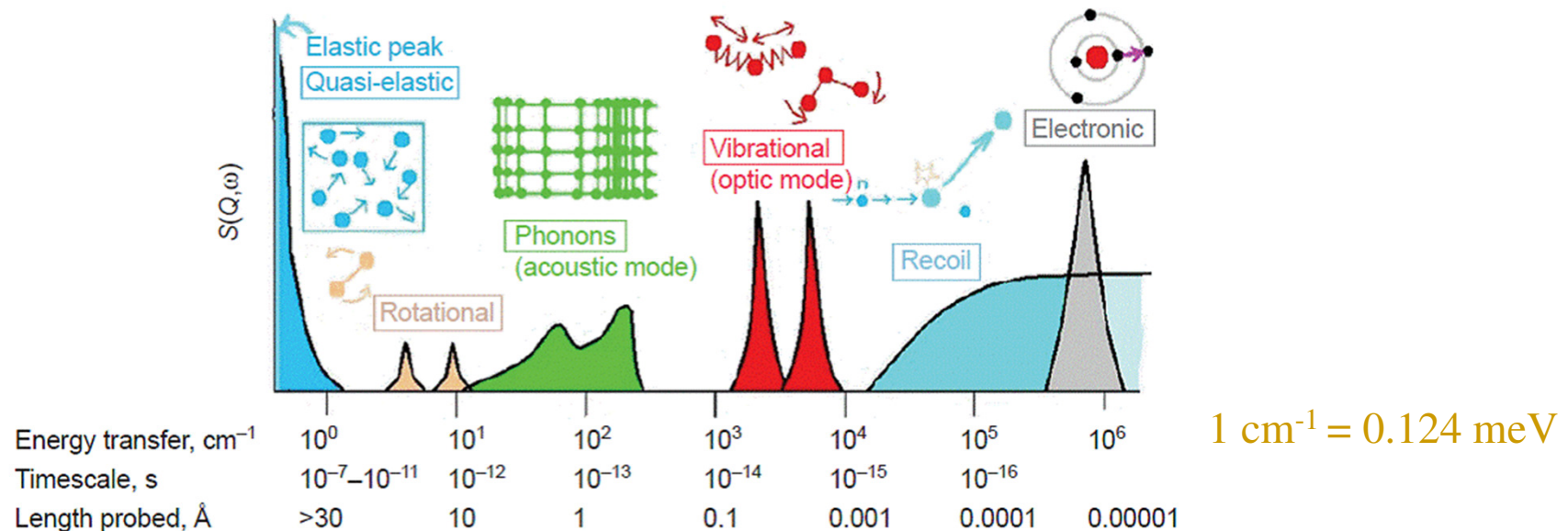


# Spectroscopy and excitations in condensed matter

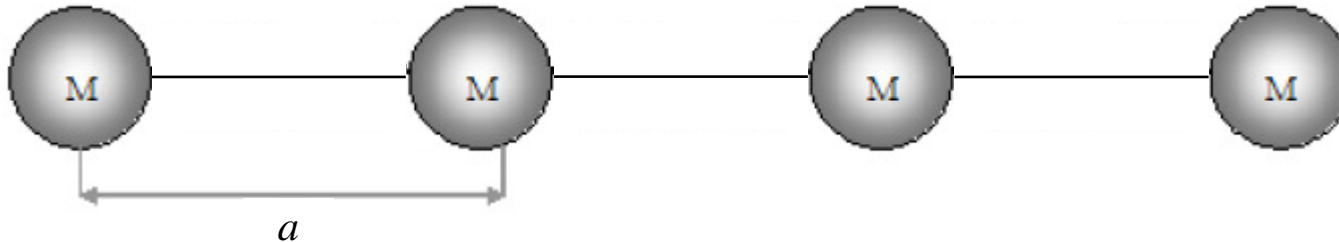
Inelastic scattering probes the elementary excitations associated to *characteristic frequencies* of the system, on variable length scales (i.e. with varying  $Q$ ).



A sample can «accept» or «give» only amounts of energy which **match** the quantized forms of its possible excitations: the scattered signal emerging from a sample tells us which energy «jumps» of the system could be probed.

# Vibrational modes in crystals

## Monatomic one-dimensional crystal



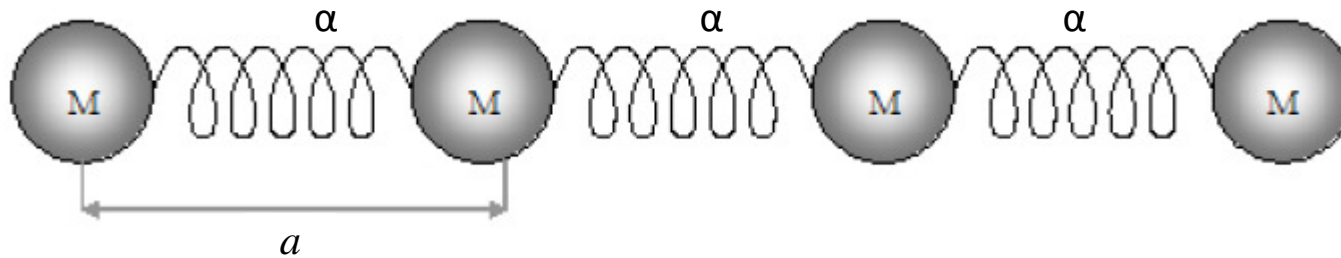
$N$  : number of lattice sites (and atoms)

$M$  : atomic mass

$a$  : lattice parameter

How the atoms of this system move? How can we describe the time dependence of the displacement,  $u_n(t)=u(na,t)$  of the  $n$ -th atom from its equilibrium position?

# Monatomic one-dimensional crystal



Harmonic potential and interaction only with neighbouring atoms:

$$U^{harm} = \frac{1}{2} \alpha \sum_n [u_n(t) - u_{n+1}(t)]^2 \quad \alpha \text{ elastic constant}$$

Equation of motion of  $N$  coupled harmonic oscillators:

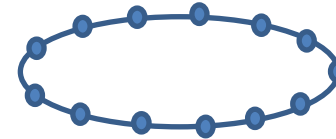
$$\begin{aligned} M \ddot{u}_n(t) &= -\frac{\partial U^{harm}}{\partial u_n(t)} = -\frac{\partial}{\partial u_n(t)} \frac{1}{2} \alpha \sum_n [u_n^2 + u_{n+1}^2 - 2u_n u_{n+1}] = \\ &= -\frac{\partial}{\partial u_n(t)} \frac{1}{2} \alpha [\dots + (u_{n-1}^2 + u_n^2 - 2u_{n-1}u_n) + (u_n^2 + u_{n+1}^2 - 2u_n u_{n+1}) + \dots] = \\ &= -\frac{1}{2} \alpha [2u_n - 2u_{n-1} + 2u_n - 2u_{n+1}] = \alpha [u_{n+1}(t) - 2u_n(t) + u_{n-1}(t)] \quad (n = 1, \dots, N) \end{aligned}$$

# Monatomic one-dimensional crystal

We look for solutions of the form

$$u_n(t) = A_q e^{i(qna - \omega t)} \quad \text{with } q = \text{wave vector}, \quad \omega = \text{angular frequency}$$

Periodic boundary condition (Born-von Karman)



$$u_{N+1}(t) = u([N+1]a, t) = u(a, t) = u_1;$$

$$u_0(t) = u(0, t) = u(Na, t) = u_N(t) \Rightarrow e^{-i\omega t} = e^{iqNa} e^{-i\omega t} \Rightarrow e^{iqNa} = 1$$

$$\Rightarrow q = \frac{m}{N} \frac{2\pi}{a} \quad \text{with } m \in \mathbb{Z} \quad (\text{positive or negative integer})$$

$q$  can take only discrete values

Note that if  $q$  is changed by  $2\pi/a$  the displacement  $u_n(t)$  is unaffected:

$$u_n(t) = e^{iqna} e^{-i\omega t} = e^{i\left(q + \frac{2\pi}{a}\right)na} e^{-i\omega t} = e^{iqna} \underbrace{e^{i2\pi n}}_1 e^{-i\omega t}$$

Consequently, there are just  $N$  values of  $q$  that yield distinct solutions

# Monatomic one-dimensional crystal

Independent (distinct) solutions: we take them to be the  $N$   $q$ -values lying between

$$-\frac{\pi}{a} \leq q \leq \frac{\pi}{a} \iff -\frac{N}{2} \leq m \leq \frac{N}{2}$$

This is the one-dimensional version of requiring  $q$  to lie in the  
FIRST Brillouin zone (1ZB)

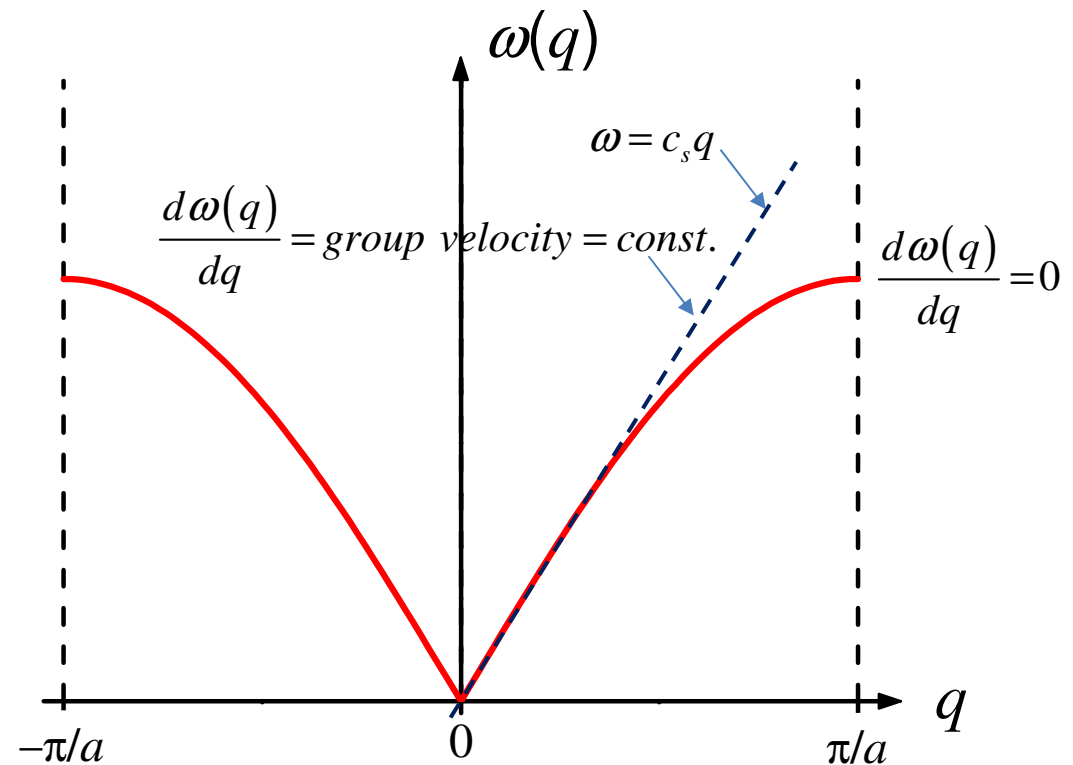
# Normal modes

$$u_n(t) = A_q e^{i(qna - \omega t)} \rightarrow M \ddot{u}_n(t) = \alpha [u_{n+1}(t) - 2u_n(t) + u_{n-1}(t)]$$

Dispersion curve:

$$\omega(q) = 2\sqrt{\frac{\alpha}{M}} \cdot \left| \sin\left(\frac{a}{2} q\right) \right|$$

*N* normal modes



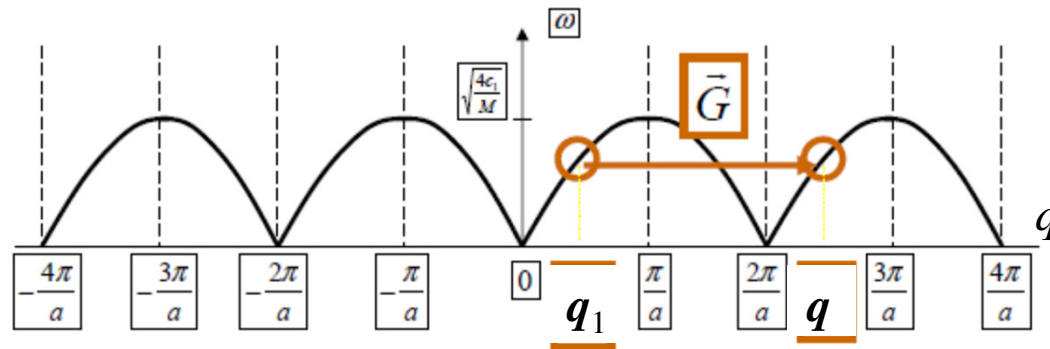
At low  $q$  (i.e. when the wavelength is large compared to the interparticle spacing  $a$ )  $\omega$  is linear in  $q$  (no «dispersion»).

# Brillouin zones (one-dimensional monatomic case)

The 1st BZ is the region in reciprocal space containing all information about the vibrations of the one-dimensional Bravais lattice.

Only the  $q$  values in the 1st BZ correspond to unique vibrational modes.  
Any  $q$  outside this zone is mathematically equivalent to a  $q_1$  value inside the 1st BZ.

This is expressed in terms of a general translation vector of the reciprocal lattice:



$$q = q_1 + \bar{G}$$

# Atomic displacements

General (classical) solution:

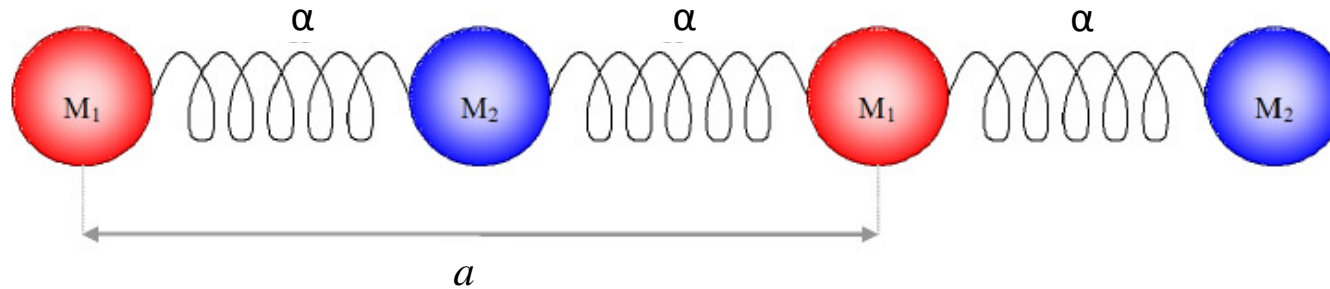
$$u_n(t) = \frac{1}{\sqrt{N}} \sum_q e^{iqna} \left[ A_q e^{-i\omega(q)t} + B_q e^{i\omega(q)t} \right] \quad (n = 1, \dots, N)$$

$$u(na, t) \propto \begin{cases} \cos(qna - \omega t) \\ \sin(qna - \omega t) \end{cases} \quad \text{We have } N \text{ distinct values of } q, \text{ each with a unique frequency } \omega(q), \text{ so there are } 2N \text{ independent solutions.}$$

However, the «normal modes» are only  $N$  because the sine solution is simply the cosine one shifted in time by  $\pi/(2\omega)$ .



# Diatomic one-dimensional crystal



$N$  : number of lattice sites

$2N$  : total number of atoms

$M_1$  : mass of atom 1

$M_2$  : mass of atom 2

$a$  : lattice parameter

$\alpha$  : elastic constant (here assumed to be the same between atom 1 and 2)

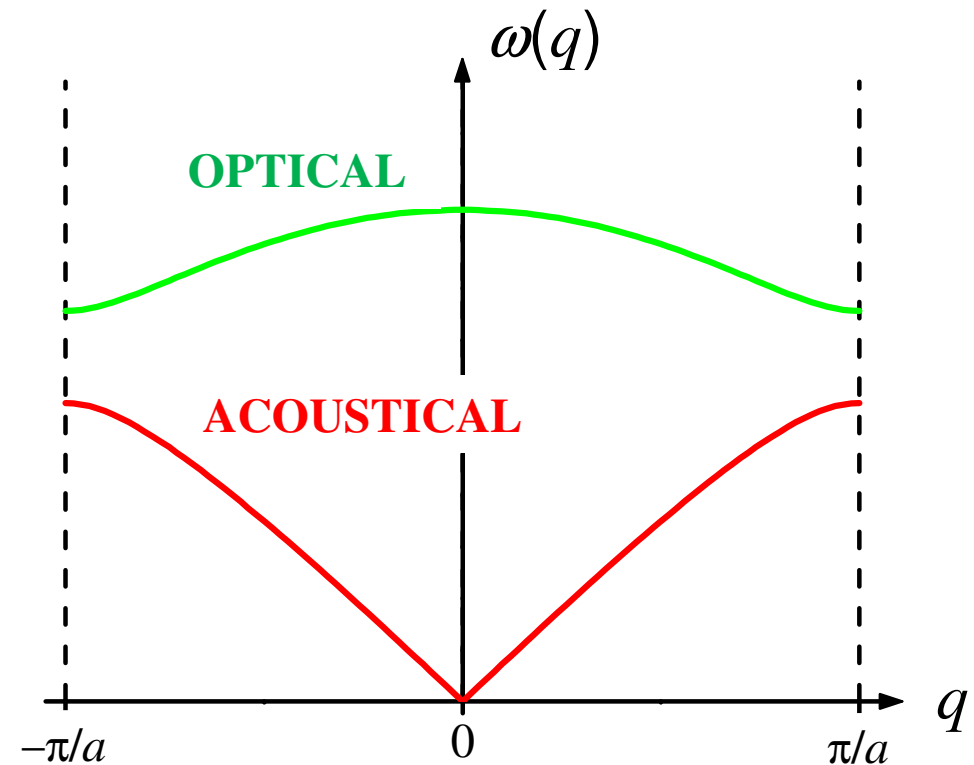
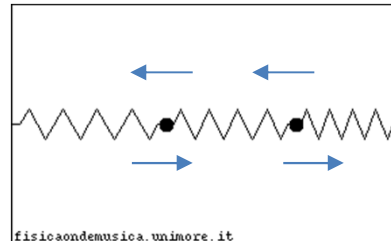
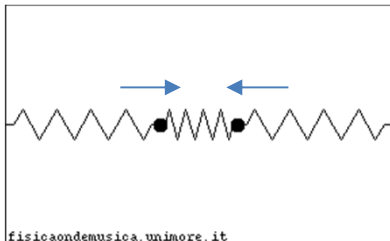
Now the normal modes in 1ZB are  $2N$

# Diatomic one-dimensional crystal

$$\omega_{\pm}(q) = \sqrt{\alpha \left\{ \left( \frac{1}{M_1} + \frac{1}{M_2} \right) \pm \sqrt{\left( \frac{1}{M_1} + \frac{1}{M_2} \right)^2 - \frac{4}{M_1 M_2} \sin^2 \left( \frac{a}{2} q \right)} \right\}}$$

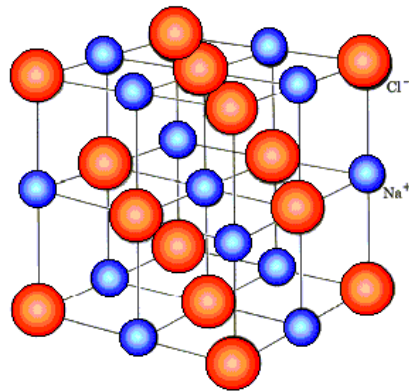
- $N$  discrete values of  $q$  in 1ZB
- 2 branches

$2N$  normal modes

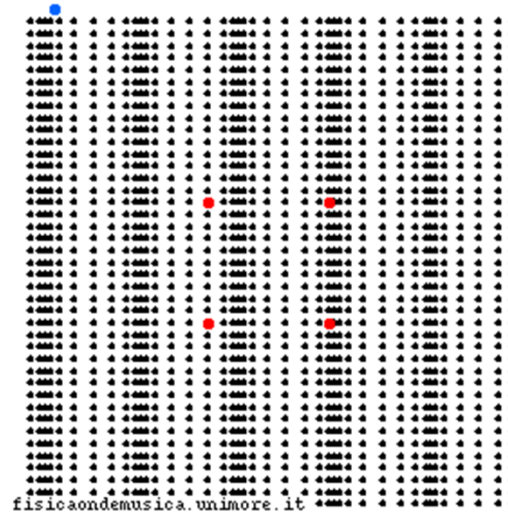


# $p$ -atomic three-dimensional crystal

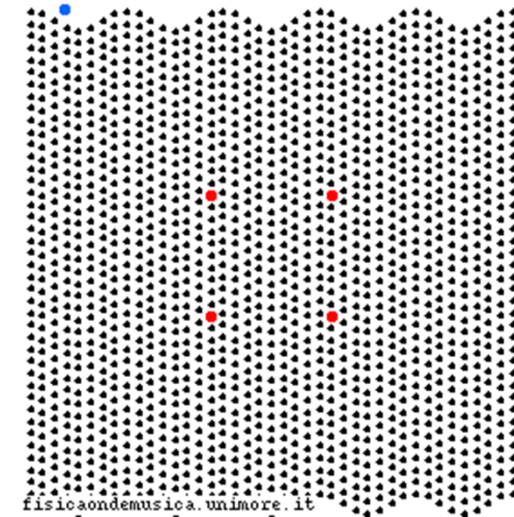
In 3 dimensions atoms can oscillate in the 3 spatial directions, so for each wave vector  $\mathbf{q}$  we have:



one longitudinal mode



two transverse modes



$N$  : n. lattice sites

$p$  : n. of atoms *per* site

$pN$  : totale number of atoms

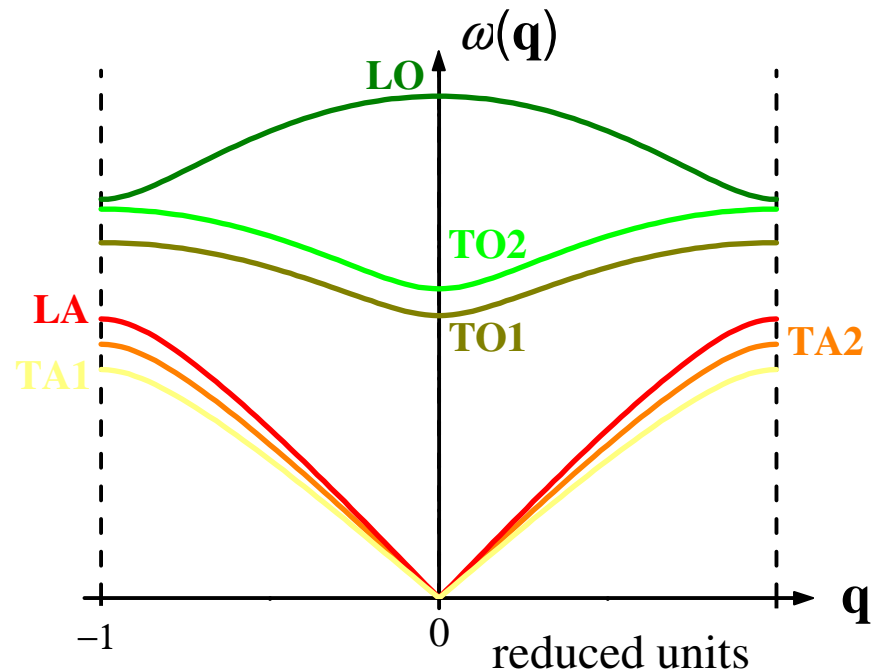
}  $3pN$  normal modes in 1ZB

$3N$  acoustic modes

$3(p-1)N$  optical modes

# $p$ -atomic three-dimensional crystal

Dispersion curve  
( $p=2$ )  
6 branches



General solution:

$$\mathbf{u}_{d,n}(t) = \frac{1}{\sqrt{NM_d}} \sum_{s,\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{l}_n} \left[ A_{d,\mathbf{q}} e^{-i\omega_s(\mathbf{q})t} + B_{d,\mathbf{q}} e^{i\omega_s(\mathbf{q})t} \right] \cdot \mathbf{e}_{s,\mathbf{q}} \quad \left( \begin{array}{l} n = 1, \dots, N \\ d = 1, \dots, p \\ s = 1, \dots, 3p \end{array} \right)$$

where  $\mathbf{l}_n$  is the position of the  $n$ -th lattice site,  
 $\mathbf{e}_{s,\mathbf{q}}$  is the polarization vector  
 $s$  is the branch index

# Normal modes

Normal mode  $(s, \mathbf{q})$  = elastic wave propagating in the crystal with angular frequency  $\omega_s(\mathbf{q})$

→  $\hbar\omega_s(\mathbf{q})$  quantum of vibrational energy: **phonon**

More rigorously, given the displacements  $\mathbf{u}_n(t)$ , one defines:

- canonical variables  $(Q_{s,\mathbf{q}}, P_{s,\mathbf{q}})$  and the classical Hamiltonian

- creation and annihilation operators:  $\hat{a}_{s,\mathbf{q}}^+$ ,  $\hat{a}_{s,\mathbf{q}}$

- Quantum Hamiltonian of  $3pN$  independent harmonic oscillators: 
$$\hat{H} = \sum_{s,\mathbf{q}} \hbar\omega_s(\mathbf{q}) \left( \hat{a}_{s,\mathbf{q}}^+ \hat{a}_{s,\mathbf{q}} + \frac{1}{2} \right)$$

If interested, see Appendix L of Neil W. Ashcroft, N. David Mermin, "Solid State Physics", Saunders College, Philadelphia, USA (1976).

Admitted energies for the single quantum oscillator  $(s, \mathbf{q})$  :

$$\left( n_{s,\mathbf{q}} + \frac{1}{2} \right) \hbar\omega_s(\mathbf{q}) \quad \text{with } n_{s,\mathbf{q}} = 0, 1, 2, \dots, \infty$$

Given  $n_{s,\mathbf{q}}$ : instead of saying that the normal mode of branch  $s$  with wave vector  $\mathbf{q}$  is in its  $n_{s,\mathbf{q}}$ -th excited state of energy  $(n_{s,\mathbf{q}} + 1/2) \hbar\omega_s(\mathbf{q})$  we *equivalently* say that  $n_{s,\mathbf{q}}$  **phonons are present in state  $(s, \mathbf{q})$**

# Phonon gas

$pN$  atoms in harmonic oscillation  
( $3pN$  normal modes)



$3pN$  quantum states  $(s, \mathbf{q})$  occupied by a potentially *infinite* number of phonons

The state of the system is defined by the **occupation numbers**  $n_{s, \mathbf{q}}$  of the total  $3pN$  available energy levels  $\hbar\omega_s(\mathbf{q})$ :

$$\left| n_{(s, \mathbf{q})_1}, n_{(s, \mathbf{q})_2}, \dots, n_{(s, \mathbf{q})_{3pN}} \right\rangle$$

Occupation numbers are determined by the temperature:

$$n_{s, \mathbf{q}}(T) = \frac{1}{e^{\frac{\hbar\omega_s(\mathbf{q})}{k_B T}} - 1} \quad \text{Bose-Einstein statistic distribution}$$