Condensed Matter Physic

Lattice vibration

Istvan Groma

ELTE

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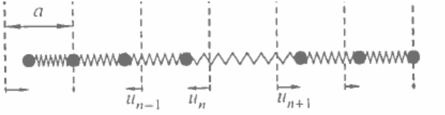
Linear chain



$$M\ddot{u}_n = D[u_{n+1} - u_n + u_{n-1} - u_n]$$

$$M\ddot{u}_n = -D[2u_n - u_{n+1} - u_{n-1}]$$

Let us try the solution in the form

$$u_n = A_n e^{j\omega t}$$

In this case

$$\omega^2 A_n = \omega_0^2 [2A_n - A_{n+1} - A_{n-1}]$$

$$\omega_0^2 = \frac{D}{M}$$

Linear chain

$$\omega^2 \begin{pmatrix} A_1 \\ A_2 \\ . \\ . \\ A_N \end{pmatrix} = \omega_0^2 \begin{pmatrix} 2 & -1 & . & . & ? \\ -1 & 2 & -1 & & \\ & . & . & . & \\ & . & . & . & \\ ? & . & . & -1 & 2 \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \\ . \\ . \\ A_N \end{pmatrix}$$

Periodic boundary conditions

$$u_{N+1} = u_1$$

$$\omega^2 \begin{pmatrix} A_1 \\ A_2 \\ . \\ . \\ A_N \end{pmatrix} = \omega_0^2 \begin{pmatrix} 2 & -1 & . & . & -1 \\ -1 & 2 & -1 & & \\ & . & . & . & \\ & . & . & . & \\ -1 & . & . & -1 & 2 \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \\ . \\ . \\ A_N \end{pmatrix}$$

Linear chain

$$A_n = A_q e^{jqan}$$

$$\omega^2 = \omega_0^2 \left[2 - e^{jqa} - e^{-jqa} \right]$$

$$\omega^2 = 2\omega_0^2 \left[1 - cos(qa) \right] = 4\omega_0^2 \sin^2 \left(\frac{qa}{2} \right)$$

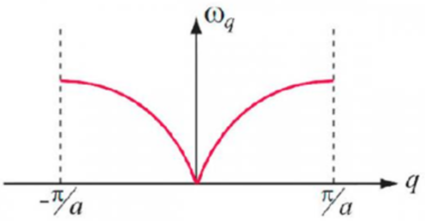
$$\omega = 2\omega_0 \left| \sin \left(\frac{qa}{2} \right) \right|$$

Due to the periodic boundary conditions

$$1 = e^{jqaN} \quad \longrightarrow \quad q_m = m \frac{2\pi}{Na}$$

Linear chain

Brilluen zone



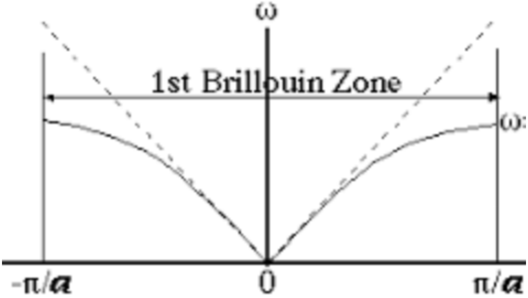
$$M\ddot{u}_n = Da^2 \frac{\frac{u_{n+1}-u_n}{a} - \frac{u_n - u_{n-1}}{a}}{a} \approx Da^2 \frac{\partial^2}{\partial x^2} u_n$$

$M = \rho a A$ ill. $E = Da/A$

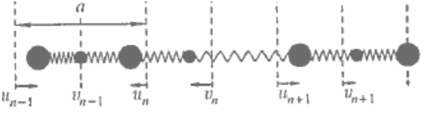
$$\rho \frac{\partial^2}{\partial t^2} u(x,t) = E \frac{\partial^2}{\partial x^2} u(x,t)$$

$$u(x,t) = u_0 e^{j(\omega t + qx)} \quad \longrightarrow \quad \omega = \left(\frac{D}{M}\right)^{1/2} a|q| = \omega_0 a|q|$$

Linear chain



Linear chain with 2 atom



$$M_1 \ddot{u}_n = -D[2u_n - v_n - v_{n-1}]$$
$$M_2 \ddot{v}_n = -D[2v_n - u_{n+1} - u_n]$$

Boundary condition

$$u_{N+1} = u_1$$
$$v_{N+1} = v_1$$

Let us try the solution in the form

$$u_n = u(q)e^{j(\omega t + qan)}$$
$$v_n = v(q)e^{j(\omega t + qan)}$$

Linear chain with 2 atom

$$-\omega^2 M_1 u(q) = -2Du(q) + D\left(1 + e^{-jqa}\right) v(q)$$
$$-\omega^2 M_1 v(q) = -2Dv(q) + D\left(1 + e^{+jqa}\right) u(q)$$

So,

$$\begin{vmatrix} 2D - \omega^2 M_1, & -2De^{-jq\frac{a}{2}} \cos\left(\frac{qa}{2}\right) \\ -2De^{+jq\frac{a}{2}} \cos\left(\frac{qa}{2}\right), & 2D - \omega^2 M_2 \end{vmatrix} = 0$$

Solution

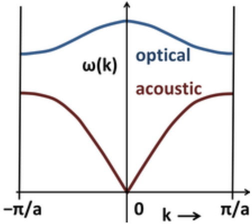
$$\omega_{\pm}^2 = \frac{D}{M_1 M_2}\left\{(M_1 + M_2) \pm \sqrt{(M_1 + M_2)^2 - 4M_1 M_2 \sin^2\left(\frac{qa}{2}\right)}\right\}$$

After introducing the notations

$$\omega_0^2 = 2D\left(\frac{1}{M_1} + \frac{1}{M_2}\right), \quad \gamma^2 = 4\frac{M_1 M_2}{(M_1 + M_2)^2} \leq 1$$

Linear chain with 2 atom

$$\omega_{\pm}^2 = \frac{1}{2}\omega_0^2 \left\{1 \pm \sqrt{1 - \gamma^2 \sin^2\left(\frac{qa}{2}\right)}\right\}$$



$$\omega_-(q \to 0) \approx \frac{1}{2}\omega_0 \gamma a |q|$$

$$\omega_+(q \to 0) \approx \omega_0$$

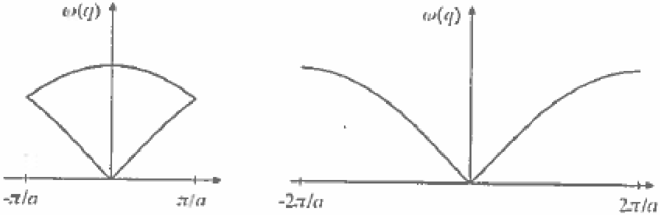
$$\omega_{\pm}^2(q = \pi/a) = \frac{1}{2}\omega_0^2 \left\{(1 \pm \sqrt{1 - \gamma^2}\right\}$$

Linear chain with 2 atom

If $M_1 = M_2$ then $\gamma = 1$

$$\omega_{\pm}^2 = \frac{2D}{M}\left[1 \pm \sqrt{1-\sin^2\left(\frac{qa}{2}\right)}\right] = \frac{2D}{M}\left[1 \pm \cos\left(\frac{qa}{2}\right)\right]$$

$$\omega_{\pm} = \begin{cases} 2\left(\frac{D}{M}\right)^{1/2}\left|\cos\left(\frac{qa}{4}\right)\right| \\ 2\left(\frac{D}{M}\right)^{1/2}\left|\sin\left(\frac{qa}{4}\right)\right| \end{cases}$$



General case

The coordinates of the atom

$$\underline{r}^{\mu}(\underline{R}_m, t) = \underline{R}_m + \underline{r}_{\mu} + \underline{u}^{\mu}(\underline{R}_m, t)$$

$\mu = 1..p$ where p is the number of atom in the primitive cell.
The energy of the system

$$\Phi = \Phi_0 + \sum_{\substack{m,n \\ \alpha,\beta \\ \mu,\nu}} \frac{1}{2} D^{\mu,\nu}_{\alpha,\beta}(\underline{R}_m, \underline{R}_n) u^{\mu}_{\alpha}(\underline{R}_m) u^{\nu}_{\beta}(\underline{R}_n)$$

where $\alpha, \beta = 1, 2, 3$
It can be rewritten

$$\Phi = \Phi_0 - \sum_{\substack{m,n \\ \alpha,\beta \\ \mu,\nu}} \frac{1}{4} D^{\mu,\nu}_{\alpha,\beta}(\underline{R}_m, \underline{R}_n)[u^{\mu}_{\alpha}(\underline{R}_m) - u^{\nu}_{\alpha}(\underline{R}_n)][u^{\mu}_{\beta}(\underline{R}_m) - u^{\nu}_{\beta}(\underline{R}_n)]$$

General case

The force is

$$F_\alpha^\mu(\underline{R}_m) = -\sum_{n,\nu,\beta} D_{\alpha,\beta}^{\mu,\nu}(\underline{R}_m, \underline{R}_n) u_\beta^\nu(\underline{R}_n)$$

If $\underline{u} = const$, then $\underline{F} = 0$ (rigid translation), so

$$\sum_{n,\nu} D_{\alpha,\beta}^{\mu,\nu}(\underline{R}_m, \underline{R}_n) = 0$$

Equations of motion

$$M_\mu \ddot{u}_\alpha^\mu(\underline{R}_m) = -\sum_{n,\nu,\beta} D_{\alpha,\beta}^{\mu\nu}(\underline{R}_m - \underline{R}_n) u_\beta^\nu(\underline{R}_n)$$

Let us search the solution in the form

$$u_\alpha^\mu(\underline{R}_m) = \frac{1}{\sqrt{M_\alpha}} e^{j\omega t} e^{j\underline{q}\underline{R}_m} u_\alpha^\mu(\underline{q})$$

General case

After substitution

$$\omega^2 \sqrt{M_\alpha} e^{j\omega t} e^{j\underline{q}\underline{R}_m} u^\mu_\alpha(\underline{q}) = \sum_{n,\nu,\beta} D^{\mu\nu}_{\alpha,\beta}(\underline{R}_m - \underline{R}_n) \frac{1}{\sqrt{M_\beta}} e^{j\omega t} e^{j\underline{q}\underline{R}_n} u^\nu_\beta(\underline{q})$$

one gets

$$\omega^2 u^\mu_\alpha(\underline{q}) = \sum_{\nu,\beta} \hat{D}^{\mu\nu}_{\alpha,\beta}(\underline{q}) u^\nu_\beta(\underline{q})$$

where

$$\bar{D}^{\mu\nu}_{\alpha,\beta}(\underline{q}) = \frac{1}{\sqrt{M_\beta M_\alpha}} \sum_n D^{\mu\nu}_{\alpha,\beta}(\underline{R}_n) e^{j\underline{q}\underline{R}_n}$$

From this

$$det\left[\bar{D}^{\mu\nu}_{\alpha,\beta}(\underline{q}) - \omega^2 \delta_{\alpha,\beta}\delta_{\mu,\nu}\right] = 0, \quad 3p \times 3p$$

General case

3p eigenvalue $\omega_\lambda^2(\underline{q})$, a $e_{\mu,\alpha}^{(\lambda)}(\underline{q})$ 3p dimension eigenvectors

$$\omega_\lambda^2(\underline{q}) = \omega_\lambda^2(-\underline{q})$$

$\underline{q}$ is in the Brilluen zone.

Normal modes

$$u_\alpha^\mu(\underline{R}_m) = \frac{1}{\sqrt{M_\mu}} \sum_{\underline{q},\lambda} e_{\mu,\alpha}^{(\lambda)}(\underline{q}) e^{j\underline{q}\underline{R}_m} Q_\lambda(\underline{q}, t)$$

$$\ddot{Q}_\lambda(\underline{q}, t) = -\omega_\lambda^2(\underline{q}) Q_\lambda(\underline{q}, t)$$

Elementary excitation = fonon

$$E = \hbar\omega$$

Heat capacity of a crystals

$$< E >= \frac{\sum_n E_n e^{-\beta E_n}}{\sum_n e^{-\beta E_n}}, \quad \beta = \frac{1}{k_B T}$$

Partition number

$$Z = \sum_n e^{-\beta E_n}$$

$$-\frac{d}{d\beta} \ln Z(\beta) = \frac{\sum_n E_n e^{-\beta E_n}}{\sum_n e^{-\beta E_n}}$$

Harmonic oscillator

$$E_n = n\hbar\omega + \frac{\hbar\omega}{2}$$

$$Z = \sum_{n=0}^{\infty} e^{-\beta\left(n\hbar\omega + \frac{\hbar\omega}{2}\right)} = \frac{e^{-\beta\frac{\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}}$$

Heat capacity of a crystals

$$-\frac{d}{d\beta}\ln\left(\frac{e^{-\beta\frac{\hbar\omega}{2}}}{1-e^{-\beta\hbar\omega}}\right)=\frac{\hbar\omega}{2}+\frac{d}{d\beta}\ln\left(1-e^{-\beta\hbar\omega}\right)$$

From this

$$<E>=\frac{\hbar\omega}{2}+\hbar\omega\frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

Neglecting zeropoint energy

$$<E>=\frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$$

Bose–Einstein distribution

$$n=\frac{1}{e^{\beta\hbar\omega}-1}$$

Heat capacity of a crystal

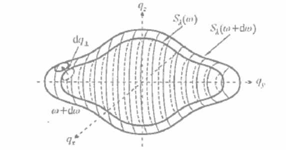
Periodic boundary conditions $\underline{u}(\underline{R}_n) = \underline{u}(\underline{R}_{n+N})$

Density of states

$$\triangle^3 q = \left| \frac{\underline{b}_1}{N_1}, \frac{\underline{b}_2}{N_2}, \frac{\underline{b}_3}{N_3} \right| = \frac{v_r}{N} = \frac{(2\pi)^3}{vN} = \frac{(2\pi)^3}{V}$$

$$\frac{1}{V} \sum_{\underline{q},\lambda} f(\omega_\lambda(\underline{q})) \approx \sum_\lambda \int \frac{dq^3}{(2\pi)^3} f(\omega_\lambda(\underline{q}))$$

Surface of $\omega_\lambda(\underline{q}) = const$



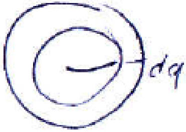
$$\triangle V_\omega = g(\omega) d\omega$$

Debye approximation

$$\frac{1}{V}\sum_{\underline{q},\lambda} f(\omega_\lambda(\underline{q})) \approx \sum_\lambda \int g(\omega_\lambda) f(\omega_\lambda(\underline{q})) d\omega_\lambda$$

Debye assumption

$$\omega_\lambda(\underline{q}) = c_\lambda |\underline{q}|$$



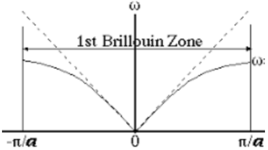
$$\frac{4\pi q^2 dq}{(2\pi)^3}$$

$$g(\omega_\lambda) = \frac{1}{2\pi^2}\frac{1}{c_\lambda^3}\omega_\lambda^2$$

Debye assumption

There are 3 branches

$$g(\omega) = \frac{1}{2\pi^2}\left[\frac{1}{c_L^3} + \frac{2}{c_T^3}\right]\omega^2 = \frac{3}{2\pi^2}\frac{\omega^2}{c_D^3}$$



Debye frequency $\omega_D = c_D q_D$

where

$$\frac{4\pi}{3} q_D^3 = \frac{(2\pi)^3}{v}$$

Debye heat capacity

$$< E >= V \int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega} - 1} \frac{3}{2\pi^2 c_D^3} d\omega$$

After variable replacement $x = \beta\hbar\omega$

$$< E >= V \frac{(k_B T)^4}{\hbar^3} \frac{3}{2\pi^2 c_D^3} \int_0^{\frac{\hbar\omega_D}{k_B T}} \frac{x^3}{e^x - 1} dx$$

If $T \to 0$

$$< E > \propto T^4$$

so

$$c_V \propto T^3$$

Debye heat capacity

$T \to \infty$

$$< E >= V \frac{(k_B T)^4}{\hbar^3} \frac{3}{2\pi^2 c_D^3} \int_0^{\frac{\hbar\omega_D}{k_B T}} x^2 dx = V \frac{(k_B T)^4}{\hbar^3} \frac{1}{2\pi^2 c_D^3} \left(\frac{\hbar\omega_D}{k_B T} \right)^3$$

$$< E >= V k_B T \frac{1}{2\pi^2} q_D^3 = V k_B T \frac{1}{2\pi^2} \frac{3}{4\pi} \frac{(2\pi)^3}{v} = 3 k_B N T$$

Classical heat capacity (Dulong-Petit)

$$c_V = 3 k_B N$$

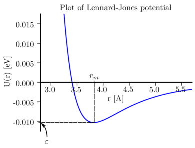
Thermal expansion

$$< u >= \frac{\int_{-\infty}^{\infty} u e^{-\beta\Phi(u)} du}{\int_{-\infty}^{\infty} e^{-\beta\Phi(u)} du}$$

If

$$\Phi(u) = \Phi_0 + \frac{D}{2} u^2$$

then $< u >= 0$
Anharmonically



$$\Phi(u) = \Phi_0 + \frac{D}{2} u^2 - \gamma u^3 + \ldots$$

Thermal expansion

$$< u >= \frac{\int_{-\infty}^{\infty} u e^{-\beta \frac{D}{2} u^2} (1 + \beta\gamma u^3) du}{\int_{-\infty}^{\infty} e^{-\beta \frac{D}{u}^2} (1 + \beta\gamma u^3) du}$$

That is

$$< u >= \frac{\int_{-\infty}^{\infty} \beta\gamma u^4 e^{-\beta \frac{D}{2} u^2} du}{\int_{-\infty}^{\infty} e^{-\beta \frac{D}{2} u^2} du}$$

By introducing the new variable

$$x = \sqrt{\beta D/2} u$$

$$< u >= \frac{\beta\gamma}{(\beta D/2)^2} \frac{\int_{\infty}^{\infty} x^4 e^{-x^2} dx}{\int_{-\infty}^{\infty} e^{-x^2} dx} = \frac{\gamma}{D^2} C k_B T$$

$$\alpha = \frac{d < u >}{dT} = \gamma C k_B / D^2 = const$$