

5. Vibrational Dynamics and Thermal Properties

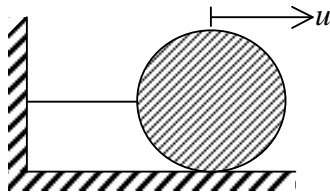
Atoms always have kinetic energy, and move around their equilibrium positions.

Three consequences:

- (i). Energy can be stored as vibrational energy, and this is reflected in the behaviour of the heat capacity.
- (ii). Motion contributes to the entropy of the solid, hence free energy, and affects the selection of structure.
- (iii). Vibrations can be transferred through the structure.
 - ⇒ sound (acoustic) waves.
 The treatment of vibrations is known as "lattice dynamics". Relies upon the properties of the simple harmonic oscillator (SHO).

5.1 Review of the SHO

Traditional example:



Mass m moving on a frictionless surface, attached to a rigid wall through a massless elastic rod.

E_y – Young's modulus for the rod material.

A – cross sectional area of rod.

l – length of rod.

5.1.1 Mechanics

Displace mass by u .

Restoring force: $F = \sigma A$

$\sigma = \text{stress} = E_y \epsilon$

ϵ is the strain $= \frac{u}{l}$

So, $F(u) = -E_y \frac{Au}{l}$

$= -Ku$

Where K is the spring constant. $K = \frac{E_y A}{l}$

Stored potential energy at displacement u :

$$V = -\int_0^u F(u') du' = \frac{1}{2} Ku^2 \quad (5.1)$$

$$\begin{aligned}
\text{Kinetic energy} & T = \frac{1}{2} m \dot{u}^2 \\
\text{Hamiltonian} & H = T + V = \frac{1}{2} m \dot{u}^2 + \frac{1}{2} K u^2
\end{aligned} \tag{5.2}$$

$$\begin{aligned}
\text{Newton's 2}^{\text{nd}} \text{ Law:} & \frac{dp}{dt} = -\frac{dV}{du} && \text{where } p = m\dot{u} \\
\Rightarrow & \ddot{u} = -\omega^2 u && \text{with angular frequency } \omega = \left(\frac{K}{m}\right)^{\frac{1}{2}}
\end{aligned}$$

$$\begin{aligned}
\text{Solution } u &= u_{\max} \cos(\omega t + \Phi) && u_{\max} = \text{amplitude} \\
& && (\omega t + \Phi) = \text{phase} \\
\text{Total energy} &= \frac{1}{2} K u_{\max}^2
\end{aligned} \tag{5.3}$$

5.1.2 Thermodynamics

Expose system to a heat bath at temperature T . Equivalent to solving an SHO with a random external driving force. Construct a partition function.

Classically:

$$\begin{aligned}
Z &= \frac{1}{h} \int du dp \exp(-H/k_B T) \\
&= \frac{1}{h} \int_{-\infty}^{\infty} du \exp\left(\frac{-Ku^2}{2k_B T}\right) \int_{-\infty}^{\infty} dp \exp\left(\frac{-p^2}{2mk_B T}\right) \\
&= \frac{1}{h} \left(\frac{2\pi k_B T}{K}\right)^{\frac{1}{2}} (2\pi m k_B T)^{\frac{1}{2}} \\
&= \frac{k_B T}{\hbar \omega}
\end{aligned}$$

$$\begin{aligned}
\text{Mean energy } \langle E \rangle &= \frac{1}{Z} \frac{1}{h} \int du dp H \exp(-H/k_B T) \\
&= -\frac{\partial \ln Z}{\partial \beta} && \text{where } \beta = 1/k_B T \\
&= \frac{\partial}{\partial \beta} \ln(\hbar \omega \beta) = 1/\beta = k_B T
\end{aligned} \tag{5.4}$$

This is just $\frac{1}{2} k_B T$ per degree of freedom: (K.E. and P.E.)

$$\text{So heat capacity is } C = \frac{d\langle E \rangle}{dT} = k_B$$

And root mean square displacement is

$$\langle u^2 \rangle = \frac{1}{Z} \frac{1}{h} \int du dp u^2 \exp(-H/k_B T) = k_B T / k = k_B T / m \omega^2 \quad \text{so as } T \uparrow, \langle u^2 \rangle \uparrow.$$

5.1.3 Quantised SHO

Now we have

$$Z = \sum_{n=0}^{\infty} \exp\left(\frac{-E_n}{k_B T}\right) = \sum_{n=0}^{\infty} \exp\left(\frac{-(n + \frac{1}{2})\hbar\omega}{k_B T}\right)$$

$$= \frac{\exp\left(\frac{-\hbar\omega}{2k_B T}\right)}{1 - \exp\left(\frac{-\hbar\omega}{k_B T}\right)} = \frac{1}{2 \sinh \frac{\hbar\omega}{2k_B T}}$$

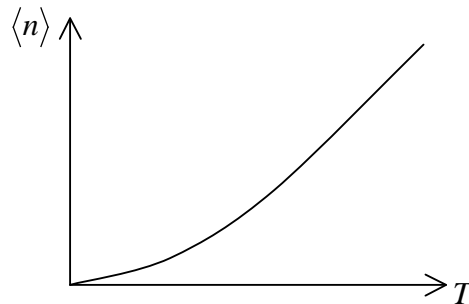
$$\langle E \rangle = \frac{-\partial \ln Z}{\partial \beta}$$

$$= \left(\langle n \rangle + \frac{1}{2}\right)\hbar\omega$$

with

$$\langle n \rangle = \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} \quad (5.5)$$

which is the mean number of quanta in the oscillator (Bose-Einstein statistics).

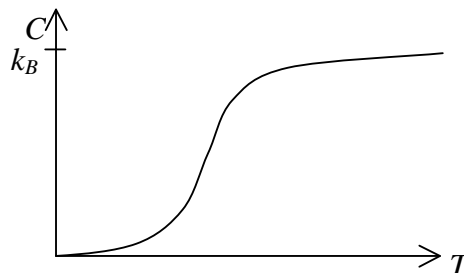


- So we increase number of quanta as $T \uparrow$.

Heat capacity

$$C = \frac{d\langle E \rangle}{dT}$$

$$= k_B \frac{\left(\frac{\hbar\omega}{k_B T}\right)^2 \exp\left(\frac{\hbar\omega}{k_B T}\right)}{\left(\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right)^2} \quad (5.6)$$



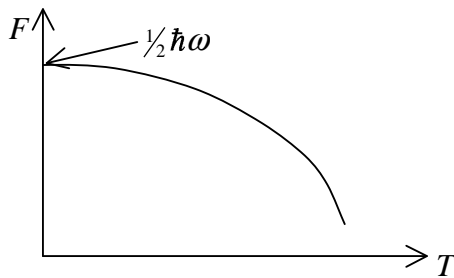
5.1.4 Helmholtz Free Energy

$$F = E - TS \quad (\text{Gibbs free energy with } p = 0)$$

We have $F = -k_B T \ln Z$

So for the SHO:

$$F = k_B T \ln \left(2 \sinh \left(\frac{\hbar \omega}{2k_B T} \right) \right) \quad (5.7)$$



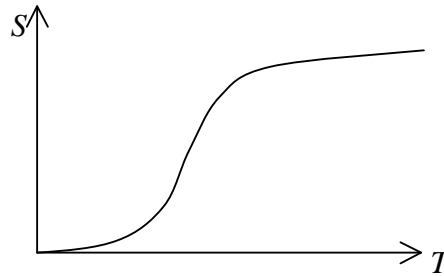
The decline in F is a reflection of the increase in entropy with T .

$$S = \frac{(E - F)}{T}$$

$$\approx k_B \left(1 + \ln \left(\frac{k_B T}{\hbar \omega} \right) \right)$$

for large T

As $T \uparrow$, $S \uparrow$ and $\langle u^2 \rangle \uparrow$.



i.e. more displacement from the mean position, more disorder.

5.2 Lattice Dynamics in the Harmonic Approximation

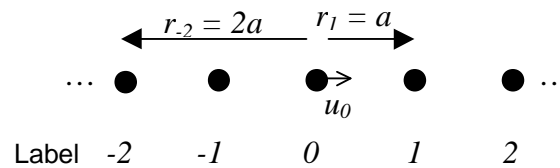
We aim to relate the vibrations of atoms in a crystalline structure to the properties of an SHO. This will allow us to determine the entropy of the structure. Also will provide phonon picture.

5.2.1 Single Atom in Motion

Consider a linear chain of N atoms of mass m , interacting through a pair potential $\phi(r)$, r is the separation.

The minimum P.E. is V_0 , at nearest neighbour separation a .

Separations from atom 0: $r_i = |i|a$



Displace atom labelled 0 from its equilibrium position by a distance u_0 to the right :

change in P.E. is $V(u_0) - V_0 = \underbrace{\sum_{i=1}^{N/2} (\phi(r_i - u_0) - \phi(r_i))}_{\text{Changes in RHS interactions}} + \underbrace{\sum_{i=1}^{N/2} (\phi(r_i + u_0) - \phi(r_i))}_{\text{Changes in LHS interactions}}$

$$= \sum_{i=1}^{N/2} \left(\phi(r_i) - \left. \frac{d\phi}{dr} \right|_{r=r_i} u_0 + \frac{1}{2} u_0^2 \left. \frac{d^2\phi}{dr^2} \right|_{r=r_i} + O(u_0^3) - \phi(r_i) \right) + \sum_{i=1}^{N/2} \left(\phi(r_i) + \left. \frac{d\phi}{dr} \right|_{r=r_i} u_0 + \frac{1}{2} u_0^2 \left. \frac{d^2\phi}{dr^2} \right|_{r=r_i} + O(u_0^3) - \phi(r_i) \right)$$

so $V(u_0) = V_0 + \frac{1}{2} K_E u_0^2 + O(u_0^4)$ where $K_E = 2 \sum_{i=1}^{N/2} \left. \frac{d^2\phi}{dr^2} \right|_{r=r_i}$

kinetic energy $T = \frac{1}{2} m \dot{u}_0^2$

$$\Rightarrow H = V_0 + \frac{1}{2} K_E u_0^2 + \frac{1}{2} m \dot{u}_0^2 + O(u_0^4) \quad (5.8)$$

If we neglect the terms of order u_0^4 , we make the “harmonic approximation”. Equivalent to an assumption that the displacement u_0 is small.

Reduces the Hamiltonian to that of an SHO (See eq. 5.2). This means we can use previous work:

$$\langle E \rangle = V_0 + k_B T \quad \text{classically} \quad (\text{See eq. 5.4})$$

or: $\langle E \rangle = V_0 + \left(\frac{1}{\exp(\hbar\omega/k_B T) - 1} + \frac{1}{2} \right) \hbar\omega$ for quantised cases (See eq. 5.5)

where: $\omega = \left(\frac{K_E}{m} \right)^{1/2}$

5.2.2 All Atoms in Motion

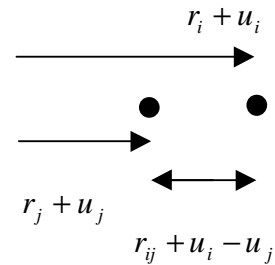
Again consider linear chain, but now displace all atoms labelled i by u_i .

Use compact notation:

$$\Delta V = \frac{1}{2} \sum_{ij} (\phi(r_{ij} + u_i - u_j) - \phi(r_{ij}))$$

where $r_{ij} = r_i - r_j$: separation between atoms i and j .

Sum is over all i and j , $\frac{1}{2}$ to avoid double counting.



Pair potential has properties:

$$\phi(-r) = \phi(r)$$

$$\Rightarrow \phi'(-r) = -\phi'(r)$$

and
$$\phi''(-r) = \phi''(r)$$

where
$$\phi'(r) = \left. \frac{d\phi}{dr} \right|_r$$

and,
$$\phi''(r) = \left. \frac{d^2\phi}{dr^2} \right|_r$$

[Check these properties with the L-J potential]

Now Taylor expand:

$$V - V_0 = \Delta V = \frac{1}{2} \sum_{ij} (u_i - u_j) \phi'(r_{ij}) + \frac{1}{2} (u_i - u_j)^2 \phi''(r_{ij}) + \mathcal{O}(u_i^3)$$

we have
$$u_i \sum_j \phi'(r_{ij}) = 0$$
 by symmetry (cancellation of equal and opposite pairs of terms)

e.g.
$$\phi'(a) + \phi'(-a) = 0$$

so,
$$\Delta V = \frac{1}{4} \sum_{ij} k_{ij} (u_i - u_j)^2$$
 with $k_{ij} = \phi''(r_{ij})$; these are the

spring constants, aka coupling constants.

Alternatively
$$\Delta V = \sum_{i>j} \frac{1}{2} k_{ij} (u_i - u_j)^2$$
 where the sum is over all pairs.

Compare this with eq. (5.1). Each pair of atoms is effectively joined together by a spring with spring constant k_{ij} .

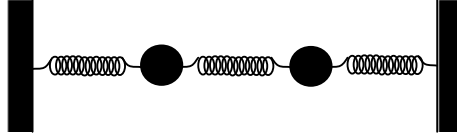
It is better to write ΔV as a quadratic form in the displacements:

$$\Delta V = \frac{1}{2} \sum_{ij} u_i D_{ij} u_j$$

Hamiltonian is now:

$$H = \underbrace{V_0}_{\text{equilibrium PE}} + \underbrace{\frac{1}{2} \sum_{ij} u_i D_{ij} u_j}_{\text{Change in PE due to displacement}} + \underbrace{\sum_i \frac{1}{2} m \dot{u}_i^2}_{\text{KE}}$$

An example: $N = 2$ chain with fixed ends.



Approximation: neglect non-nearest neighbour interactions. Label atoms 1 and 2 with displacements u_1 and u_2 .

$$\Delta V = \frac{1}{2} K(u_1)^2 + \frac{1}{2} K(u_1 - u_2)^2 + \frac{1}{2} K(u_2)^2$$

K is the nearest neighbour spring constant.

$$\begin{aligned} \Delta V &= \frac{K}{2} (2u_1^2 + 2u_2^2 - 2u_1u_2) \\ &= \frac{K}{2} (u_1 u_2) \begin{pmatrix} 2 & -1 \\ -1 & 2 \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \end{pmatrix} \end{aligned}$$

$$= \sum_{ij} \frac{1}{2} u_i D_{ij} u_j$$

$$D_{11} = 2K$$

with $D_{22} = 2K$

$$D_{12} = D_{21} = -K \quad (D \text{ is deliberately made symmetric})$$

Transform H to a harmonic oscillator form by diagonalising the D matrix.

Define $v = \Lambda u$ where u and v are N component vectors (elements u_i and v_i), and Λ is an $N \times N$ orthogonal matrix. v are linear combinations of the atomic displacements.

$$(\Lambda^{-1})^T = \Lambda \quad \text{definition of an orthogonal matrix.}$$

We have $u = \Lambda^{-1}v$ and $\dot{u} = \Lambda^{-1}\dot{v}$

And $\sum_i \dot{u}_i^2 = \dot{u}^T \dot{u}$

But $\dot{u}^T = (\Lambda^{-1}\dot{v})^T = \dot{v}^T (\Lambda^{-1})^T = \dot{v}^T \Lambda$

So $\dot{u}^T \dot{u} = \dot{v}^T \Lambda \Lambda^{-1} \dot{v} = \dot{v}^T \dot{v}$

More importantly:

$$\frac{1}{2} \sum_{ij} u_i D_{ij} u_j = \frac{1}{2} u^T D u$$

$$= \frac{1}{2} v^T \Lambda D \Lambda^{-1} v \quad \text{where } M = \Lambda D \Lambda^{-1}$$

$$= \frac{1}{2} v^T M v$$

Choose Λ such that M is diagonal with diagonal elements λ_i . These are the eigenvalues of M and D , since Λ is an orthogonal matrix. Λ is the matrix of eigenvectors of D .

Then:
$$H = V_0 + \sum_i \frac{1}{2} \lambda_i v_i^2 + \sum_i \frac{1}{2} m \dot{v}_i^2$$

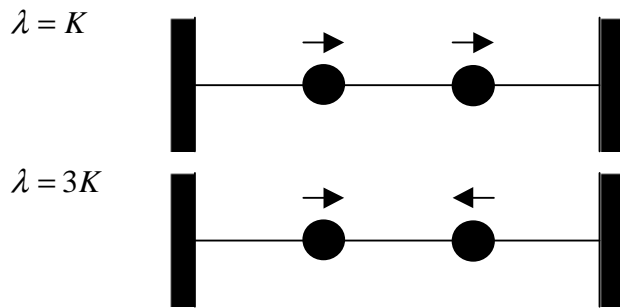
So, after much effort, we have transformed H to look like the Hamiltonian of N simple harmonic oscillators. The position and velocity coordinates v_i and \dot{v}_i are called normal coordinates, which are linear combinations of the atomic coordinates. The oscillatory modes of motion described by these coordinates are called normal modes. They are the natural modes of oscillation of the structure. Each can be excited independently.

The N oscillators have angular frequencies $\omega_i = \left(\frac{\lambda_i}{m}\right)^{\frac{1}{2}}$.

e.g. for the $N = 2$ chain, $D = K \begin{pmatrix} 2 & -1 \\ -1 & 2 \end{pmatrix}$

Eigenvalues $\lambda = K, 3K$. Eigenvectors $\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$

$$\omega_1 = \left(\frac{K}{m}\right)^{\frac{1}{2}}, \omega_2 = \left(\frac{3K}{m}\right)^{\frac{1}{2}}$$



Alternatively, solve equations of motion: $\frac{dp_i}{dt} = -\frac{\partial H}{\partial u_i}$ (Newton's second law)

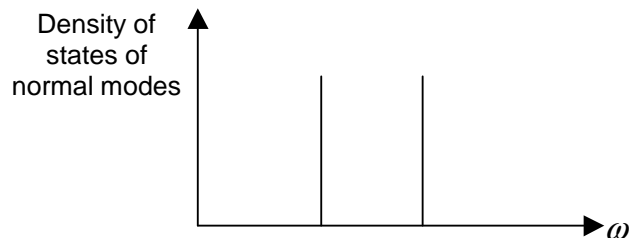
i.e. $m\ddot{u} = -\sum_j D_{ij}u_j$

and by inserting a trial oscillatory displacement pattern $u_i = A_i \cos \omega t$ we then need to solve

$$-\omega^2 mA_i = -\sum_j D_{ij}A_j$$

which is the same problem of finding the eigenvalues $m\omega^2$ and eigenvectors A_i of the matrix D .

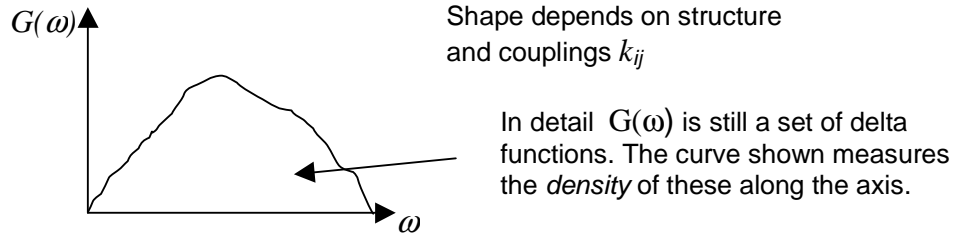
Either way, we can derive the frequency spectrum, which in this example takes the form of two delta functions. (Delta functions are infinitely high, infinitely narrow peaks located at the point where the argument is zero. Main property is $\int_{-\infty}^{\infty} \delta(x - x_0) dx = 1$)



For N atoms in the 1-d chain, there are N delta functions. For large N , it is useful to introduce a density of states $G(\omega)$, such that $G(\omega) d\omega$ is the number of frequencies (i.e. delta functions) lying in the range $\omega \rightarrow \omega + d\omega$.

So, for $N = 2$
$$G(\omega) = \delta(\omega - \omega_1) + \delta(\omega - \omega_2)$$

More generally



Can be extended to 3-d. In the harmonic approximation, H is equivalent to $3N$ simple harmonic oscillators. There is a density of states $G(\omega)$ in 3-d too.

What are these normal mode frequencies useful for? Calculating thermodynamic properties, since we know the properties of single oscillators.

$$E = V_0 + \int d\omega G(\omega) \left[\left(\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1 \right)^{-1} + \frac{1}{2} \right] \hbar\omega$$

$$F = V_0 + \int d\omega G(\omega) k_B T \ln \left(2 \sinh\left(\frac{\hbar\omega}{2k_B T}\right) \right)$$

How do we calculate the frequency spectrum, or density of states?

5.3 Models of normal mode frequencies

5.3.1 The Einstein Model

Einstein analysed the dynamics of an atom assuming all other atoms were stationary (mean field approximation).

H is combination of Hamiltonians from equation (5.8).

$$H = V_0 + \sum_i \frac{1}{2} K_E (u_{ix}^2 + u_{iy}^2 + u_{iz}^2) + \sum_i \frac{1}{2} m (\dot{u}_{ix}^2 + \dot{u}_{iy}^2 + \dot{u}_{iz}^2)$$

i.e. single atom in motion case extended to 3-d.

$$\Rightarrow \text{All } 3N \text{ oscillators have frequency } \omega_E = \left(\frac{K_E}{m} \right)^{\frac{1}{2}}. \text{ Einstein frequency.}$$

Density of states: $G(\omega) = 3N\delta(\omega - \omega_E)$. $3N$ modes for N atoms in 3-d.