C. 1D crystal: Chain of Identical atoms

Equilibrium,

$$\cdots \quad \underset{O}{} \quad \overset{\leftarrow a \rightarrow}{\underset{O}{}} \quad \underset{O}{} \quad \underset{O}{\overset{M}{}} \quad \underset{O}{} \cdots$$

$$\cdots \quad \underset{x_{n-2}^0}{(n-2)a} \quad \underset{x_{n-1}^0}{(n-1)a} \quad \underset{x_n^0}{na} \quad \underset{x_{n+1}^0}{(n+1)a} \quad \underset{x_{n+2}^0}{(n+2)a} \cdots$$

$$\cdots\, oooo \underset{|}{O} oooo \underset{|}{O} oooo \underset{|}{O} oooo \underset{|}{O} oooo \underset{|}{O} ooo \cdots$$

$$\underset{u_{n-2}}{\overset{|\rightarrow}{}} \quad \underset{u_{n-1}}{\overset{|\rightarrow}{}} \quad \underset{u_n}{\overset{|\rightarrow}{}} \quad \underset{u_{n+1}}{\overset{|\rightarrow}{}} \quad \underset{u_{n+2}}{\overset{|\leftarrow}{}}$$

u_n = displacement of nth atom from equilibrium=$u_n(t)$

(assume motion in one direction[+]; longitudinal)

• There are two viewpoints (or two systems) that one may consider:

(i) an infinite chain

or

(ii) a finite (very long) chain of N atoms with N≫1

Physics should be the same for N≫1

[+] If we consider motion only in y-direction (or z-direction), i.e. transverse motion, the treatment is the same.

• We take the Harmonic approximation, i.e., the springs obey Hooke's law or potential energy terms are quadratic.[+]

Assume only <u>nearest-neighbor interactions</u>, i.e., spring connects only two nearest neighboring atoms

<u>Force</u> on the nth atom consists of:

$$\underbrace{-K(u_n - u_{n-1})}_{\substack{\text{from spring to} \\ \text{the left of } n^{th} \text{ atom}}} - \underbrace{K(u_n - u_{n+1})}_{\substack{\text{from spring to the} \\ \text{right of } n^{th} \text{ atom}}}$$

Equation of motion (n^{th} atom):

$$\boxed{M \frac{d^2 u_n}{dt^2} = K(u_{n+1} - 2u_n + u_{n-1})} \qquad (9)$$

↳ For an <u>infinite chain</u>, every atom takes on an equation of motion of the same form

$$(n = -\infty, \cdots, 0, \cdots, n = +\infty)$$

⇒ an infinite set of equations

[+] Recall for a mass-and-spring system, the restoring force $F = -Kx$ (Hooke's law) and the potential energy is $\frac{1}{2}Kx^2$ (quadratic in x).

• To look for normal modes, the atoms in each mode have the same time-dependence $e^{-i\omega t}$, where the allowed ω get to be determined.

Write: $u_n(t) = u_n\, e^{-i\omega t}$ (10)

    • no time dependence
    • amplitude in the nth primitive cell

Eq.(9) becomes:

$$-\omega^2 u_n = \frac{K}{M}\left(u_{n+1} - 2u_n + u_{n-1}\right) \qquad (11)$$

and similar equations for other atoms.

Eq.(11) is:

$$\underbrace{\frac{K}{M}\begin{pmatrix} \ddots & & & & \\ \cdots & -1 & +2 & -1 & 0 & 0 & \cdots \\ \cdots & 0 & -1 & +2 & -1 & 0 & 0 & \cdots \\ & 0 & 0 & -1 & +2 & -1 & 0 & 0 & \cdots \\ & & 0 & 0 & -1 & +2 & -1 & 0 & \cdots \\ & & & 0 & 0 & -1 & +2 & -1 & 0 & \cdots \end{pmatrix}}_{\displaystyle \frac{K}{M}}\begin{pmatrix} \vdots \\ u_2 \\ u_1 \\ u_0 \\ u_{-1} \\ u_{-2} \\ \vdots \end{pmatrix} = \omega^2 \begin{pmatrix} \vdots \\ u_2 \\ u_1 \\ u_0 \\ u_{-1} \\ u_{-2} \\ \vdots \end{pmatrix} \qquad (12)$$

$$\overleftrightarrow{M}\,\vec{u} = \omega^2\,\vec{u}$$

an eigenvalue problem.

• A crystal (and the matrix $\overleftrightarrow{M}$) has the property of discrete translational symmetry

  ■ translating the crystal by $m\vec{a} = \vec{R}$,   a lattice vector
     any integer   (any $\vec{R}$)

    we will get the same set of equations of motion

   OR $\overleftrightarrow{M}$ looks the same as your head moves left or right!

   Technically, $\overleftrightarrow{M}$ commutes with translational operators.

Key point: For eigenvalue problem of this kind, we have the following result.

$$\vec{u}_{\vec{R}} = \vec{u}_{\vec{R}=0}\, e^{\vec{u}\cdot\vec{R}}$$

   amplitude in the primitive cell at $\vec{R}$ amplitude in the primitive cell at $\vec{R}=0$ ← the two amplitudes are related by a factor that is slight to be an exponential

For $\vec{u}_{\vec{R}}$ to remain finite, the vector $\vec{u}$ must be of the form

$$\vec{u} = i\vec{q}$$

$$\boxed{\overline{U}_{\vec{R}} = \overline{U}_{\vec{R}=0}\, e^{i\vec{q}\cdot\vec{R}}} \qquad \text{(BT)}$$

- This result is called the Bloch's theorem, which is the most important theorem in solid state physics.

- It says $\overline{U}_{\vec{R}}$ and $\overline{U}_{\vec{R}=0}$ are related by a phase factor $e^{i\vec{q}\cdot\vec{R}}$.

- Here $\vec{q}$ serves as a label for a normal mode, i.e., we expect to find $\omega(\vec{q})$.

- $\vec{q}$ is a quantity $\sim$ 1/length, thus $\vec{q}$ is a vector that lives in the reciprocal space.

- As a label, some $\vec{q}$'s are redundant! For example, the mode $\vec{q} + \vec{G}$ is the same as $\vec{q}$, since $e^{i\vec{G}\cdot\vec{R}} = 1$

- ∴ It is sufficient to consider $\vec{q}$ being in one primitive cell of the reciprocal lattice. The choice is:

$$\boxed{\vec{q} \text{ in 1st Brillouin Zone.}} \qquad (13)$$

Now, we go back to Eq.(11)

$$-\omega^2 \overline{U}_n = \frac{K}{M}\left(\overline{U}_{n+1} - 2\overline{U}_n + \overline{U}_{n-1}\right) \qquad (11)$$

Apply Bloch's theorem: (see Eq.(BT))

$$\overline{U}_n = A e^{iqna} \qquad (14)$$

Equivalently,
$$U_n(t) = A e^{iqna}\, e^{-i\omega t}$$
for $M\dfrac{d^2 u(t)}{dt^2} = K(U_{n+1} - 2U_n + U_{n-1})$

$$\boxed{\begin{array}{l} \text{Eq.(11) becomes:} \\[4pt] -\omega^2 A e^{iqna} = \dfrac{K}{M}\left(A e^{iqna}\, e^{iqa} - 2A e^{iqna} + A e^{iqna}\, e^{-iqa}\right) \end{array}}$$

$$\Rightarrow \quad \omega^2 = \frac{2K}{M}(1 - \cos qa)$$

$$\Rightarrow \quad \omega^2 = \frac{4K}{M}\sin^2\left(\frac{qa}{2}\right) = \omega^2(q) \qquad (15)$$

$$\Rightarrow \quad \boxed{\omega(q) = \sqrt{\frac{4K}{M}}\left|\sin\frac{qa}{2}\right|} \qquad (16)$$

normal mode frequencies labelled by q → "phonon dispersion relation" (1D, 1 atom per unit cell)

(q is thus a "quantum number")   (q is thus a wave vector (number))

Dispersion relation [ω vs q]

$\vec{a}_1 = a\hat{z}$ $\Rightarrow$ $\vec{b}_1 = \frac{2\pi}{a}\hat{z}$
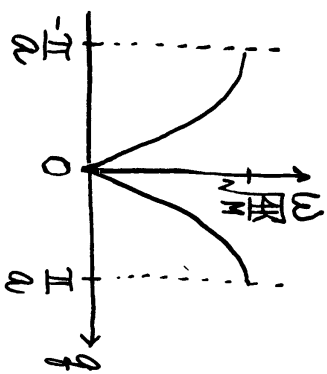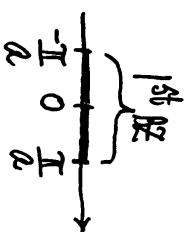
$\omega = \sqrt{\frac{4K}{M}}\left|\sin\frac{qa}{2}\right|$

$\omega_{cutoff} = \sqrt{\frac{4K}{M}}$ $\quad$ (1D monatomic chain)

No propagating mode with $\omega > \omega_{cutoff}$

Each normal mode involves all atoms

$u_m(t) = A\, e^{iqma}\, e^{-i\sqrt{\frac{4K}{M}}\left|\sin\frac{qa}{2}\right|t}$ $\qquad$ (17)

for the mode $\omega(q)$.

- For $q \to q + v\cdot\frac{2\pi}{a}$, $\leftarrow$ any G
  $\qquad\qquad\quad\uparrow$ integer

  $u_m(t)$ remains unchanged. Thus, restricting q to
  $q \in$ 1st BZ is sufficient.

- But real crystal is not infinite.
  How about a finite crystal?

D. 1D Finite Crystal : Long finite chain / Periodic Boundary condition

- Consider a chain of N identical atoms ($N \gg 1$, eg. $N\sim 10...$)

  Equation of motion (n^{th} atom):

  $$M\frac{d^2 u_n}{dt^2} = K(u_{n+1} - 2u_n + u_{n-1}) \qquad (18)$$

  A similar equation holds for the other atoms.

- One may wonder:
  What about the atoms at the two ends? $\leftarrow$ "surface"

  Their equation of motion should be different!
  Yes, that is right, strictly speaking.

  For $N \gg 1$, we expect that these "surface effects"
  are NOT important.

- In solid state physics, a standard way to
  treat a finite crystal is to impose the
  periodic boundary condition.[+]

[+] An alternative is to impose fixed-boundary condition, i.e. the atoms
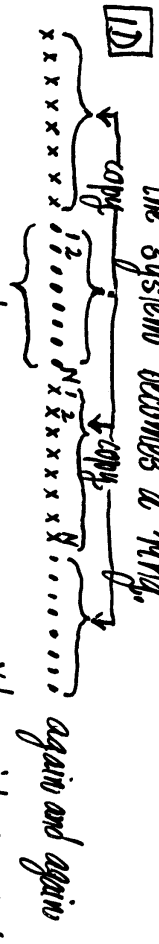at the two ends are fixed. The physics is unchanged for $N \gg 1$.

Aside: Periodic Boundary Condition

To eliminate edge effects, we impose periodic B.C.:

$$\boxed{u_j = u_{j+N}} \qquad \text{periodic B.C.}$$
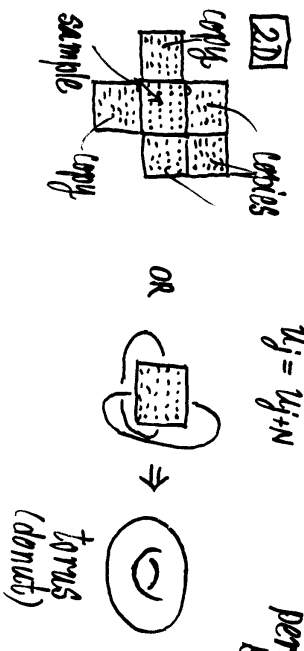
• We consider a finite N-atom chain (N≫1).

• We want to mimic an infinite system by repeatedly joining N-atom chains together. Equivalently, we join the Nth atom back to the 1st atom by a spring K, and the system becomes a ring.

1D:

x x x x x x x x x

$\underbrace{}_{\text{copy}}$

$\underbrace{x x x x x \cdots x x^{8} \cdots x x x x x x x}_{\text{copy} \qquad \text{copy}}$ ... again and again

N-atom chain $u_j = u_{j+N}$

[sample size]

Note: periodic B.C. leads to a new period which is of the order of size of sample Na. The periodicity inside a crystal has period a.

$[Na \gg a.]$
$\underset{\sim}{N} \gg 1$ ← intrinsic

OR

$\vdots \quad {}^{N} \vdots {}^{2} \atop \ddots$ ⇒ N copies

$u_j = u_{j+N}$
periodic B.C.

2D:

copies → sample → copy

or

  ⇒ torus (donut)

• Using periodic B.C., then all atoms obey the same equation of motion

$$\boxed{M\frac{d^2 u}{dt^2} = K(u_{n+1} - 2u_n + u_{n-1}) \quad \text{for all } n \quad (n=1,\cdots,N)} \qquad (19)$$

Following Eq.(14), we look for normal mode solutions:[+]

$$u_n(t) = A\, e^{iqna}\, e^{-i\omega t} \qquad (20)$$

i.e., • all atoms oscillate with same amplitude
• atoms at different primitive cells oscillate with a different phase.
• all atoms carry the same $e^{-i\omega t}$
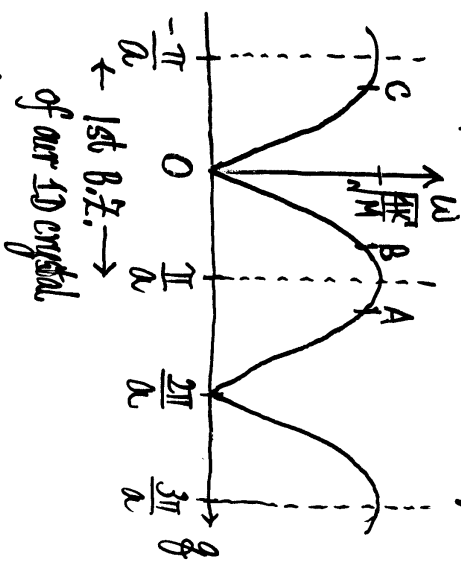• ω and q are related through eg. of motion

Subst. into Eq.(19):

$$\omega^2(q) = \frac{4K}{M}\sin^2\left(\frac{qa}{2}\right)$$

$$\Rightarrow \boxed{\omega(q) = \sqrt{\frac{4K}{M}}\left|\sin\frac{qa}{2}\right|} \qquad (21)$$

same phonon dispersion relation as before.

[+] As usual, complex notation is used. It is the real part of u_n that should be interpreted as the physical displacement.

Dispersion relation [ω vs q]

$$\omega = \sqrt{\frac{4K}{M}}\,\left|\sin\frac{qa}{2}\right|$$

1st B.Z. of our 1D crystal

- normal modes with wavenumbers at A, B, C all have same ω and correspond to some instantaneous atomic displacements.

- B represents a wave moving to the right. A and C represent a wave moving to the left.

Features:

- A cutoff $\omega_{cutoff} = \sqrt{\frac{4K}{M}}$ corresponding to the maximum possible frequency of waves.

- Each q has a finite ω given by the dispersion relation ω(q).

- Each normal mode oscillation involves all the N atoms, in general.

- These normal modes are independent of each other.
  [non-identical independent oscillators — easy to do SM]

- Linear ω-q relation at small q (long wavelengths).
  For q→0 (λ>>a):
  $$\omega = \sqrt{\frac{4K}{M}}\,\sin\frac{qa}{2} \approx \sqrt{\frac{4K}{M}}\cdot\frac{qa}{2}$$
  $$= \left(\sqrt{\frac{K}{M}}\cdot a\right)\cdot q \qquad (2e)$$

$$v = \sqrt{\frac{K}{M}}\cdot a, \quad a = \sqrt{\frac{M}{K}}\sqrt{\frac{Ka}{a}} = \sqrt{\frac{C}{\rho}} = \text{sound velocity}$$

$$C = \text{elastic modulus}$$
$$\rho = \text{density}$$

- Small q ⟹ long wavelength
  ⟹ λ >> a
  ⟹ continuum limit (discreteness is not important)
  wave equation ⟹ $\omega = v\,q$

- $$\omega^2(q) = \frac{4K}{M}\sin^2\left(\frac{qa}{2}\right)$$
  $$\omega^2(-q) = \frac{4K}{M}\sin^2\left(\frac{qa}{2}\right) = \omega^2(q)$$
  this is a general property of phonon dispersion relation
  ["inversion symmetry"]

- As discussed,
  $$q \to q' = q + v\cdot\frac{2\pi}{a} \qquad v:\text{integer}$$
  $$\omega(q') = \omega(q)$$
  and $u_n(t)$ are the same for q and q'
  ⟹ sufficient to take $q \in 1^{st}$ B.Z.
  any reciprocal lattice vector G

Thus, the phonon dispersion relation is represented as
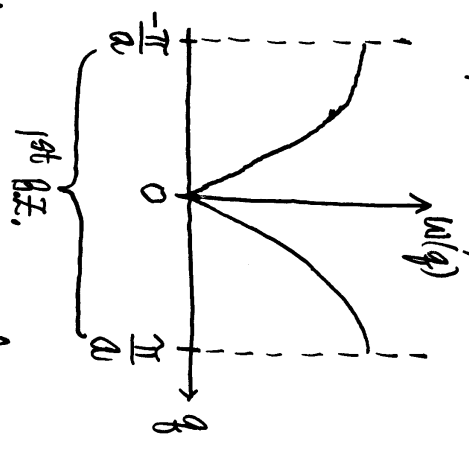
- $q \in$ 1st B.Z. , λ goes from $\lambda \gg a$ to $\lambda \sim 2a$

$$q' = q \, , \quad q' = q + v' \cdot \frac{2\pi}{a} \Rightarrow \lambda' < 2a \text{ to } \lambda' \ll a$$

and it is unnecessary!

The wave represented by the solid curve conveys no information not given by the dashed curve. Only wavelengths longer than $2a$ are needed to represent the motion.

larger q'

smaller q
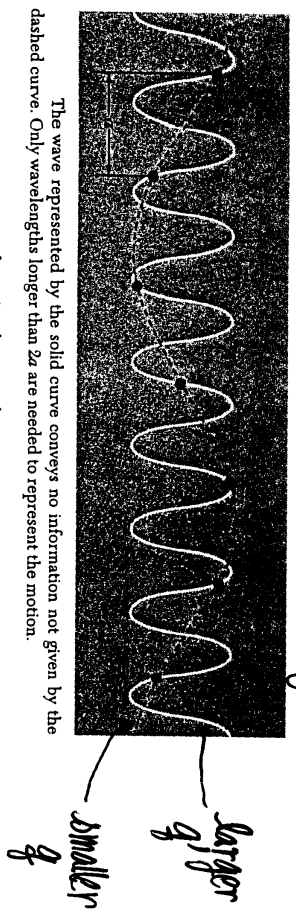
- q and q' describe the same mode

- But there remains one question.
For a finite chain of N atoms, we only expect
to have only N normal modes.
How come? This is a consequence of periodic B.C.

Q: How many allowed modes are there? [Mode counting]

Periodic B.C. $\Rightarrow u_n = u_{n+N}$

$$\Rightarrow A e^{iqna} e^{-i\omega t} = A e^{iqna} e^{iqNa} e^{-i\omega t} \quad \leftarrow \text{ consequence of periodic B.C.}$$

$$\Rightarrow \boxed{e^{iqNa} = 1}$$

Note: N = total number of unit cells in the 1D crystal

$$Na = L = \text{sample size}$$

$$\therefore \quad e^{iqL} = 1$$
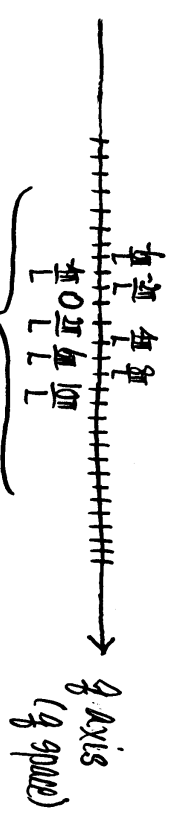
Require $qNa = 2\pi \cdot \text{integer} = 2\pi \cdot p$

$$\Rightarrow \boxed{q = \frac{2\pi}{Na} \cdot p = \frac{2\pi}{L} \cdot p} \quad p = \text{integer} \quad (*)$$
$$(0, \pm 1, \pm 2, \cdots)$$

↳ The allowed q-values are given by (*).
For each allowed q, ω is given by the dispersion relation.

densely packed allowed q-values

$$\cdots \quad \frac{-4\pi}{L} \quad \frac{-2\pi}{L} \quad 0 \quad \frac{2\pi}{L} \quad \frac{4\pi}{L} \quad \cdots$$

q-axis
(q space)

Important concept →
- Each allowed q-value occupies $\frac{2\pi}{L}$ of q-space
- Density of allowed modes (DOS) in q-space
$$= \frac{L}{2\pi} \, , \text{ i.e. there are } \frac{L}{2\pi} \text{ allowed } q\text{-values per unit "length" of } q\text{-space.}$$

Choosing q-values in a certain range

Why?   N unit cells + 1 atom per unit cell + longitudinal motion only

⇒ N degrees of freedom

Expect N normal modes

∴ there should be N physically distinguishable values of q

⇒ further restrict q to a certain range.

Each q-value occupies $\frac{2\pi}{l} = \frac{2\pi}{Na}$ q-space

⇒ ┌───┐
   │ There are N allowed q-values in a range $\frac{2\pi}{a}$ in q-space. │
   └───┘

• The range is chosen to be:

↳ ∴ Take a range of "length" $\frac{2\pi}{a}$ and the allowed q-values in the range cover all N normal modes.

$$\boxed{-\frac{\pi}{a} < q \le \frac{\pi}{a}}$$
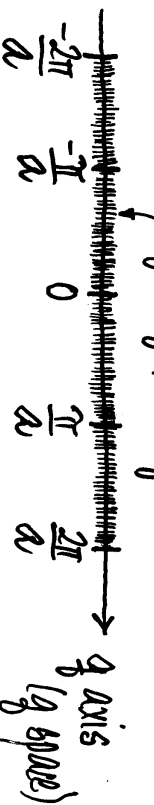
i.e. chose the N q-values that are inside the <u>1st Brillouin Zone</u>

∴ there are N allowed q-values (thus N normal modes) in the 1st B.Z.
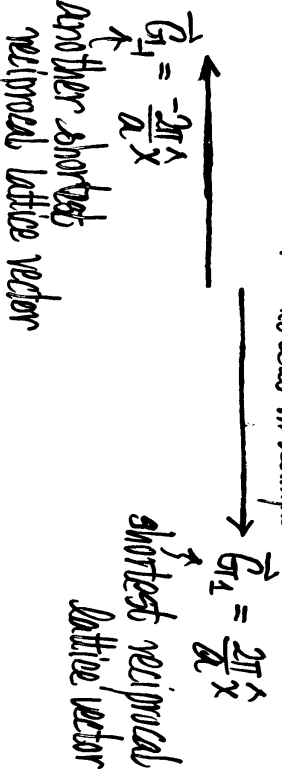
✝ One could take $-\frac{\pi}{a} \le q < \frac{\pi}{a}$, it really doesn't matter.

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densely (evenly) packed q-values

$$\frac{-2\pi}{a} \quad -\frac{\pi}{a} \quad 0 \quad \frac{\pi}{a} \quad \frac{2\pi}{a} \quad \text{q axis (q space)}$$

reciprocal lattice points
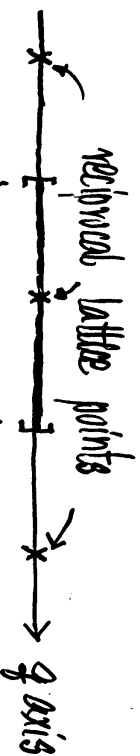
1st Brillouin Zone
(N allowed q-values in 1st BZ)
unit cells in sample

$\vec{G}_1 = \frac{2\pi}{a}\hat{x}$
$\vec{b}_1 = \frac{2\pi}{a}\hat{x}$
shortest reciprocal lattice vector

$\vec{G}_1 = \frac{-2\pi}{a}\hat{x}$
Another shortest reciprocal lattice vector

• Any allowed value q' outside the 1st BZ is related to an allowed value q inside the 1st B.Z. by:

$$\vec{q}' = \underbrace{\vec{q}}_{\text{inside 1st BZ}} + \underbrace{(\text{integer})\cdot\frac{2\pi}{a}}_{\text{a reciprocal lattice vector } \vec{G}}$$

outside 1st BZ

The motion described by q' is

$$e^{iq'an} = e^{iqan}\cdot e^{i2\pi\cdot integer} = e^{iqan} \qquad \text{this is a result of } e^{i\vec{G}\cdot\vec{R}} = 1$$

⇒ q' and q describe the <u>same normal mode</u>

Summary-

- # normal modes = # degrees of freedom

- $\omega(q)$ is governed by eq. of motion

- normal mode oscillation involves all atoms (collective excitation)

- Periodicity or discrete translational symmetry,

  $\Rightarrow$ Bloch's theorem and $\vec{q} \in 1^{st}$ BZ.

- Finite crystal is handled by periodic boundary condition

  $\Rightarrow$ q takes on discrete value $\frac{2\pi}{L} \cdot p$

  N>>1 $\Rightarrow$ N (# primitive cells) allowed q-values in 1st B.Z.

  $\Rightarrow$ allowed q values are very close to each other

  $\Rightarrow$ can draw $\omega(q)$ as a continuous function

- Each q-value occupies $\frac{2\pi}{L}$ q-space

  $\Rightarrow \left(\frac{L}{2\pi}\right)$ allowed q-values per unit "length" of q-space

- $\omega(q) = \omega(-q)$

- $\omega(q) \xrightarrow[q \to 0]{} v \cdot q$ (v = sound velocity)

  an estimate on ω range: $v \sim 1000 \, ms^{-1}$
  $q \sim$ a few Å (longest q)
  $\Rightarrow \omega \sim 10^{12}$ Hz (IR range)

$$\omega(q) = \sqrt{\frac{4K}{M}} \left| \sin\frac{qa}{2} \right|$$
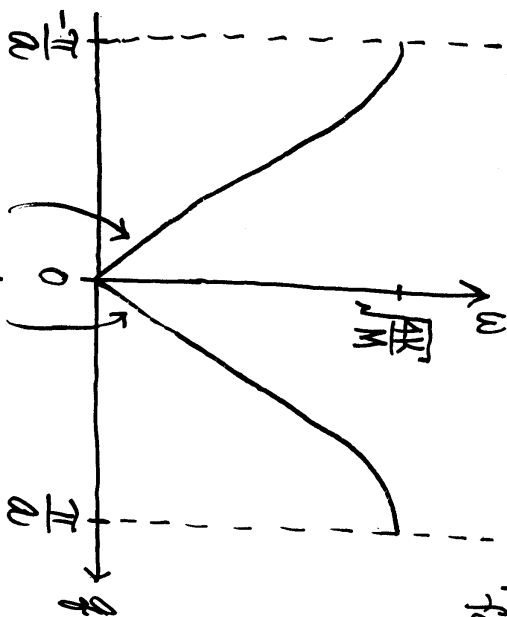
"phonon" dispersion relation
for 1D monatomic chain

$\Rightarrow$ N>1
q (while discrete)
looks continuous

$q << \frac{1}{a}$ or $\lambda >> a$ (long wavelength limit)
$\downarrow$
continuum limit where
$\omega = v_s \cdot q$ (acoustic branch)

Q: How many allowed ω-values are there in the
range ω to $\omega + d\omega$?
This is $D(\omega) \, d\omega$
$\uparrow$
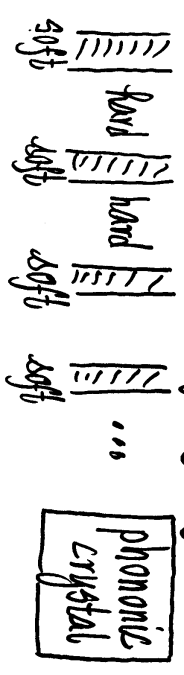DOS (density of states) in ω-space.

Further considerations

- How about crystal with a basis of 2 atoms, 3 atoms?

- Higher dimension (2D, 3D)?

- Allowing for transverse as well as longitudinal motions?

- Other wave propagation (matrix eigenvalue) problem in periodic structures?

  e.g. EM waves in alternating layers of dielectrics

  ε_2 | ε_2 | ε_2 | ...
  ε_1 | ε_1 | ε_1
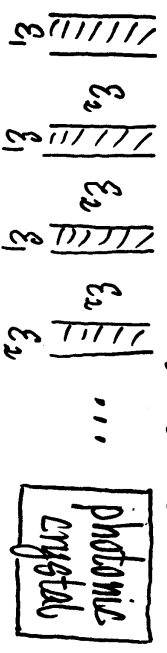
  photonic crystal

  Elastic waves in alternating layers of materials

  soft | hard | hard | ...
  soft | soft | soft
  soft | soft | soft

  phononic crystal

  Photonic and phononic crystals are hot topics in research.