Scuola di Dottorato in Ingegneria Leonardo da Vinci – a.a. 2009/10

PROPRIETÀ MECCANICHE, OTTICHE, ELETTRONICHE DEI MATERIALI ALLE PICCOLE E PICCOLISSIME SCALE

Versione 1 – Settembre 2010 – http://www.df.unipi.it/~fuso/dida

Parte 3
Descrizione classica e quantistica dei solidi: proprietà (termo)meccaniche ed effetti su scala locale

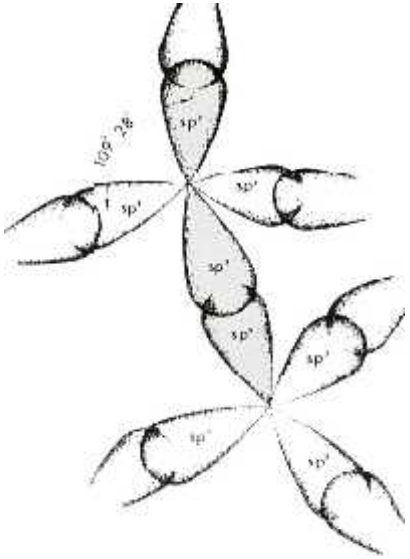
Lu 13.09.10 13-14 aula DIC
Lu 20.09.10 13-16 B32
Ve 24.09 14-15 aula 6 DCCI

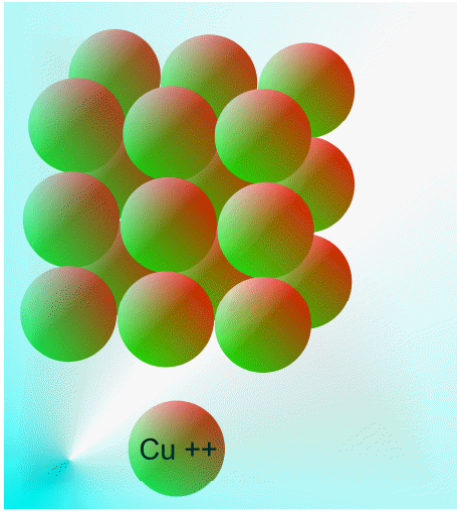
Outlook

What we are interested in:
- description of the behavior for a solid at the local (ultra-small!) scale

Restrictions (for the moment!):
- the solid is a *crystal*, i.e., single atoms (or molecules) are regularly arranged in space
- the sample is huge in all three directions (it's a *bulk crystal*, for the moment!)

Assumption:
-Electron and "ions" (i.e., lattice sites) can be considered separately, i.e.:
- the total Hamiltonian is sum of Hamiltonians and
-wavefunctions are multiplied





Electron wavefunction → transport properties
Lattice wavefunction → termo(mechanical) properties

Interaction force/potential

A.N. Cleland, Foundations of Nanomechanics, Springer (2002)

Interatomic force/potential: typical example Lennard-Jones

r_0 being the equilibrium distance

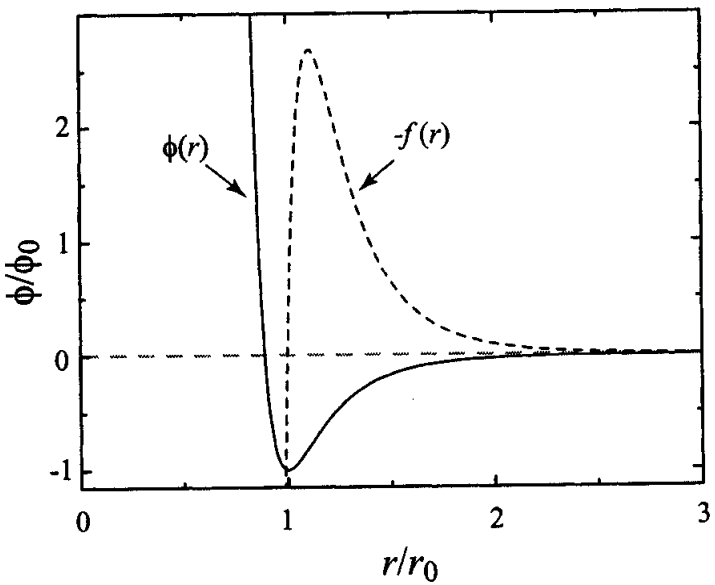


Fig. 1.1. Lennard–Jones model interaction force $-f(r)$ and potential energy $\phi(r)$, as a function of distance r/r_0. Note we have plotted the negative of the force, so that a positive value corresponds to an attractive force. The vertical axis is for the potential, in units of the potential at the minimum, $\phi_0 = -\phi(r_0)$.

As we shall see, it is often more useful to deal with the interaction potential energy $\phi(r)$ rather than the force $f(r)$, which is defined through the relation

$$f(r) \equiv -\frac{\mathrm{d}\phi}{\mathrm{d}r}. \tag{1.1}$$

Note that this differential equation defines the potential energy only up to an additive constant, whose value is arbitrary and has no physical meaning. The potential energy can also be described as the negative of the work done by the force for a displacement $r - r_0$ from the point of zero potential energy r_0, or

$$\phi(r) = -W = -\int_{r_0}^{r} f(r)\,\mathrm{d}r, \tag{1.2}$$

which is equivalent to (1.1).

As a specific example, we will consider the model known as the *Lennard–Jones* interaction, which applies to atoms interacting through the van der Waals interaction. The interaction potential energy for the Lennard–Jones model has the algebraic form

$$\boxed{\phi(r) = -\frac{A}{r^6} + \frac{B}{r^{12}},} \tag{1.3}$$

with the parameter A determining the strength of the attractive interaction, and B the repulsive interaction. The attractive $1/r^6$ dependence is characteristic of the van der Waals interaction, while the repulsive $1/r^{12}$ dependence is somewhat phenomenological. The repulsive interaction is strongest for small r, with the atoms close together, and decreases more rapidly with r than the attractive interaction, which therefore dominates for large r. The zero for the potential energy $\phi(r)$ is chosen so that the energy is zero when the atoms are infinitely far apart. The force corresponding to (1.3) is

$$\boxed{f(r) = 6\,\frac{A}{r^7} - 12\,\frac{B}{r^{13}}.} \tag{1.4}$$

Attractive/repulsive character depending on distance

Harmonic approximation (small displacements)

1.1.1 External Forces

We can now imagine what happens if we try to pull our two atoms apart. Let's say that we apply equal and opposite external forces $f_{\rm ext}$ to each atom. The atoms will move apart until they reach a new equilibrium point r_0', where their attractive interaction balances the external force, $-f(r_0') = f_{\rm ext}$. If the external force is too large, above the maximum value of $-f(r)$ in Fig. 1.1, there will be no equilibrium point and the atoms will unbind.

Another way to understand this is to define the potential energy associated with the external force, $\phi_{\rm ext}(r) = -f_{\rm ext} r$. Note that the zero for the external potential is chosen at $r = 0$. Note there is no factor of two in this expression: Both atoms are acted upon by the external force, but each atom is only displaced from $r = 0$ by $r/2$, so the work done by the force, which is the negative of the potential energy, is $W = 2 \times f_{\rm ext} r/2$.

The total potential energy is then $U_{\rm tot} = \phi(r) + \phi_{\rm ext}(r)$. For $f_{\rm ext} = 0$, the total potential energy is the same as the interaction potential. For small $f_{\rm ext}$, the minimum for the total potential $U_{\rm tot}$ will shift to the new equilibrium point r_0'; for $f_{\rm ext}$ too large, no minimum occurs. In Fig. 1.2, we show a family of potential energy curves for different external forces, showing how the minimum energy point moves away from r_0 until it disappears at large enough $f_{\rm ext}$ (see Exercise 1.2).

Note that as soon as we apply the external force, the energy minimum at r_0' becomes *metastable*; the atoms can achieve a lower total energy if they can cross over the potential barrier and escape to infinity. This provides interesting questions in the case where we allow the atoms to have non-zero temperature, so that there is a certain probability that they can be thermally activated over the potential barrier; the same question occurs when we consider quantum mechanical *tunnelling*, through the barrier, also allowing the atoms to escape.

In addition to the question of binding, it is often useful to know how a solid, or in our case, the two atoms, respond to very weak forces, such that the atoms only displace a very small amount from their equilibrium positions, from r_0 to r_0'. We can use our model Lennard–Jones interaction to see how this works. For a very weak force $f_{\rm ext}$, the very small shift in the equilibrium point allows us to approximate the interaction potential by using a *Taylor series* expansion of the potential:

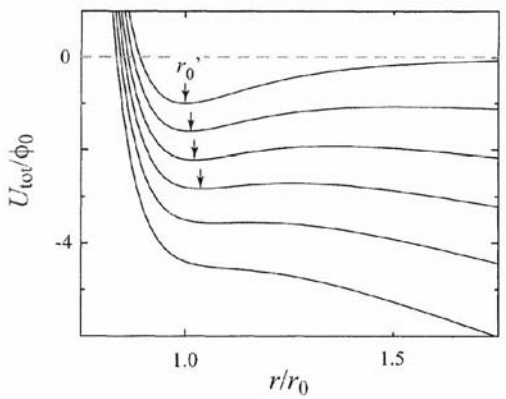


Fig. 1.2. Total potential energy $U_{\rm tot}$ for the Lennard–Jones potential in the presence of a constant external force; the family of curves is for external forces ranging from zero (*top*) to a force larger than the maximum Lennard–Jones binding force (*bottom*). The arrows indicate the new equilibrium point r_0' for each value of the external force. Vertical axis is in units of the interaction potential at the minimum point.

$$\begin{aligned}\phi(r) &= \phi(r_0) + \left.\frac{d\phi}{dr}\right|_{r_0}(r-r_0) + \frac{1}{2!}\left.\frac{d^2\phi}{dr^2}\right|_{r_0}(r-r_0)^2 \\ &\quad + \frac{1}{3!}\left.\frac{d^3\phi}{dr^3}\right|_{r_0}(r-r_0)^3 + \ldots \\ &\approx \phi(r_0) + \frac{1}{2}\left.\frac{d^2\phi}{dr^2}\right|_{r_0}(r-r_0)^2, \qquad (1.5)\end{aligned}$$

where in the second, approximate equality, we have used the fact that $d\phi/dr(r_0) = 0$, and we have dropped the higher order terms in the Taylor expansion. We are thus left with a *harmonic potential* approximation for the interaction, that depends quadratically on the square of the displacement $u = r - r_0$ from equilibrium.

For the Lennard–Jones potential, the curvature is given in terms of the equilibrium spacing and binding energy by

$$\left.\frac{d^2\phi}{dr^2}\right|_{r_0} = 72\,\frac{E_b}{r_0^2}. \qquad (1.6)$$

In Fig. 1.3 we show the harmonic approximation to the Lennard–Jones potential; the approximation is seen to work well for very small displacements from equilibrium, but rapidly fails as one moves further away.

In the presence of a weak external force, the equilibrium point shifts to where $dU_{\rm tot}/dr = 0$; using the expansion (1.5) for the interaction potential, this is when

At the first order, potential is parabolic, force is linear (and restoring), i.e., harmonic

Relative motion of the dimer

We now consider the dynamical behavior of the atoms in our model interaction potential. What this means is that we will allow the atoms to move, so that they have a kinetic energy T in addition to the potential energy $U = \phi(r)$.

We assume that the *center of mass* of our system remains at rest. With the atoms at distances r_1 and r_2 from the origin, their separation is $r = r_2 - r_1$. If the atoms have masses M_1 and M_2, the location of the center of mass $r_{\rm cm}$ is the weighted sum of their locations, or

$$r_{\rm cm} \equiv \frac{M_1 r_1 + M_2 r_2}{M_1 + M_2}. \qquad (1.9)$$

Center of mass

The atom positions can be written in terms of $r_{\rm cm}$ and r as

$$\left.\begin{aligned} r_1 &= r_{\rm cm} - \frac{M_2}{M_1+M_2}\, r, \\ r_2 &= r_{\rm cm} + \frac{M_1}{M_1+M_2}\, r. \end{aligned}\right\} \qquad (1.10)$$

If the center of mass is at rest, so $\dot{r}_{\rm cm} = 0$ (where we use the notation $\dot{r} = {\rm d}r/{\rm d}t$), then the atom velocities must satisfy

$$M_1 \dot{r}_1 = -M_2 \dot{r}_2. \qquad (1.11)$$

Conservation of the impulse

The kinetic energy can then be written

$$\begin{aligned} T &= \frac{1}{2} M_1 \dot{r}_1^2 + \frac{1}{2} M_2 \dot{r}_2^2 \\ &= \frac{1}{2}\mu \dot{r}^2, \end{aligned} \qquad (1.12)$$

using the *reduced mass* $1/\mu = 1/M_1 + 1/M_2$. With the momentum $p = \mu\dot{r}$, the kinetic energy is

$$T = \frac{p^2}{2\mu}. \qquad (1.13)$$

The Hamiltonian for the system, $H = T + U$, is then

$$H = \frac{1}{2\mu} p^2 + \phi(r), \qquad (1.14)$$

and Hamilton's equations of motion (see e.g. Goldstein [2]) then yield

$$\mu \ddot{r} = -\frac{{\rm d}\phi}{{\rm d}r}(r) = f(r). \qquad (1.15)$$

Interaction force

Let's again consider only very small displacements $u = r - r_0$ from the equilibrium spacing r_0. Using the Taylor expansion (1.5) for the interaction potential, the equation of motion for $u(t)$ is easily shown to be

$$\mu \ddot{u} = -\left.\frac{{\rm d}^2\phi}{{\rm d}r^2}\right|_{r_0} u. \qquad (1.16)$$

This is the equation of motion of a *simple harmonic oscillator*, and has the usual harmonic solution of the form

$$u(t) = u_0 \cos(\omega_0 t + \varphi), \qquad (1.17)$$

where the resonance frequency ω_0 is given by

$$\omega_0 = \sqrt{\frac{1}{\mu}\frac{{\rm d}^2\phi}{{\rm d}r^2}}, \qquad (1.18)$$

Oscillation frequency

and the amplitude u_0 and phase φ are determined by the initial conditions. A convenient shorthand for writing harmonic solutions of the form (1.17) is to use complex exponential notation, of the form

$$u(t) = u_0 {\rm e}^{-{\rm i}\omega_0 t}, \qquad (1.19)$$

where the amplitude u_0 can be complex, to allow for the phase factor φ, and the actual solution is obtained by taking the real part of (1.19).

We see that the natural resonance frequency ω_0 of our system is determined by the reduced mass μ and by the curvature of the interaction potential ${\rm d}^2\phi/{\rm d}r^2$, just as the displacement due to a static external force, (1.8), is inversely proportional to the same curvature. This close relation is due to our use of the harmonic approximation for the potential; another way to represent the interaction in this approximation is to think of the atoms as being linked by a simple linear spring, with spring constant k given by

$$k = \left.\frac{{\rm d}^2\phi}{{\rm d}r^2}\right|_{r_0}. \qquad (1.20)$$

The equilibrium length of the spring is r_0, and the potential energy for separation r is thus $U = k(r - r_0)^2/2 = ku^2/2$, the same as for the harmonic approximation, with the trivial change that our zero of energy is now at the equilibrium point r_0 rather than at infinite separation. Both the response to weak external forces, and the natural dynamic resonant response (1.15), are captured by this simple model, shown schematically in Fig. 1.4.

For the Lennard–Jones potential, and two argon atoms, with masses $M_1 = M_2 = 2\mu = 6.6 \times 10^{-23}$ g, we have already calculated a spring constant $k = 52$ meV/Å^2 = 0.83 N/m; we now find a natural resonance frequency $\omega_0/2\pi = 0.8$ THz. This is somewhat low for a mechanical atomic resonance frequency; the shallow van der Waals interaction has a gentle curvature, reducing the frequency from that for covalently or ionically bonded atoms, which typically have resonance frequencies of order 10 THz = 10^{13} Hz. The spring constants for such bonds are correspondingly larger, with k in the range of 10-100 N/m.

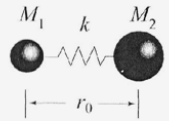


Fig. 1.4. Spring model for the interaction potential between two atoms.

Neglecting center of mass dynamics, the internuclear distance oscillates at some frequency (upon externally applied small perturbations) determined by the potential curvature

Trimers

1.2 The Three Atom Chain

We now add a third atom to our system, and for simplicity assume all the atoms are identical, with mass M. We arrange the atoms in a line, and again restrict motion to one dimension, along the line of atoms. We further assume that the force which holds the three atoms together is a *two-particle* interaction, depending only on the positions r_1 and r_2 of, say, atoms 1 and 2. Hence we write the interaction potential energy as $\phi(r_1, r_2)$. Furthermore, we assume the potential is a function only of the distance between the atoms, so that $\phi(r_1, r_2) = \phi(r_2 - r_1)$. For three identical atoms, the total potential energy U in the absence of any external forces is then given by

$$U(r_1, r_2, r_3) = \phi(r_2 - r_1) + \phi(r_3 - r_2) + \phi(r_1 - r_3). \tag{1.21}$$

We will further assume that the potential interaction is very short-range, so that we only need include the interactions between atoms adjacent to one another; for a chain with the atoms in the sequence $(1, 2, 3)$, as shown in Fig. 1.5, this means we can drop the third term in (1.21).

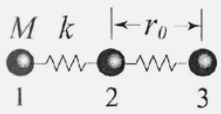


Fig. 1.5. Spring model for the three atom chain.

Our final simplification will be to replace each potential interaction by its harmonic approximation, so that for atoms 2 and 3,

$$\phi(r = r_3 - r_2) = \frac{1}{2}\left.\frac{d^2\phi}{dr^2}\right|_{r_0} (r - r_0)^2, \tag{1.22}$$

choosing the zero of energy at the equilibrium separation $r_3 - r_2 = r_0$.

As discussed above, the response of the two-atom potential to both weak external forces and for small dynamic motion is entirely equivalent to that when the atoms are connected by a linear spring with spring constant k, whose value is given by the curvature of $\phi(r)$. We therefore find that our simplified, one-dimensional three atom system now consists of three masses M connected by linear springs k, as shown in Fig. 1.5.

1.2.1 External Force on a Trimer

We first consider what happens when we pull on either end of the chain with equal and opposite external forces f_{ext}, as shown in Fig. 1.6. By symmetry, atom 2, in the middle of the chain, does not move. The two end atoms 1 and 3 will be displaced until the restoring force provided by their interaction with atom 2 matches that of the external force. The displacement u_1 of atom 1 from its rest point is therefore identical to that obtained when pulling on the two atom chain,

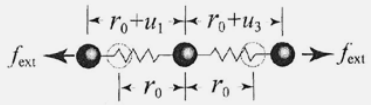


Fig. 1.6. Three atom chain stretched by an external force f_{ext}.

$$\begin{aligned} u_1 &= r_2 - r_1 - r_0 = f_{ext}/k \\ &= \frac{1}{d^2\phi/dr^2} f_{ext}, \end{aligned} \tag{1.23}$$

with an identical expression for $u_3 = r_3 - r_2 - r_0$.

1.2.2 Strain in the Trimer

We are now in a position to define the *strain*, a very useful quantity when describing distortions of solid objects. The strain, which we will write as e (we will be careful to distinguish this from the electron charge), is defined as the fractional displacement of a point in the solid from its rest point. For our three-atom chain, the strain e between atoms 1 and 2 is then

$$e = \frac{u_1}{r_0} = \frac{f_{ext}}{kr_0}. \tag{1.24}$$

Definition of strain

The strain between atoms 3 and 2 is the same, $e = u_3/r_0 = f_{ext}/kr_0$. The strain is a dimensionless quantity, and for a uniform external force applied to a uniform object, will be constant through the object.

1.2.3 Dynamic Motion

We now briefly explore the dynamic behavior of our three atom chain; we will assume, as we did with the two-atom system, that the center of mass of the system is at rest. The dynamic motion can be described by the relative displacements u_1, u_2 and u_3 of the atoms from their rest points; the center of mass condition is then, for equal mass atoms,

$$\dot{u}_1 + \dot{u}_2 + \dot{u}_3 = 0. \tag{1.25}$$

The momentum associated with each atom is $p_n = M\dot{u}_n$.

The kinetic energy of the three atoms, and their (nearest-neighbor) spring interactions, yield the Hamiltonian

$$H = T + U = \frac{1}{2M}\left(p_1^2 + p_2^2 + p_3^2\right) + \frac{k}{2}(u_1 - u_2)^2 + \frac{k}{2}(u_2 - u_3)^2. \tag{1.26}$$

The corresponding equations of motion are

Neglecting center of mass dynamics, a *three* particle system requires *two* coordinates

Oscillations of the trimer

$$\left.\begin{aligned} M\ddot{u}_1 &= k(u_2 - u_1), \\ M\ddot{u}_2 &= k(u_1 - 2u_2 + u_3), \\ M\ddot{u}_3 &= k(u_2 - u_3). \end{aligned}\right\} \quad \text{Equations of motion} \tag{1.27}$$

To solve these coupled equations, we look for the *normal modes* of the system, the solutions where all the degrees of freedom (u_1, u_2 and u_3) have the same, harmonic, time dependence. Using the convenient exponential notation, this means we look for solutions of the form

$$u_n = A_n e^{-i\omega t}, \qquad (n = 1 \text{ to } 3) \tag{1.28}$$

where the common frequency ω and the (complex) amplitudes A_n are still to be determined. Inserting these solutions in (1.27), we find the linear system of equations

$$\left.\begin{aligned} -M\omega^2 A_1 &= k(A_2 - A_1), \\ -M\omega^2 A_2 &= k(A_1 - 2A_2 + A_3), \\ -M\omega^2 A_3 &= k(A_2 - A_3), \end{aligned}\right\} \tag{1.29}$$

where we have cancelled out the common time dependence. Defining the frequency $\omega_0 = (k/M)^{1/2}$, the system of equations (1.29) can be written as an *eigenvalue-eigenvector equation*,

$$\left(\frac{\omega}{\omega_0}\right)^2 \begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix} = \begin{bmatrix} 1 & -1 & 0 \\ -1 & 2 & -1 \\ 0 & -1 & 1 \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix}. \tag{1.30}$$

Search for oscillations
→ System of linear eqs

The eigenvalues are the three values of ω/ω_0 that yield non-trivial solutions to this equation, and the eigenvectors the set of amplitudes (A_1, A_2, A_3) that correspond to each eigenvalue; we refer the reader unfamiliar with this approach to a text on linear algebra, or a book on mathematical physics, such as that of Arfken [3] or Morse and Feshbach [4].

With $z = (\omega/\omega_0)^2$, we subtract the term on the left from both sides, leaving the equation

$$\begin{bmatrix} 1-z & -1 & 0 \\ -1 & 2-z & -1 \\ 0 & -1 & 1-z \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix} = 0. \tag{1.31}$$

This has a non-trivial solution only if the determinant of the matrix is zero:

$$\det \begin{vmatrix} 1-z & -1 & 0 \\ -1 & 2-z & -1 \\ 0 & -1 & 1-z \end{vmatrix} = -z^3 + 4z^2 - 3z = 0. \tag{1.32}$$

This is known as the *characteristic equation*. The solutions to this cubic equation are the set $z = (\omega/\omega_0)^2 = 0$, 1 and 3.

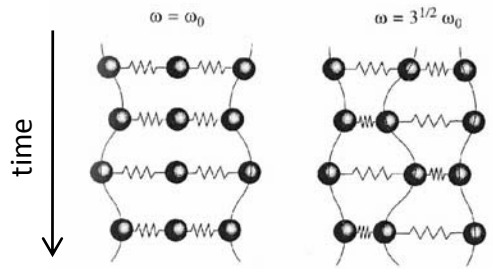
Let us deal first with the non-zero solutions. If we take the solution $z = 1$, i.e. $\omega = \omega_0$, the corresponding eigenvector (A_1, A_2, A_2) is obtained from (1.31). We find that the amplitudes must satisfy $A_1 = -A_3$ and $A_2 = 0$. The overall amplitude of the eigenvector is arbitrary; the eigenvector equation (1.31) only tells us the *relative* amplitudes of motion for the three atoms. It is convenient to make the length of the eigenvector (A_1, A_2, A_3) equal to unity, that is, to *normalize* the solution, so we find the solution pair

$$\omega = \omega_0 \leftrightarrow \begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix} = \begin{bmatrix} 1/\sqrt{2} \\ 0 \\ -1/\sqrt{2} \end{bmatrix}. \quad \text{First normal mode} \tag{1.33}$$

The second non-zero frequency is $z = 3$ or $\omega = \sqrt{3}\omega_0$; we find the corresponding eigenvector must satisfy $A_2 = -2A_1 = -2A_3$, so the normalized solution is

$$\omega = \sqrt{3}\omega_0 \leftrightarrow \begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix} = \begin{bmatrix} -1/\sqrt{6} \\ 2/\sqrt{6} \\ -1/\sqrt{6} \end{bmatrix}. \quad \text{Second normal mode} \tag{1.34}$$

The final frequency is $\omega = 0$. Inserting this solution in (1.31), we find the corresponding eigenvector $(A_1, A_2, A_3) = (1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3})$. This last solution, with equal values for all the displacement amplitudes A_n, is actually somewhat special: The zero frequency solution corresponds to an overall motion of the center of mass, where the actual time dependence is not an exponential $e^{-i\omega t}$, but instead has the form $u_n = at + b$, corresponding to the uniform translation of the chain at constant velocity. This can be seen by inserting this solution into the original system of equations (1.27); however, it violates our condition on the center of mass, (1.25), unless the velocity a is zero. We therefore ignore this now trivial solution; we have, after all, found



Normal modes as a basis set (eigenfunctions) for describing the oscillatory dynamics

Fig. 1.7. The two normal modes for the three atom chain. The time axis runs vertically; note that if the time axis were proportional, the oscillations for the higher frequency mode on the right would be three times faster than for that on the left. The relative amplitudes and phase of motion for the three atoms are however correct.

two independent solutions to a system with two independent degrees of freedom, the third degree of freedom having been removed by our condition on the center of mass motion.

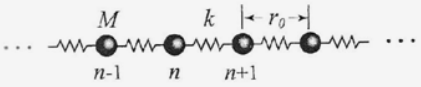
We note that if we had used the center of mass equation to eliminate one degree of freedom, say u_2, in terms of the other two, and then written the corresponding Hamiltonian and two equations of motion, we would have obtained the same two (nontrivial) eigenfrequencies and eigenvectors found above.

In Fig. 1.7 we illustrate the two normal modes, (1.33) and (1.34).

Linear atom chain (1D)

1.3 An N-mer Molecule: The N Atom Linear Chain

We now turn to an N-atom one-dimensional chain, where the atoms are connected by linear springs k with equilibrium spacing r_0; the atoms all have mass M (see Fig. 1.8). The nth atom will have relative displacement u_n from its equilibrium point, so the potential energy in the spring connecting it to its $(n+1)$th neighbor is $\phi = k(u_n - u_{n+1})^2/2$. Motion is restricted, as before, to along the line of atoms.



Linear atom chain

Fig. 1.8. Model for the N atom chain, with masses M connected by springs k. Equilibrium spacing is r_0.

If we apply a force f_{ext} to the ends of the chain, we find the usual result that each atom displaces by an amount

$$u_n = f_{\text{ext}}/k. \tag{1.35}$$

The strain is therefore again uniform, with value $\epsilon = f_{\text{ext}}/kr_0$.

We now look at the dynamic behavior of the chain, and try to find the normal mode solutions. The potential energy U of the whole chain of N atoms, summing over atoms n, is give

$$U = \frac{1}{2}\sum_{n=1}^{N-1} k(u_{n+1} - u_n)^2,$$

First neighbour harmonic interaction assumed

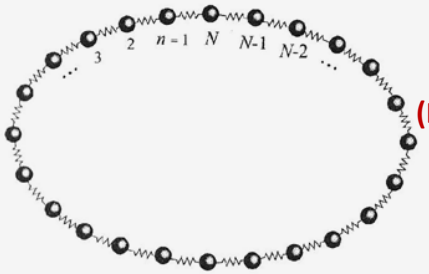
and the total kinetic energy T, in terms of the momenta $p_n = M\dot{u}_n$, by the sum

$$T = \frac{1}{2M}\sum_{n=1}^{N} p_n^2. \tag{1.37}$$

Hamilton's equations of motion are given by

$$\left.\begin{aligned} M\ddot{u}_1 &= k(u_2 - u_1), \\ M\ddot{u}_n &= k(u_{n+1} - 2u_n + u_{n-1}) \quad (n = 2 \text{ to } N-1), \\ M\ddot{u}_N &= k(u_{N-1} - u_N). \end{aligned}\right\} \tag{1.38}$$

We notice from (1.38) that the atoms $n = 1$ and $n = N$ need special treatment, as they only have one neighboring atom. This presents an annoying aspect of the problem, and dealing with it subtracts somewhat from the message we are trying to convey. We therefore take this problem and transform it somewhat: We connect the atom $n = 1$ to the atom $n = N$ by a spring k, so that effectively the chain of atoms is now a ring, shown in Fig. 1.9. Performing this sleight of hand is known as applying *periodic boundary conditions*.



Periodic boundary conditions (Born-Von Karman) assumed to simplify the mathematics

Fig. 1.9. Ring of N atoms, with atom 1 connected to atom N.

Our new equations of motion, with this modification, are

$$\left.\begin{aligned} M\ddot{u}_1 &= k(u_2 - 2u_1 + u_N), \\ M\ddot{u}_n &= k(u_{n+1} - 2u_n + u_{n-1}) \quad (n = 2 \text{ to } N-1), \\ M\ddot{u}_N &= k(u_{N-1} - 2u_N + u_1). \end{aligned}\right\} \tag{1.39}$$

The eigenmodes of the chain are those where all the atoms move at the same frequency,

$$u_n = \frac{A_n}{\sqrt{N}} e^{-i\omega t}, \tag{1.40}$$

where A_n is the amplitude associated with the nth atom, and has units of length; the factor $1/\sqrt{N}$ will prove convenient later.

Inserting this in the system of equations (1.38), we find the eigenvector-eigenvalue equation

Symmetry in the chain

Assuming first neighbour interaction and Born-von Karman, we define a *periodic potential* , with a periodicity given by the average (equilibrium) interatomic spacing (called **R** here)

In the (simple) 1D linear chain, the Bravais lattice is produced out of the **R** vector representing the interactomi average (equlibrium) distance: we'll see later the extension to more realistic situations

0.2 Teorema di Bloch

Gli autostati ψ di un hamiltoniano monoelettronico o, più in generale, di un sistema con data periodicità

$$\mathcal{H}\psi = \left[-\frac{\hbar^2}{2\,m}\nabla^2 + U(\mathbf{r})\right]\psi = \epsilon\,\psi$$

dove

$$U(\mathbf{r}+\mathbf{R}) = U(\mathbf{r})$$

per tutti gli $\mathbf{R}$ nel reticolo di Bravais possono essere descritti da un'onda piana (che rappresenta la soluzione in assenza di potenziale) moltiplicata per una funzione con la stessa periodicità del reticolo di Bravais:

Plane wave

$$\boxed{\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\bullet\mathbf{r}}\,u_{n\mathbf{k}}(\mathbf{r})}$$

Envelope function (periodic)

con $u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$ per tutti gli $\mathbf{R}$ del reticolo di Bravais.

La combinazione delle due equazioni precedenti porta come conseguenza che

$$\psi_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = e^{i\mathbf{k}\bullet\mathbf{R}}\,\psi_{n\mathbf{k}}(\mathbf{r})$$

la presenza dell'indice n indica che per ogni valore di $\mathbf{k}$ esiste un numero grande di soluzioni.

http://edu.sm.chim.unifi.it/gc/CFST-PDF/bloch1.pdf

Demonstration of the Bloch theorem

Definiamo un operatore di traslazione $\mathbf{T_R}$, per ogni vettore del reticolo di Bravais, che agisce su una funzione $f(\mathbf{r})$ traslandone l'argomento di $\mathbf{R}$

$$\mathbf{T_R}\, f(\mathbf{r}) = f(\mathbf{r}+\mathbf{R})$$

Esaminiamo le proprietà dell'operatore traslazione

1. $\mathbf{T_R}$ commuta con l'hamiltoniano: $\mathbf{T_R}\mathcal{H} = \mathcal{H}\mathbf{T_R}$

$$\mathbf{T_R}(\mathcal{H}\,\psi) = \mathcal{H}(\mathbf{r}+\mathbf{R})\,\psi(\mathbf{r}+\mathbf{R})$$

poichè l'hamiltoniano è periodico

$$= \mathcal{H}(\mathbf{r})\,\psi(\mathbf{r}+\mathbf{R}) = \mathcal{H}(\mathbf{r})\,\mathbf{T_R}\,\psi(\mathbf{r})$$

2. $\mathbf{T_R}$ è additivo

$$\begin{aligned} \mathbf{T_R}\,\mathbf{T_{R'}}\,\psi(\mathbf{r}) &= \mathbf{T_R}\,\psi(\mathbf{r}+\mathbf{R'}) = \psi(\mathbf{r}+\mathbf{R'}+\mathbf{R}) && (1)\\ &= \mathbf{T_{R+R'}}\,\psi(\mathbf{r}) && (2)\\ &= \mathbf{T_{R'}}\,\psi(\mathbf{r}+\mathbf{R}) && (3)\\ &= \mathbf{T_{R'}}\mathbf{T_R}\,\psi(\mathbf{r}) && (4) \end{aligned}$$

e quindi

$$\mathbf{T_R}\mathbf{T_{R'}} = \mathbf{T_{R'}}\mathbf{T_R} = \mathbf{T_{R+R'}}$$

3. $\mathbf{T_R}$ commuta con l'hamiltoniano per qualsiasi vettore di Bravais, quindi gli autostati dell'hamiltoniano possono essere scelti in modo tale da essere contemporaneamente autostati di tutti i $\mathbf{T_R}$

$$\begin{aligned} \mathcal{H}\,\psi &= \varepsilon\,\psi && (5)\\ \mathbf{T_R}\psi &= c(\mathbf{R})\psi && (6) \end{aligned}$$

4. dalle proprietà di $\mathbf{T_R}$ si ha

$$\begin{aligned} \mathbf{T_{R'}}\mathbf{T_R}\,\psi &= c(\mathbf{R})\mathbf{T_{R'}}\psi = c(\mathbf{R})c(\mathbf{R'})\psi && (7)\\ \mathbf{T_{R'}}\mathbf{T_R}\,\psi &= \mathbf{T_{R+R'}}\psi = c(\mathbf{R}+\mathbf{R'})\psi && (8) \end{aligned}$$

e quindi

$$c(\mathbf{R})c(\mathbf{R'}) = c(\mathbf{R}+\mathbf{R'})$$

Questo suggerisce che c sia scritto in forma esponenziale

5. consideriamo la norma delle funzioni ψ e $\mathbf{T_R}\psi$

$$\left|\int \psi(\mathbf{r}+\mathbf{R})d\mathbf{r}\right|^2 = \left|\int c(\mathbf{R})\,\psi(\mathbf{r})d\mathbf{r}\right|^2 = |c(\mathbf{R})|^2\left|\int \psi(\mathbf{r})d\mathbf{r}\right|^2$$

poichè le due funzioni $\psi(\mathbf{r}+\mathbf{R})$ e $\psi(\mathbf{r})$ differiscono solo per il cambio di origine si deve avere che le due norme sono uguali e quindi la norma di $c(\mathbf{R})$ è 1. Questo suggerisce che

$$c(\mathbf{R}) = e^{-2\pi i x} = e^{2\pi i x}$$

dove x deve essere scelto in modo opportuno

6. consideriamo un versore del reticolo di Bravais δ_i, possiamo scrivere

$$c(\delta_i) = e^{-2\pi i x_i}$$

In genere un vettore del reticolo di Bravais può essere scritto

$$\mathbf{R} = n_1\delta_1 + n_2\delta_2 + n_3\delta_3$$

per cui

$$c(\mathbf{R}) = c(\delta_1)^{n_1}\,c(\delta_2)^{n_2}\,c(\delta_3)^{n_3}$$

ossia

$$c(\mathbf{R}) = e^{-2\pi i(n_1x_1+n_2x_2+n_3x_3)} = e^{-2\pi i\mathbf{k}\cdot\mathbf{R}}$$

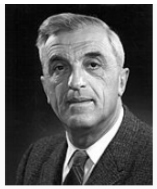
dove

$$\mathbf{k} = x_1\delta_1 + x_2\delta_2 + x_3\delta_3$$

e i δ_i sono i vettori di base del reticolo reciproco. Pertanto abbiamo

$$\mathbf{T_R}\psi(\mathbf{r}) = \psi(\mathbf{r}+\mathbf{R}) = c(\mathbf{R})\psi = e^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r})$$

C.V.D



Felix Bloch (1905-1983)

Born	October 23, 1905 Zürich, Switzerland
Died	September 10, 1983 (aged 77) Zürich, Switzerland
Nationality	Swiss
Fields	Physics
Institutions	Stanford University
Alma mater	ETH Zürich and University of Leipzig
Doctoral advisor	Werner Heisenberg
Known for	NMR Bloch wall Bloch's Theorem
Notable awards	Nobel Prize for Physics (1952)

Bloch theorem provides a straigthforward way to point out the consequences of periodicity, which is one of the most striking aspect of solid state (especially, crystal lattices)

Linear chain II

$$\left(\frac{\omega}{\omega_0}\right)^2 \begin{bmatrix} A_1 \\ A_2 \\ A_3 \\ A_4 \\ \vdots \end{bmatrix} = \begin{bmatrix} 2 & -1 & 0 & 0 & \dots \\ -1 & 2 & -1 & 0 & \dots \\ 0 & -1 & 2 & -1 & \dots \\ 0 & 0 & -1 & 2 & \dots \\ \vdots & \vdots & \vdots & & \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ A_3 \\ A_4 \\ \vdots \end{bmatrix}. \qquad (1.41)$$

Using the assumption of normal modes has transformed the coupled differential system of equations (1.38) into an N-dimensional linear system (1.41). This is a rather horrendous system to solve. We can however use the fact that the chain of atoms is extremely regular, with each atom equivalent to its neighbors (this holds for the atoms 1 and N as well, due to our joining them together). This *translational symmetry* allows us to apply a version of a theorem known as *Bloch's theorem*, about which we will say more later. This theorem says that we can look for normal modes that have the form

$$u_n = \frac{A}{\sqrt{N}} e^{iqr_n} e^{-i\omega t}, \qquad (1.42)$$

Bloch's wave (+ oscillation)

where A is the overall amplitude (with dimensions of distance) and r_n the equilibrium position of the nth atom, $r_n = nr_0$. The spatial dependence of the mode, that is, the dependence on the index n, is sinusoidal, with *wavevector* q, or wavelength $\lambda = 2\pi/q$. This is equivalent to saying that the amplitudes A_n in the normal modes (1.40) depend on the index n through $A_n = Ae^{iqr_n}$. As we shall see, the equations of motion will force a relationship between the frequency ω and the wavevector q, although the amplitude A is arbitrary, as it is for the three-atom chain.

Inserting the form (1.42) into the equations of motion (1.39), we find a set of three equations,

$$\left.\begin{aligned} -\omega^2 &= \omega_0^2 \left(e^{iqr_0} + e^{i(N-1)qr_0} - 2\right), \\ -\omega^2 &= \omega_0^2 \left(2\cos qr_0 - 2\right) \\ -\omega^2 &= \omega_0^2 \left(e^{-iqr_0} + e^{-i(N-1)qr_0} - 2\right). \end{aligned}\right\} \qquad (1.43)$$

This set of three equations for the two unknowns ω and q appears to overdetermine the problem. However, the third equation is simply the complex conjugate of the first, and as the frequency ω is real (not complex), it merely emphasizes that the right side of these equations must also be real. Hence we find that q must be given by

$$q = \frac{2\pi}{r_0}\frac{m}{N},$$

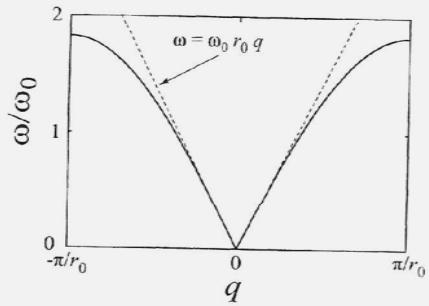
Quantization of the wavevector
$q_m = m\,(2\pi/r_0)/N$

for integer values m; we will write these discrete values as q_m. With this condition, the first and third equations are the same as the middle equation, which gives us the relation between ω_m and q_m:

$$\frac{\omega_m}{\omega_0} = \sqrt{2 - 2\cos q_m r_0}$$

Periodicity in space implies periodicity in q

Wavevector and oscillation frequency are related through the *dispersion law*



Acoustic modes

Fig. 1.10. The eigenfrequency solution $\omega(q)$ of the simple linear chain. The dotted line shows the linear solution at small wavevector q Note that the values of q are actually discrete, but for a large number N of atoms, the spacing is very fine, and the discreteness can be ignored.

In Fig. 1.10 we display this solution, along with the linear approximation that applies for small values of the wavevector q. We have only plotted the solution for $-\pi/r_0 < q < \pi/r_0$, and we have ignored the discreteness in the values of q specified by (1.44)

Normal modes of oscillation follow specific rules and acquire a *collective* character

Linear chain III

The values of q are discrete, given by the set q_m, because they relate to the motion of a finite number of atoms; there cannot be more than N values of q. The spacing of the values of q is set by (1.44), but this equation does not limit the range of q. However, if we examine the Bloch form (1.42), we see that values of q larger than π/r_0, and smaller than $-\pi/r_0$, do not represent physically different displacements. If we take q larger than π/r_0, the displacements u_n are the same as if we take $q' = q - 2\pi/r_0$:

$$\begin{aligned} u_n &= \frac{A}{\sqrt{N}} e^{iqnr_0} e^{-i\omega t} \\ &= \frac{A}{\sqrt{N}} e^{iq'nr_0 + i2\pi n} e^{-i\omega t} \\ &= \frac{A}{\sqrt{N}} e^{iq'nr_0} e^{-i\omega t}. \end{aligned} \tag{1.46}$$

Eigenfunctions

A similar argument applies if $q < -\pi/r_0$, where we would take $q' = q + 2\pi/r_0$. It is therefore not physically meaningful to take q outside the range $-\pi/r_0 < q < \pi/r_0$. From the relation (1.44), we therefore see that the index m can range from $-N/2$ to $N/2$, yielding N distinct values for q, as desired.

The solutions (1.42) are written using complex notation; the actual displacements are of course real, and are obtained by taking the real part of (1.42).

The most general form for the displacement for the nth atom, in other words for motion that is not restricted to a single normal mode, is built by superposing all the normal modes with arbitrary amplitude and relative phase,

$$u_n = \frac{1}{\sqrt{N}} \sum_{m=-N/2}^{N/2} |A_m| \cos(q_m r_n - \omega_m t + \varphi_m). \tag{1.47}$$

General solution for the collective displacement

There is a physical difference between positive and negative values of q (or m). For $q > 0$, the solution (1.47) is a travelling wave moving towards larger n, counterclockwise in Fig. 1.9; the *phase* of the cosine remains constant if, as time t increases, n increases as well. For $q < 0$, the wave travels towards smaller n, or clockwise, in the periodic chain. Our solutions therefore include waves travelling in both directions around the periodic chain. This result is not obtained for the original problem, with the end atoms not connected to one another: In that case, one finds *standing waves*, as we discuss in Sect. 1.3.3.

1.3.1 Normal Mode Coordinates

In the previous section, we determined the relation between the normal mode frequencies and wavevectors. In that section, the relative displacements u_n of each atom provided the coordinates in which the system's motion was described. Another way to look at this system is to treat the amplitude of each normal mode as a coordinate of the system, leaving the amplitudes as time-dependent variables. The idea is to write (1.42) in the form

$$\begin{aligned} u_n(t) &= \frac{1}{\sqrt{N}} \sum_{m=-N/2}^{N/2} \mathcal{U}_m(t) e^{iq_m r_n} \\ &= \frac{1}{\sqrt{N}} \sum_{m=-N/2}^{N/2} \mathcal{U}_m(t) e^{2\pi i mn/N}, \end{aligned} \tag{1.48}$$

where the amplitudes $\mathcal{U}_m$ are time-dependent. We can invert (1.48) to find an expression for the mode amplitudes $\mathcal{U}_m$ in terms of the atom displacements u_n:

$$\mathcal{U}_m(t) = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} u_n(t) e^{-2\pi i mn/N}. \tag{1.49}$$

The proof that this relation is equivalent to (1.48) is left to the exercises (see Exercise 1.11).

The momentum associated with each atom is $p_n = M\dot{u}_n$; we can define a momentum $\mathcal{P}_m$ associated with the normal mode amplitudes $\mathcal{U}_m$ using the definition of the *canonical momentum*,

$$\mathcal{P}_m = \frac{\partial \mathcal{L}}{\partial \dot{\mathcal{U}}_m} = \frac{\partial T}{\partial \dot{\mathcal{U}}_m}, \tag{1.50}$$

Crystal momentum

Normal modes of oscillations in the lattice can be regarded as *collective* excitation of the crystal, with proper energy, momentum, etc.

They move at a phase velocity experimentally corresponding to the *speed of sound* in the solid

Further variants I

1.3.3 Fixed Boundary Conditions

We have treated the problem of the N atom chain using periodic boundary conditions. It is perhaps more appealing to see how this problem is treated using more "realistic" boundary conditions; we will therefore briefly treat the problem of fixed boundary conditions, where we connect atoms 1 and N by springs to fixed, rigid supports, shown in Fig. 1.13.

Fixed boundary conditions

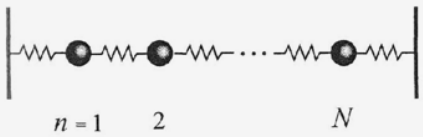


Fig. 1.13. Fixed boundary conditions for a chain with N atoms.

The equations of motion for this system are

$$\left.\begin{aligned} M\ddot{u}_1 &= k(u_2 - 2u_1), \\ M\ddot{u}_n &= k(u_{n+1} - 2u_n + u_{n-1}) \quad (n = 2 \text{ to } N-1), \\ M\ddot{u}_N &= k(u_{N-1} - 2u_N). \end{aligned}\right\} \tag{1.62}$$

The solutions to this system of equations are not travelling waves but standing waves, made up of equal amplitudes of the right- and left-going waves found for periodic boundary conditions. These have the form

$$u_n = \frac{A}{\sqrt{N}} \sin qr_0 n \, e^{i\omega t}. \tag{1.63}$$

Inserting this in (1.62), we find after some trigonometric manipulations the pair of equations

$$\left.\begin{aligned} \omega^2 &= 4\omega_0^2 \sin^2 qr_0/2, \\ \tan Nqr_0 &= -\tan qr_0 . \end{aligned}\right\} \tag{1.64}$$

$$q = m\frac{2\pi}{(N+1)r_0} \qquad (1 \le m \le N)$$

Assuming fixed boundary conditions:

- Quantization is still recovered, i.e., the quantum character does not depend on artificial boundary conditions;
- Standing waves are found instead of travelling waves (reflection at the borders…)
- The obtained dispersion relation is slightly different

Further variants II

1.4 Linear Chain with Optical Modes

The last one-dimensional problem we will discuss is what happens if we add a second set of atoms of mass M' to the one dimensional chain, alternating these with the original atoms of mass M; as we shall see, this generates a new set, or *branch*, of frequencies, which are known as *optical modes* to distinguish them from the *acoustic modes* discussed so far.

The masses are linked by identical linear springs k, and the masses have equilibrium spacing r_0, as sketched in Fig. 1.18. We number the masses in pairs, so that the nth atom with mass M has displacement u_n, while nth atom with mass M' has displacement v_n. The equations of motion can be shown to be

$$\left.\begin{aligned} M\ddot{u}_n &= k(v_{n+1} - 2u_n + v_{n-1}), \\ M'\ddot{v}_n &= k(u_{n+1} - 2v_n + u_{n-1}). \end{aligned}\right\} \qquad (1.74)$$

We will take periodic boundary conditions, so the $n = 1$ atom of mass M is coupled to the $n = N$ atom of mass M'; this is not reflected in (1.74), but we will enforce this at the end of the calculation, when we determine the set of allowed values of the wavevector.

More than one species is present in the chain

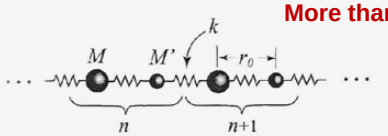


Fig. 1.18. Model for a linear chain with alternating atoms of mass M and M'. The index n counts pairs of atoms.

The displacements are written in Bloch form,

$$\left.\begin{aligned} u_n(t) &= \frac{A}{\sqrt{N}}\, e^{iqn2r_0 - i\omega t} \\ v_n(t) &= \frac{B}{\sqrt{N}}\, e^{iqn2r_0 - i\omega t}, \end{aligned}\right\} \qquad (1.75)$$

where the amplitudes A and B can be complex. We define two frequencies ω_0 and ω_0',

$$\left.\begin{aligned} \omega_0 &= \sqrt{k/M} \\ \omega_0' &= \sqrt{k/M'}, \end{aligned}\right\} \qquad (1.76)$$

and using these and the forms (1.75), the equations of motion become

$$\left.\begin{aligned} \omega^2 A &= 2\omega_0^2 A - 2\omega_0^2 \cos(2qr_0)\, B \\ \omega^2 B &= -2\omega_0'^2 \cos(2qr_0)\, A + 2\omega_0'^2 B. \end{aligned}\right\} \qquad (1.77)$$

This is a 2×2 eigenvalue-eigenvector equation, where the values of ω are the eigenvalues and the amplitude pairs (A, B) the eigenvectors. Written in matrix form, the equation is

$$\begin{bmatrix} 2\omega_0^2 - \omega^2 & -2\omega_0^2 \cos(2qr_0) \\ -2\omega_0'^2 \cos(2qr_0) & 2\omega_0'^2 - \omega^2 \end{bmatrix} \begin{bmatrix} A \\ B \end{bmatrix} = 0. \qquad (1.78)$$

The characteristic equation, obtained by setting the determinant of the matrix of coefficients to zero, is given by

$$\omega^4 - 2(\omega_0^2 + \omega_0'^2)\omega^2 + 4\omega_0^2\omega_0'^2 \sin^2 2qr_0 = 0. \qquad (1.79)$$

The two eigenfrequencies for each value of wavevector q are thus given by

$$\omega_\pm^2(q) = \omega_0^2 + \omega_0'^2 \pm \sqrt{\omega_0^4 + \omega_0'^4 + 2\omega_0^2\omega_0'^2 \cos 4qr_0}. \qquad (1.80)$$

There are two solutions, ω_+ and ω_-, for each value of the wavevector q. These two solutions are shown in Fig. 1.19, as a function of q, for a frequency ratio $\omega_0'/\omega_0 = 1.3$ (corresponding to a mass ratio $M/M' = 1.3^2 = 1.69$). The lower set of solutions, $\omega_-(q)$, looks very similar to that for the single mass chain, but the upper set, $\omega_+(q)$, is rather different. For small wavevectors q, $\omega_-(q)$ increases linearly with q, while $\omega_+(q)$ is constant, and then falls gradually. The two frequencies approach one another at the limits of the plot, as $q \to \pm\pi/4r_0$. There is a band of frequencies between the maximum value of ω_- and the minimum of ω_+ for which there are no solutions; this gap in the frequency spectrum is characteristic of this type of problem, and is known as a *bandgap*.

The range of q in Fig. 1.19 is $-\pi/4r_0 < q < \pi/4r_0$. We have not yet determined the spacing of the values of q; this is set by the periodic boundary conditions, where we have u_1 connected to v_N. The equations for these two atoms are

$$\left.\begin{aligned} -\omega^2 u_1 &= \omega_0^2(v_1 - 2u_1 + v_N) \\ -\omega^2 v_N &= \omega_0'^2(u_1 - 2v_N + u_N). \end{aligned}\right\} \qquad (1.81)$$

Substituting the forms (1.75) in this pair of equations ultimately yields the condition

$$\boxed{q_m = \frac{\pi}{2(N-1)r_0}\, m,} \qquad (1.82)$$

Quantization condition

for integer values m. There are thus N values of q (counting $q = 0$), and as there are two frequencies ω_- and ω_+ for each value of q, we find $2N$ independent values, equal to the number of degrees of freedom.

The two distinct frequencies, and the spectral gap in their dispersion relation, is characteristic of the perturbation in the periodicity of the linear chain, here from the variation in atomic mass. An equivalent result appears if the spring constant alternates between two values, k and k', even if the masses are identical (see Exercise 1.15). The lower set of frequencies $\omega_-(q)$ is known as the *acoustic* band, while the upper set $\omega_+(q)$ is known as the *optical band*. For all the normal modes in the acoustic band, the two atoms in the unit cell move in the same direction, so that the displacements u_n and v_n have the same sign. For a normal mode in the optical band, by contrast, the two atoms move in opposite directions, so u_n and v_n have opposite signs. If the charge on the atoms is different, as for example in an ionic system where neighboring atoms have opposite charge, or in a chain where the bonding electrons are closer to one atom than its neighbor, the optical band motion will couple to the electric field in an electromagnetic wave, through the induced dipole moment. The upper frequency band is therefore optically active; this is the origin of the terminology.

“Optical” branches

Modi normali in un reticolo con base

$$y_1(na) = na + u_1(na)$$

$$y_2(na) = na + d + u_2(na)$$

K: costante elastica 1-2
G: costante elastica 2-1

$$m\frac{d^2u_1(na)}{dt^2} = -K[u_1(na) - u_2(na)] - G[u_1(na) - u_2([n-1]a)]$$

$$m\frac{d^2u_2(na)}{dt^2} = -K[u_2(na) - u_1(na)] - G[u_2(na) - u_1([n+1]a)]$$

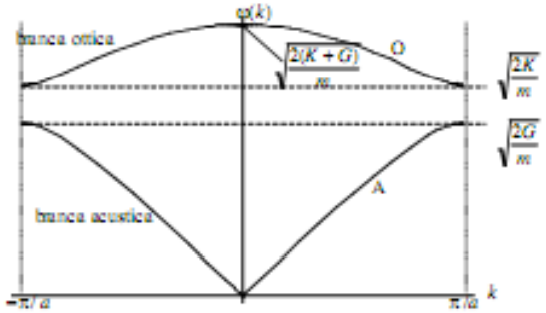
$$u_1(na) = \varepsilon_1 e^{i(kna-\omega t)}$$

$$u_2(na) = \varepsilon_2 e^{i(kna-\omega t)}$$

$$\begin{cases} [m\omega^2 - (K+G)]\varepsilon_1 + (K + Ge^{-ika})\varepsilon_2 = 0 \\ (K + Ge^{ika})\varepsilon_1 + [m\omega^2 - (K+G)]\varepsilon_2 = 0 \end{cases}$$

$$\omega = \frac{K+G}{m} \pm \frac{1}{m}\sqrt{K^2 + G^2 + 2KG\cos(ka)}$$

$$\frac{\varepsilon_2}{\varepsilon_1} = \mp\frac{K + Ge^{ika}}{|K + Ge^{ika}|}$$



A. Carnera - 2005

Acoustic and optical phonons [edit]

In solids with more than one type of atom (with either different masses or bonding strengths) in the smallest unit cell, there are two types of phonons: acoustic phonons and optical phonons. Acoustic phonons, which are the phonons described above, have frequencies that become small at the long wavelengths, and correspond to sound waves in the lattice. Longitudinal and transverse acoustic phonons are often abbreviated as LA and TA phonons, respectively.

Optical phonons, which also arise in crystals with more than one type of atom in the unit cell, always have some minimum frequency of vibration, even when their wavelength is large. They are called *optical* because in ionic crystals (like sodium chloride) they are excited very easily by infrared radiation. This is because they correspond to a mode of vibration where positive and negative ions at adjacent lattice sites swing against each other, creating a time-varying electrical dipole moment. Optical phonons that interact in this way with light are called *infrared active*. Optical phonons which are *Raman active* can also interact indirectly with light, through Raman scattering. Optical phonons are often abbreviated as LO and TO

http://www.padova.infm.it/carnera/Didattica/Struttura%202004-2005/Files%20pdf/Fononi05.pdf

When the unit cell consists of two different atoms (or sites), “optical phonons” appear
Optical means barely that an electric dipole can be associated to the oscillation

Phonons and collective excitations

→Creating and destroying phonons:

$$\hat{a}_s^\dagger(\mathbf{q})\left|n_s(\mathbf{q})\right\rangle = \sqrt{n_s(\mathbf{q})+1}\left|n_s(\mathbf{q})+1\right\rangle$$

$$\hat{a}_s(\mathbf{q})\left|n_s(\mathbf{q})\right\rangle = \sqrt{n_s(\mathbf{q})}\left|n_s(\mathbf{q})-1\right\rangle$$

→Arbitrary number of phonons can be excited in each mode → phonons are bosons:

$$\left|n_s(\mathbf{q})\right\rangle = \sqrt{\left(\prod_{\mathbf{q},s}\frac{1}{n_s(\mathbf{q})!}\right)}\prod_{\mathbf{q},s}\left[\hat{a}_s^\dagger(\mathbf{q})\right]^{n_s(\mathbf{q})}\left|0\right\rangle$$

Mathematics can be developed to define quantum operators formally similar to those adopted for the photon description of the radiation field:

- Phonon similar to photons
- They both are "bosons"

In contrast to quasiparticles, collective excitations are bosons, and they bear no resemblance to constituent particles of real system. They involve collective (i.e., coherent) motion of many physical particles.

- **Phonon:** Corresponds to coherent motion of all the atoms in a solid — quantized lattice vibrations with typical energy scale of $\hbar\omega = 0.1\ \mathrm{eV}$
- **Exciton:** Bound state of an electron and a hole with binding energy $e^2/\varepsilon a = 0.1\mathrm{eV}$
- **Plasmon:** Collective excitation of an entire electron gas relative to the lattice of ions; its existence is a manifestation of the long-range nature of the Coulomb interaction. The energy scale of plasmons is $\hbar\sqrt{ne^2/m_e} \sim 5-20\mathrm{eV}$
- **Magnon:** Collective excitation of the spin degrees of freedom on the crystalline lattice. It corresponds to a spin wave, with an energy scale of $\hbar\omega \sim 0.001-0.1\mathrm{eV}$

http://www.physics.udel.edu/~bnikolic/teaching/phys624/phys624.html

Quantum character of phonons

To recapitulate:

- Lattice vibrations, in the harmonic approximation, described as normal modes of the crystal;
- Each normal mode has the same Hamiltonian as a harmonic oscillator;
- The energy in each normal mode k is $(n_k + \frac{1}{2})\hbar\omega_k$;

The collective excitation of the crystal lattice can be regarded as a sort of quasi-particle with quantum character

Energy quantization as for photons: $E = (n+1/2)h\nu$
(but the quantum energy is by far smaller)

We want now to demonstrate, in a striking manner, the quantum character of phonons

We will evaluate the internal energy of a lattice at temperature T associated with phonons

In general:

$$< E >= \sum_{\text{all freq}} (\text{quantum of energy}) \times (\text{average number of normal modes}) \times (\text{density of modes per energy})$$

Assuming continuous variables
(i.e., assuming very many, slightly spaced, energy levels):

$$< E >= \int_{\text{all freq}} h\nu \bar{n}_\nu g(\nu) d\nu$$

Density of states I

The density of states is a measure of how many states are allowed for a certain value of a quantity (typically, wavenumber, frequency, energy…)

We found for the linear chain (one dimensional problem):
Quantization of the wavevector $q_m = m\,(2\pi/r_0)/N$
Assuming continuous variables and considering that $L = r_0 N$ is the total size of the sample we have:

$$q = n\,2\pi/L$$

The allowed states are uniformly distributed in the reciprocal (q) space with spacing $2\pi/L$

4.4 Three dimensions – g(E)

Apply periodic boundary conditions along x, y and z. The number of states in the reciprocal space volume $\mathrm{d}k_x\mathrm{d}k_y\mathrm{d}k_z$ is then

$$\frac{L_x L_y L_z}{(2\pi)^3}\,\mathrm{d}k_x\mathrm{d}k_y\mathrm{d}k_z = \frac{V}{8\pi^3}\,\mathrm{d}k_x\mathrm{d}k_y\mathrm{d}k_z,$$

for crystal volume V. Now assume that the crystal is *isotropic* – ω depends only on magnitude of k, not its direction. Then

$$\mathrm{d}k_x\mathrm{d}k_y\mathrm{d}k_z = 4\pi k^2\mathrm{d}k$$

and the number of states with modulus of wavevector between k and $k + \mathrm{d}k$ is

$$g(k)\mathrm{d}k = \frac{V}{8\pi^3}\,4\pi k^2\mathrm{d}k = \frac{V}{2\pi^2}\,k^2\mathrm{d}k$$

Here we've accounted for all directions, so no extra factor of 2 as in one dimension when going to $g(\omega)$.

Density of states II

Density of states as a function of frequency

We want: $g(\nu)d\nu = g(k)dk \rightarrow g(\nu) = g(k)\, dk/d\nu$

<u>Note:</u> $(d\nu/dk)$ is the *group velocity* of the perturbation

Assuming a non-dispersive material, $(d\nu/dk) = 2\pi v_{sound}$, speed of sound

<u>Note:</u> speed of sound is typically depending on direction and on the mode (transversal or longitudinal)

1-Dimensional

Define the density of states in frequency: number of allowed states between ω and $\omega + \mathrm{d}\omega$ is $g(\omega)\,\mathrm{d}\omega$. This must be the same as the number in the region of k-space containing states in that frequency interval, so in $0 < k < \pi/a$

$$g(\omega)\,\mathrm{d}\omega = g(k)\,\mathrm{d}k,$$

or

$$g(\omega) = g(k)\frac{dk}{d\omega} = g(k)/\frac{d\omega}{dk}.$$

Allowing also for the states with negative k we get in one dimension

$$g(\omega) = 2\,\frac{L}{2\pi}\,\frac{dk}{d\omega}.$$

$$\frac{d\omega}{dk} = v_g,$$

the group velocity of the wave. *Non-dispersive system* v_g is constant, so

$$g(\omega) = \frac{L}{\pi v_g} = \text{constant}.$$

3-Dimensional

But we do have to include all the modes (acoustic, optic, longitudinal, transverse), each with its own dispersion relation, so

$$g(\omega) = \frac{V}{2\pi^2}\sum_s k(\omega_s)^2/\frac{\mathrm{d}\omega_s}{\mathrm{d}k},$$

where s denotes the mode. *Non-dispersive system* If we assume that

$$\omega_s(k) = v_s k,$$

i.e. the sound speed does not depend on frequency, we have

$$k(\omega_s) = \frac{\omega}{v_s},$$

and

$$\frac{\mathrm{d}k}{\mathrm{d}\omega_s} = \frac{1}{v_s},$$

so

$$g(\omega) = \frac{V}{2\pi^2}\sum_s \frac{\omega^2}{v_s^3}.$$

$$\boxed{g(\nu)d\nu = 4\pi V \sum_{\text{acoustic modes}} \frac{\nu^2}{v_{sound}^2}}$$

Normalization (Debye model)

In the linear chain, the total number of normal modes of oscillation was *N*
In the 3D case, we expect a maximum number *3N*

It must be: $$3N = \int_{\text{allowed frequencies}} g(\nu)\,d\nu$$

Integral limits:

$$0, \nu_D \text{ with: } \int_0^{\nu_D} g(\nu)\,d\nu = 3N$$

that is:

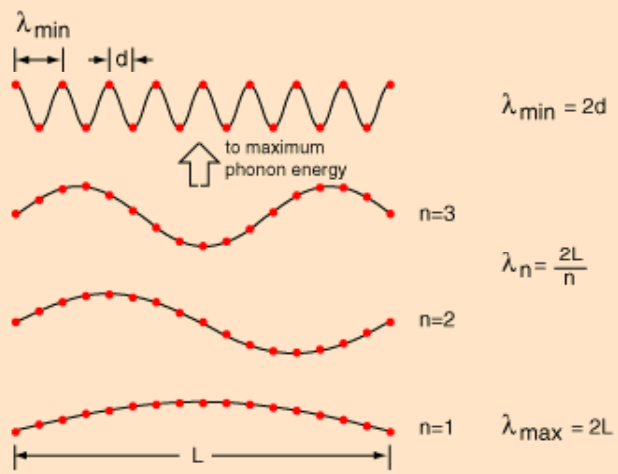
$$\nu_D = \sqrt[3]{\frac{9N v_{sound}^2}{4\pi V}} \quad \text{(assuming only one acoustic mode)}$$

A maximum allowed frequency is defined for phonons (not for photons!)

The Debye frequency depends on the material properties (density, speed of sound)
A Debye temperature can be defined as
$T_D = h\nu_D/k_B$

The occurrence of the maximum allowed frequency is in agreement with the presence of a minimum allowed wavelength for the acoustic vibrations

Considering a solid to be a periodic array of mass points, there are constraints on both the minimum and maximum wavelength associated with a vibrational mode.



Specific heat of the "phonon gas"

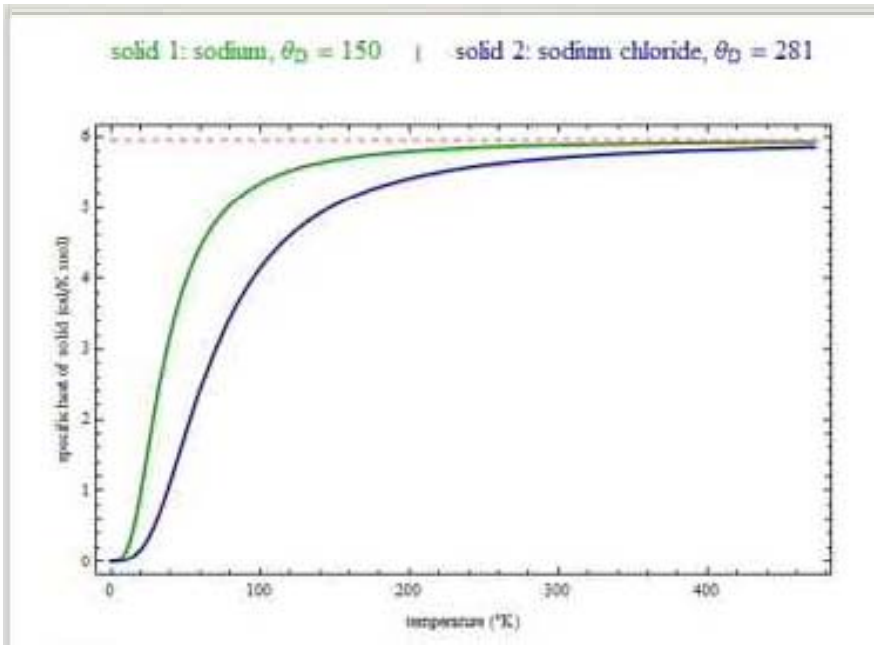
We have, thus: $$< E >= \int_{\text{all allowed freq}} h\nu\, \bar{n}_\nu g(\nu)d\nu \rightarrow \int_0^{\nu_D} h\nu \bar{n}_\nu g(\nu)d\nu$$

Since phonons are bosons, statistics is of the Bose-Einstein kind: $$\bar{n}_\nu = \frac{1}{e^{\frac{h\nu}{k_B T}} - 1}$$

By definition, the specific heat is: $$c = \frac{1}{N}\frac{\partial < E >}{\partial T} = \frac{1}{N}\frac{\partial}{\partial T}\int_0^{\nu_D} \frac{h\nu}{e^{\frac{h\nu}{k_B T}} - 1} g(\nu)d\nu$$

One gets:
For $T > T_D$: $c \rightarrow 3k_B$ (Dulong and Petit!)
For $T < T_D$: $c \rightarrow 0$ like T^3

The striking agreement with experimental data confirms the quantum character of phonons



Debye temperature/speed of sound

Speed of sound
(longitudinal perturbations)

Medium	Velocity (m/s)
Aluminum	4877
Brass	3475
Brick	4176
Concrete	3200 - 3600
Copper	3901
Cork	366 - 518
Diamond	12000
Glass	3962
Glass, Pyrex	5640
Gold	3240
Hardwood	3962
Iron	5130
Lead	1158
Lucite	2680
Rubber	40 - 150
Steel	6100
Water	1433
Wood (hard)	3960
Wood	3300 - 3600

Debye temperature

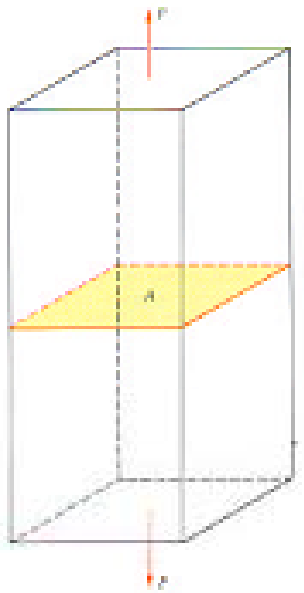
Aluminium	428 K
Cadmium	209 K
Chromium	630 K
Copper	343.5 K
Gold	165 K
Iron	470 K
Lead	105 K
Manganese	410 K
Nickel	450 K
Platinum	240 K

Silicon	645 K
Silver	215 K
Tantalum	240 K
Tin (white)	200 K
Titanium	420 K
Tungsten	400 K
Zinc	327 K
Carbon	2230 K
Ice	192 K

Debye temperature is associated with speed of sound, which is in turn associated with stiffness of the bonds and with macroscopic mechanical properties

Reminders of conventional (macro) mech prop

STRESS



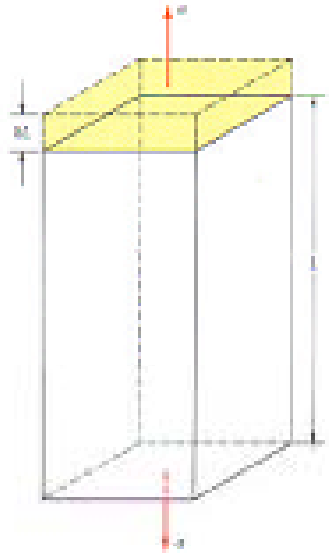
Lo sforzo (stress)

sforzo = la forza per unità di superficie della sezione trasversale passante per un punto particolare del materiale.

$\sigma = F/A$

STRAIN

La deformazione è la conseguenza di uno sforzo applicato a un materiale.



La deformazione è generalmente indicata col simbolo ε: se un'asta di lunghezza iniziale L viene allungata di un tratto δl, è soggetta alla deformazione

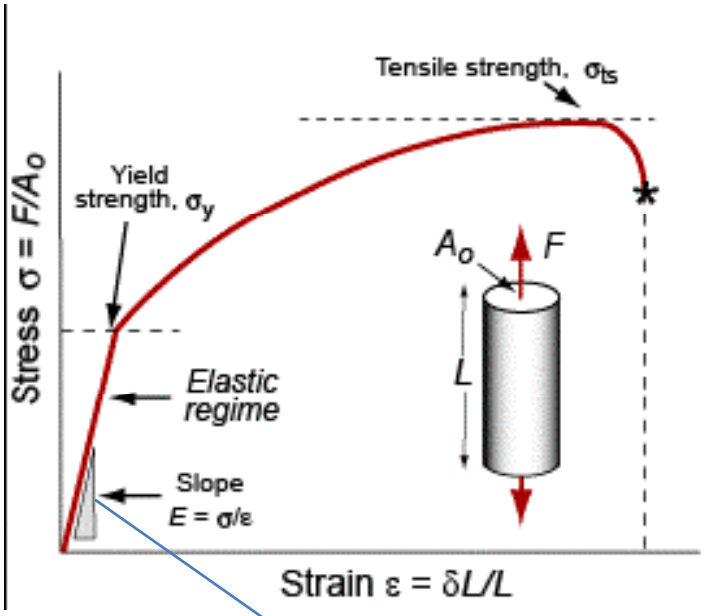
$\varepsilon = \delta l/L$

la deformazione è un rapporto fra due lunghezze, è una grandezza adimensionale.

Stress: applied perturbation
$\sigma = F/A$
(dimension: pressure)

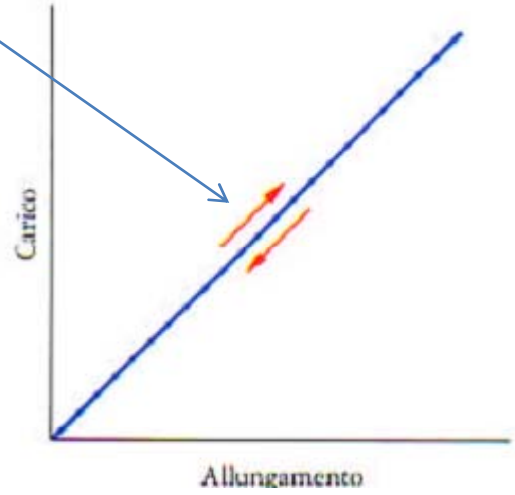
Strain :measured deformation
$\varepsilon = \delta L/L$
(adimensional)

Tensile strain vs stress measurements



Hooke (pure elastic):
strain proportional to stress

«ut tensio, sic vis »



$|F|=k|\Delta l|$

Young's modulus

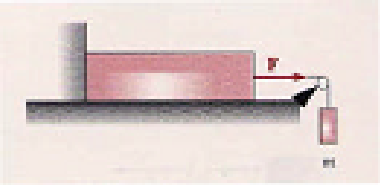
Young's modulus is a measurement of the elastic behavior (typically, upon 1D perturbation)

$$E = \frac{\sigma}{\varepsilon}$$

(dimension: pressure)

Elasticita' per trazione e compressione

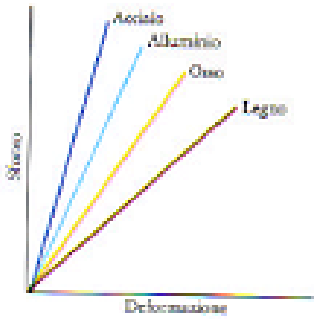
Un semplice dispositivo per studiare il comportamento in *trazione*



La legge di Hooke fornisce

$\sigma = E\varepsilon$

La quantita' E e' chiamata **modulo di Young**, del materiale e fornisce una misura della durezza del materiale. Maggiore e' il suo valore , maggiore e' la resistezza del materiale alla deformazione di tipo tensile.



Il modulo di Young (E) è dato dalla pendenza della prima parte della curva stress-deformazione e ha un valore caratteristico per ciascun materiale.

Substance	E, Young's modulus (Pa)	G, Shear modulus (Pa)	k, bulk's modulus (Pa)	Poisson's ratio
Aluminium	7.0×10^{10}	2.4×10^{10}	7.5×10^{10}	0.34
Cast bronze	8.1×10^{10}	3.4×10^{10}	9.6×10^{10}	0.18
Copper	12.3×10^{10}	4.5×10^{10}	13.1×10^{10}	0.34
Gold	8.0×10^{10}	2.8×10^{10}	16.6×10^{10}	0.42
Lead	1.6×10^{10}	0.54×10^{10}	5.0×10^{10}	0.45
Silver	7.8×10^{10}	2.8×10^{10}	10.9×10^{10}	0.37
Steel	20.6×10^{10}	8.9×10^{10}	18.1×10^{10}	0.33
Tin	4.5×10^{10}	1.67×10^{10}	5.1×10^{10}	0.31
Quarz fiber	5.2×10^{10}	3.0×10^{10}	1.4×10^{10}	0.37
Glass, crown	7.0×10^{10}	3.0×10^{10}	5.0×10^{10}	0.24
Phosphor bronze	12.0×10^{10}	4.3×10^{10}	-	0.36

Per confronto si noti che il valore di E per il caucciu' e' ~10^7 Pa.

Weak dependence on the material (but Young does depend on material!)

Rough microscopic picture I

Drilling down: the origins of moduli. Atoms bond together, some weakly, some strongly. If they bind strongly enough they form solids; the stronger the bond, the higher is the melting point of the solid. Think of the bonds as little springs (Figure 3). The atoms have an equilibrium spacing a_o ; a force F pulls them apart a little, to $a_o + \delta$, but when it is released they jump back to their original spacing. The same happens in compression because the energy of the bond increases no matter in which direction the force is applied, as the lower part of the figure suggests. The bond energy is a minimum at the equilibrium spacing. A spring that stretches by δ under a force F has a stiffness, S, defined by

$$S = \frac{F}{\delta}$$

and this is the same in compression as in tension.

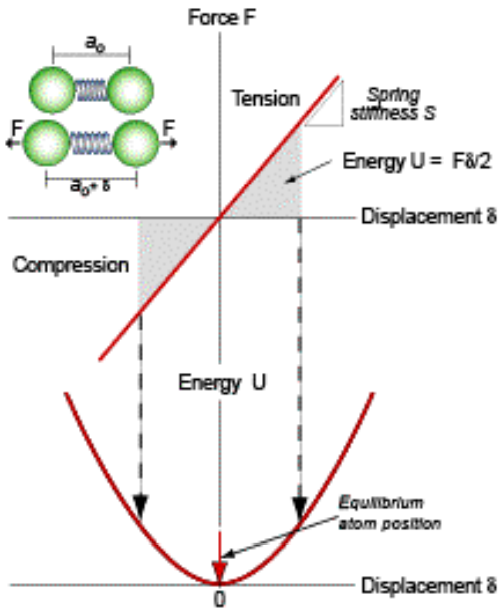


Figure 3. Stretching or compressing an atomic bond raises its energy. Its resistance to stretch is its stiffness, S.

Table 1 lists the stiffnesses of the different bond types; these stiffnesses largely determine the value of the modulus, E . The covalent bond is particularly stiff (S = 20–200 N/m); diamond, for instance, has a very high modulus because the carbon atom is small (giving a high bond density) and its atoms are linked by the stiffest springs (S = 200 N/m). The metallic bond is a little less stiff (S =15–100 N/m) and metal atoms are often close-packed, giving metals high moduli too, though not as high as that of diamond. Ionic bonds, found in many ceramics, have stiffnesses comparable with those of metals, giving them, also, high moduli. Polymers contain both strong diamond-like covalent bonds along the polymer chain and weak hydrogen or Van-der-Waals bonds (S = 0.5–2 N/m) between the chains; it is the weak bonds that stretch when the polymer is deformed, giving them low moduli.

http://www.grantadesign.com/education/sciencenote.htm

Rough microscopic picture II

When a force F is applied to a pair of atoms, they stretch apart by δ. A force F applied to an atom corresponds to a stress $\sigma = F/a_o^2$ where a_o is the atom spacing. A stretch δ between two atoms separated by a_o corresponds to a strain $\varepsilon = \delta / a_o$. Substituting these into the last equation gives

$$\sigma = \frac{S}{a_o} \varepsilon$$

Table 1 Bond stiffnesses, S

Bond type	Examples	Bond Stiffness S (N/m)	Young's Modulus E (GPa)
Covalent	Carbon-carbon bond	50 – 180	200 – 1000
Metallic	All metals	15 – 75	60 – 300
Ionic	Alumina, Al_2O_3	8 – 24	32 – 96
Hydrogen bond	Polyethylene	6 – 3	2 – 12
Van der Walls	Waxes	0.5 - 1	1 - 4

Comparing this with the definition of Young's modulus reveals that E is roughly

$$E = \frac{S}{a_o}$$

The largest atoms ($a_o = 4 \times 10^{-10}$ m) bonded with the weakest bonds (S = 0.5 N/m) will have a modulus of roughly

$$E = \frac{0.5}{4 \times 10^{-10}} \approx 1\ GPa$$

This is the *lower limit* for true solids and many polymers do have moduli of about this value; metals and ceramics have values 50–1000 times larger because, as Table 1 shows, their bonds are stiffer.

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Rubber as a counterexample

One class of materials – elastomers (rubber) – have moduli that are much less than 1 GPa. An elastomer is a tangle of long-chain molecules with occasional cross-links, as in Figure 4 (a), as explained in ***Density and atom packing***. The bonds between the molecules, apart from the cross-links, are weak – so weak that, at room temperature, they have melted. We describe this by saying that the glass temperature T_g of the elastomer – the temperature at which the bonds first start to melt – is below room temperature. Segments are free to slide over each other, and were it not for the cross-links, the material would have no stiffness at all.

Temperature favors randomness. That is why crystals melt into disordered fluids at their melting point. The tangle of Figure 4 (a) has high randomness, or expressed in the terms of thermodynamics, its *entropy* is high. Stretching it, as at (b), aligns the molecules – some parts of it now begin to resemble the crystallites shown in the notes on ***Density and atom packing***. Crystals are ordered, the opposite of randomness; their entropy is low. The effect of temperature is to try to restore disorder, making the material try to revert to a random tangle, and the cross-links give it a "memory" of the disordered shape it had to start with. So there is a resistance to stretching – a stiffness – that has nothing to do with bond-stretching, but with strain-induced ordering. A full theory is complicated – it involves the statistical mechanics of long-chain tangles – so it is not easy to calculate the value of the modulus. The main thing to know is that the moduli of elastomers are low because they have this strange origin and that they increase with temperature (because of the increasing tendency to randomness), whereas those of true solids decrease (because of thermal expansion).

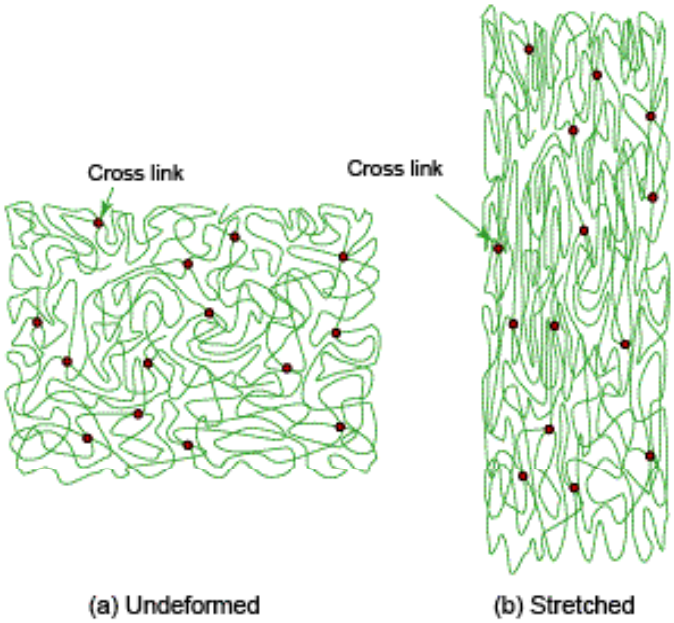

Figure 4. The stretching of an elastomer causes alignment, producing crystal-like regions. Thermal vibration drives the structure back to the one on the left, restoring its shape.

Top

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Energy and hysteresis

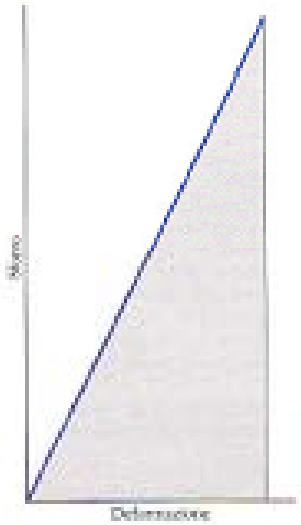
•Quando un materiale elastico viene deformato, immagazzina energia.

•Questènergia viene restituita quando la deformazione viene meno.

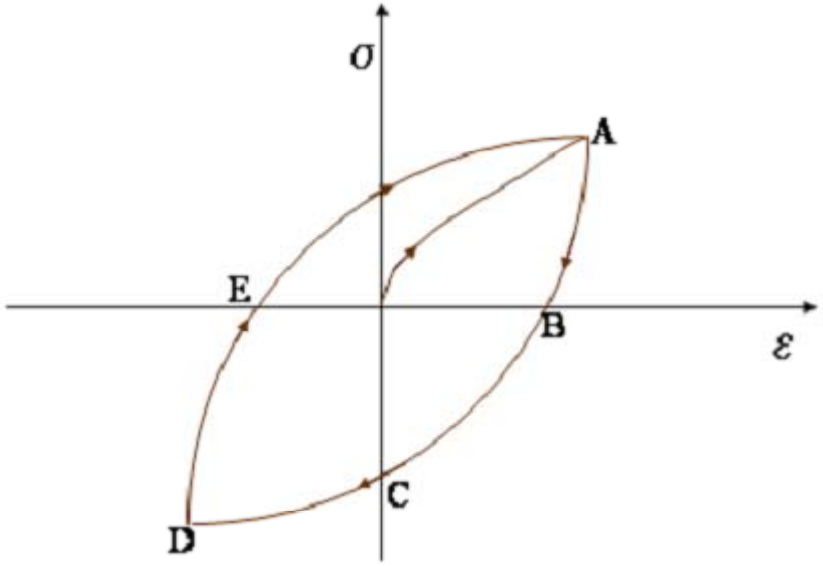
•L'energia E immagazzinata in un materiale elastico, hookiano, soggetto a uno sforzo assiale σ, che produce una deformazione ε, è da

$$e = \frac{\sigma\varepsilon}{2} = \frac{1}{2E}\sigma^2 \quad [\mathrm{J/m^3}]$$

Elastic energy density



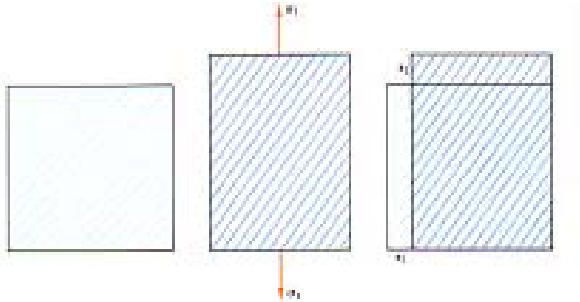
E è lárea sottesa alla curva sforzo-deformazione



Elastic hysteresis is often seen in stress strain loops
→ Some energy is "dissipated"
← Rearrangement of the atomic structure upon deformation is involved

Materiale tratto da Laura Andreozzi - http://www.df.unipi.it/~andreozz/stc/elast.pdf

Poisson's ratio



Quando un solido viene allungato da uno sforzo di trazione σ_1, subisce una deformazione primaria e, nella direzione di σ_1, ma si contrae anche lateralmente con una deformazione secondaria ε_2. Il coefficiente di Poisson ν è uguale a $\varepsilon_2/\varepsilon_1$

ε_2 ed ε_3 dirette lungo gli assi perpendicolari alla direzione dello sforzo σ_1:

$\varepsilon_2 = \varepsilon_3 = -\nu\varepsilon_1 = -\nu(\sigma_1/E)$

Poisson's ratio: $\nu = -\dfrac{\varepsilon_2}{\varepsilon_1}$

Quindi: $\varepsilon_2 = \varepsilon_3 = -\nu\varepsilon_1 = -\nu\dfrac{\sigma_1}{E}$

Poisson's ratio su scala differenziale.

Volume: $V = xyz$

$$\frac{d\ln(V)}{d\ln(x)} = \frac{d\ln(x)}{d\ln(x)} + \frac{d\ln(y)}{d\ln(x)} + \frac{d\ln(z)}{d\ln(x)} = 1 + \frac{d\ln(y)}{d\ln(x)} + \frac{d\ln(z)}{d\ln(x)}$$

ma:

$$\frac{d\ln(y)}{d\ln(x)} = \frac{dy/y}{dx/x} = \frac{\varepsilon_2}{\varepsilon_1} = -\nu$$

$$\frac{d\ln(z)}{d\ln(x)} = \frac{dz/z}{dx/x} = \frac{\varepsilon_2}{\varepsilon_1} = -\nu$$

cioè:

$$\frac{d\ln(y)}{d\ln(x)} = \frac{d\ln(z)}{d\ln(x)} = -\nu$$

Allora, se $\Delta V = 0$

$0 = 1 - 2\nu \rightarrow\rightarrow \nu = 0.5$

Coefficiente di Poisson	
Materiale	_
acciaio	0.30
alluminio	0.33
caucciu'	0.50
ferro	0.30
ottone	0.35
piombo	0.40
platino	0.38
rame	0.34
vetro per finestre	0.25

Poisson ratio	Interpretazione
0.5	No volume change during stretch
0.0	No lateral contraction
0.49 - 0.499	Typical values for elastomers
0.2 - 0.4	Typical value for plastics

Ideal system (isotropic): $\nu = 0.5$
Tipycally $0<\nu<0.5$ (with remarkable exceptions for artificial and natural systems)

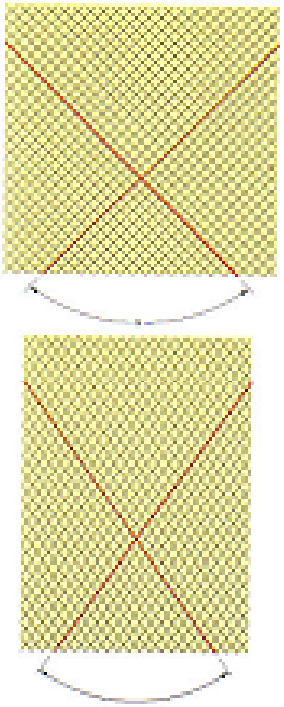
Materiale tratto da Laura Andreozzi - http://www.df.unipi.it/~andreozz/stc/elast.pdf

Negative Poisson's ratio

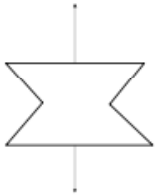
Anisotropia e coefficiente di Poisson

In un materiale omogeneo, isotropo il coefficiente di Poisson non può essere superiore a 0,5.

Tuttavia molti materiali biologici hanno una morfologia molecolare molto complicata che li rende anisotropi (questi materiali hanno cioè differenti proprietà elastiche nelle differenti direzioni). Per esempio, come possiamo verificare tastando i muscoli del braccio, che si ingrossano considerevolmente quando vengono contratti, il coefficiente di Poisson può essere molto più grande di 0,5; spesso è vicino a 1,0.



Auxetics are materials that, have a negative Poisson's ratio, i.e. when stretched, become thicker perpendicularly to the applied force. This occurs because they contain hinge-like structures which flex when stretched. Such materials are expected to have interesting mechanical properties such as high energy absorption and fracture resistance. This may be useful in applications such as body armor, packing material, knee and elbow pads, robust shock absorbing material, and sponge mops.



Auxetics can be illustrated with an inelastic string wound around an elastic cord. When the ends of the structure are pulled apart, the inelastic string straightens while the elastic cord stretches and winds around it, increasing the structure's effective volume.

The term *auxetic* derives from the Greek word αὔξητικός (auxetikos) which means, "that which tends to increase," and has its root in the word αὔξησις, or *auxesis*, meaning "increase" (noun). This terminology was coined by Professor Ken Evans of the University of Exeter. Auxetic materials can be single molecules or a particular structure of macroscopic matter.

Scientists have known about auxetic materials for over 100 years but have only recently given them special attention. The earliest published example of a synthetic auxetic material was in *Science* in 1987, "Foam structures with a negative Poisson's ratio" by R.S. Lakes from the University of Iowa. The use of the word *auxetic* to refer to this property probably began in 1991.

Typically, auxetic materials have low density, which is what allows the hinge-like areas of the auxetic microstructures to flex.

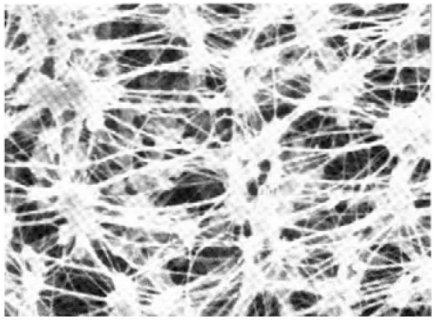
Examples of auxetic materials include:

- Certain rocks and minerals
- Living bone tissue (although this is only suspected)
- Specific variants of polytetrafluorethylene polymers such as Gore-Tex

The history of Gore-Tex started in 1958 when Wilbert Gore identified a market opportunity for polytetrafluoroethylene, or PTFE. This is better known to us as DuPont Teflon. His idea was to use it as insulation for electronic wires. Mr. Gore and his wife set up shop in the basement of their home to make PTFE-insulated ribbon cables.

In 1969, Mr. Gore's son Bob discovered that PTFE could be stretched to form a strong, porous material. This discovery came after long experimentation using high temperature and a slow stretching technique. Perhaps in frustration, the high temperature and FAST STRETCH production secret was discovered. the unique properties of this material have led to a wide variety of applications. It was patented and has the trademark GORE-TEX.

Gore-Tex expanded PTFE is chemically inert. It has a low friction coefficient, which means it is smooth to the touch. It functions over a wide temperature range and has good aging qualities. It is porous, air permeable, strong, hydrophobic, biocompatible and weather durable.



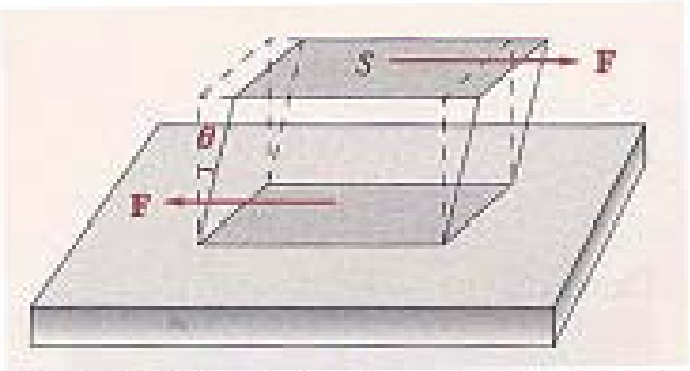
Gore-Tex expanded PTFE Structure of Nodes Interconnected with Fibrils (6700X)
Courtesy of W.L. Gore and Associates

Materiale tratto da Laura Andreozzi - http://www.df.unipi.it/~andreozz/stc/elast.pdf

Shear modulus

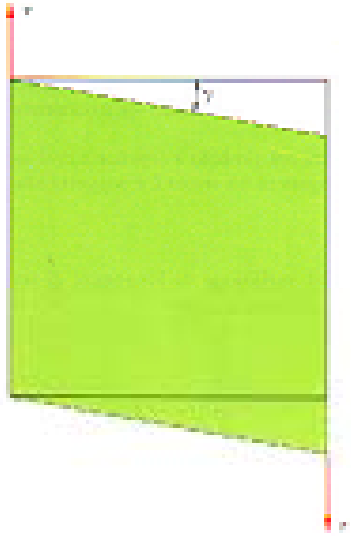
Elasticita' di scorrimento

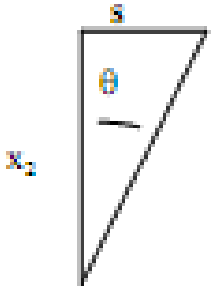
Se la trazione può essere intuitivamente associata all'azione di tirare e la compressione a un'azione di spinta, il taglio è associato a uno scorrimento, o più precisamente a una resistenza alla tendenza a scorrere quando viene applicata una forza.



Lo sforzo di taglio τ è la forza di taglio per unità di superficie della sezione del materiale su cui la forza agisce

La deformazione di taglio γ è l'angolo di deformazione del materiale causato dall'applicazione di uno sforzo di taglio τ. La deformazione di taglio è un angolo generalmente espresso in radianti





La deformazione di shear γ e' definita come lo spostamento della superficie superiore del blocco s diviso il suo spessore (nello schema x_2):

$\gamma = s / x_2$

Per piccole deformazioni:

$\theta = s / x_2$

- **Legge di Hooke** $\tau = G\gamma$

G (Pa) e' il modulo di taglio o di rigidita' (shear modulus).

G e' dello stesso ordine di grandezza di E.

Dalla teoria della elasticita' $G = E/2(1+\nu)$.
Poiche' $0 \leq \nu \leq 0.5$, allora $2G \leq E \leq 3G$.

NOTA
La sollecitazione di scorrimento mantiene il volume rigorosamente costante.

τ: shear force per surface unit
γ: deformation angle

$$\tau = \gamma G$$

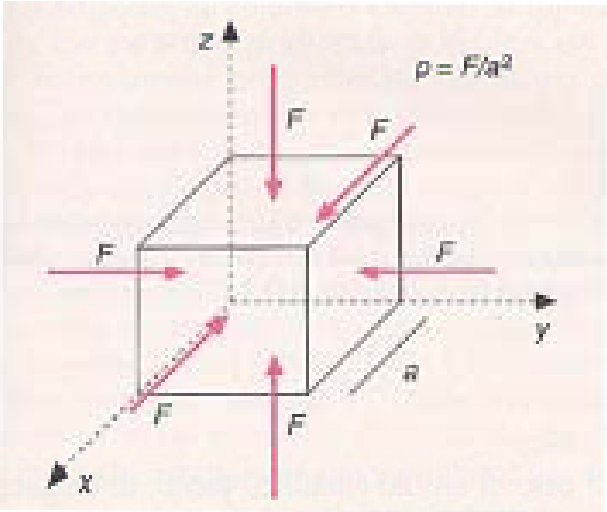
***G*: shear modulus**

Materiale tratto da Laura Andreozzi - http://www.df.unipi.it/~andreozz/stc/elast.pdf

Bulk modulus

Compressione uniforme e modulo di compressibilita'

Se la pressione viene variata di una quantita' Δp si avra' in corrispondenza una variazione di volume ΔV fino al volume V



Il **modulo di compressibilita'** k (o *bulk modulus*, Pa) e' definito dalla relazione:

$$\text{bulk modulus}: \quad k = -V\frac{\Delta p}{\Delta V}$$

Il segno negativo indica che ad un aumento della pressione corrisponde una diminuzione del volume e viceversa.

Dalla teoria dell'elasticita' : $$k = \frac{E}{3(1-2\nu)}$$

modulo di compressibilita' isoterma	
Materiale	k (Pa)
acciaio	1.6 10^11
acqua	2.1 10^9
alluminio	7 10^10
ferro	1.7 10^11
mercurio	2.8 10^10
ottone	6.1 10^10
rame	1.4 10^11
tungsteno	2.0 10^11
vetro per finestre	5.0-5.5 10^10

TABLE 2.2 Relations among the Elastic Constants for Isotropic Materials

Elastic Constants	In Terms of: E, ν	E, G	K, ν	K, G	λ, μ
E	$= E$	$= E$	$= 3(1-2\nu)K$	$= \frac{9K}{1+3K/G}$	$= \frac{\mu(3+2\mu/\lambda)}{1+\mu/\lambda}$
ν	$= \nu$	$= -1 + \frac{E}{2G}$	$= \nu$	$= \frac{1-2G/3K}{2+2G/3K}$	$= \frac{1}{2(1+\mu/\lambda)}$
G	$= \frac{E}{2(1+\nu)}$	$= G$	$= \frac{3(1-2\nu)K}{2(1+\nu)}$	$= G$	$= \mu$
K	$= \frac{E}{3(1-2\nu)}$	$= \frac{E}{9-3E/G}$	$= K$	$= K$	$= \lambda + \frac{2\mu}{3}$
λ	$= \frac{E\nu}{(1+\nu)(1-2\nu)}$	$= \frac{E(1-2G/E)}{3-E/G}$	$= \frac{3K\nu}{1+\nu}$	$= K - \frac{2G}{3}$	$= \lambda$
μ	$= \frac{E}{2(1+\nu)}$	$= G$	$= \frac{3(1-2\nu)K}{2(1+\nu)}$	$= G$	$= \mu$

μ e λ sono le *costanti elastiche di Lame'*.

Materiale tratto da Laura Andreozzi - http://www.df.unipi.it/~andreozz/stc/elast.pdf

Speed of sound/elasticity

Speed of sound is the distance traveled per a unit of time by a sound wave propagating through an elastic medium. In dry air at 20 °C (68 °F), the speed of sound is 343 metres per second (1,125 ft/s). This equates to 1,236 kilometres per hour (768 mph), or about one kilometer in three seconds or approximately one mile in five seconds. The speed of sound in air is referred to as *Mach 1* by aerospace professionals.

In solids, sound waves propagate as two different types. A *longitudinal wave* is associated with compression and decompression in the direction of travel, which is the same process as all sound waves in gases and liquids. A *transverse wave*, often called shear wave, is due to elastic deformation of the media perpendicular to the direction of wave travel, and thus has a polarization in this direction. In general, transverse waves occur as a pair of orthogonal polarizations. These different waves (compression waves and the different polarizations of shear waves) may have different speeds at the same frequency. Therefore, they arrive at an observer at different times, an extreme example being an earthquake, where sharp compression waves arrive first, and rocking transverse waves seconds later.

The speed of elastic waves in all media is determined by the media's compressibility and density. The speed of shear waves, which can occur only in solids, are determined by the solid material's stiffness, compressibility and density.

Speed of sound in solids

[ec

In a solid, there is a non-zero stiffness both for volumetric and shear deformations. Hence, it is possible to generate sound waves with different velocitie dependent on the deformation mode. Sound waves generating volumetric deformations (compressions) and shear deformations are called longitudina waves and shear waves, respectively. In earthquakes, the corresponding seismic waves are called P-waves and S-waves, respectively. The sound velocities of these two type waves are respectively given by[15]:

$$c_l = \sqrt{\frac{K + \frac{4}{3}G}{\rho}} = \sqrt{\frac{E(1-\nu)}{\rho(1+\nu)(1-2\nu)}}$$

$$c_s = \sqrt{\frac{G}{\rho}},$$

where K and G are the bulk modulus and shear modulus of the elastic materials, respectively. Note that the speed of longitudinal/compression waves depends both on the compression and shear resistance properties of the material, while the speed of shear waves depends on the shear properties only.

Typically, compression or P-waves travel faster in materials than do shear waves, and in earthquakes this is the reason that onset of an earthquake is often preceded by a quick upward-downward shock, before arrival of waves that produce a side-to-side motion. E is the Young's modulus, and ν is Poisson's ratio.

For example, for a typical steel alloy, K = 170 GPa, G = 80 GPa and ρ = 7700 kg/m^3, yielding a longitudinal velocity c_l of 6000 m/s.[15] This is in reasonab agreement with c_l=5930 m/s measured experimentally for a (possibly different) type of steel.[16]

The shear velocity c_s is estimated at 3200 m/s using the same numbers.

Medium	(m/s)
Aluminum	4877
Brass	3475
Brick	4176
Concrete	3200 - 3600
Copper	3901
Cork	366 - 518
Diamond	12000
Glass	3962
Glass, Pyrex	5640
Gold	3240
Hardwood	3962
Iron	5130
Lead	1158
Lucite	2680
Rubber	40 - 150
Steel	6100
Water	1433
Wood (hard)	3960
Wood	3300 - 3600

Conclusions

- ✓ At the nanometer scale, an idela solid (bulk, crystalline, defect-free) can be modeled as a network of rigid spheres interacting through an harmonic potential
- ✓ Normal modes of vibration are sustained by the system
- ✓ Macroscopically, they are connected to acoustic vibrations; microscopically phonons can be introudced
- ✓ Phonons give evidence of thermophysical effects (specific heat): according to Debye, a critical temperature exists discriminating classical and quantum behaviors, which depends on the speed of sound (stiffness and density)
- ✓ Macroscopic mechanical properties depend on speed of sound as well
- ✓ The quantum description required at the ultra-small scale is reflected into macroscopic mechanical properties