P_i \ln P_i}$$

where  $P_i$  is the prob to be in state  $i$

Note: above was derived for canonical ensemble.

But it also holds for the microcanonical ensemble.

In microcanonical, the prob to be in state  $i$  is  $1/\Omega(E)$

for a state with  $E_i = E$ , and zero otherwise. Equally likely to be in any state with energy  $E$

$$\Rightarrow -k_B \sum_i p_i \ln p_i = -k_B \sum_i \left(\frac{1}{\Omega}\right) \ln\left(\frac{1}{\Omega}\right)$$

↑ sum over only states in energy shell about  $E$ .

But the terms in the sum are all equal, and the number of terms is just the number of states at energy  $E$ , i.e.  $\Omega$ .

$$\begin{aligned} \Rightarrow -k_B \sum_i \left(\frac{1}{\Omega}\right) \ln\left(\frac{1}{\Omega}\right) &= -k_B \left(\frac{1}{\Omega}\right) \ln\left(\frac{1}{\Omega}\right) \sum_i 1 \\ &= -k_B \left(\frac{1}{\Omega}\right) \ln\left(\frac{1}{\Omega}\right) (\Omega) = -k_B \ln\left(\frac{1}{\Omega}\right) \end{aligned}$$

$$= k_B \ln \Omega$$

$$\text{So } -k_B \sum_i p_i \ln p_i = k_B \ln \Omega = S(E) \quad \text{entropy in microcanonical ensemble}$$

$$\text{So } \boxed{S = -k_B \sum_i p_i \ln p_i} \quad \text{works for both microcanonical and canonical ensembles!}$$