Properties of Materials

Last Time

Types of Systems and Types of Processes

Division of Total Energy into Kinetic, Potential, and Internal

Types of Work: Polarization

Linear Isotropic Polarizable Materials

Types of Work: Magnetization

Linear Isotropic Non-Ferromagnetic Materials
Chemical Work

If we consider an open chemical system, then we can change the internal energy of a body by alterations of the composition.

For instance, we know that salt has a maximum solubility in water (it is about 300 g/l). If a salt crystal is placed in contact of an open system of water of fixed volume, then chemical work is performed by the dissolution of the salt crystal (or precipitation of salt if the water system is supersaturated).

We will discuss chemical work at length later in the course—but it may be useful to ask yourself the following:

Question: What is the natural “force” against which one must to work to add molecules to a system? Should this force depend on the type of molecule being added to the system? Should the value of the force depend on the chemical composition of the system to which the molecules are being added?

Figure 7-1: Illustration of the concept of chemical work. Each “syringe” contains one chemical component, to change the composition of the system work must be performed on the system that is proportional to the extensive quantity $dN_i$ where $i$ represents the $i$-th chemical component.

It may be useful to think of a particular case. Consider a regular kitchen sponge that has been dried out in the oven for a few days and then exposed to a humid environment. Is there a force driving water molecules from the vapor into the sponge? When does the force disappear?
Consider a sponge that has been soaking in liquid water and then placed in the desert—is there a force on the water molecules driving them one way or another?

--- Elastic Work ---

A spring is an example of a one-dimensional material—it resists or exerts force in one direction only. A volume of material can exert forces in all three directions simultaneously—and the forces need not be the same in all directions. A volume of material can also be “squeezed” in many different ways: it can be squeezed in only one or in only two directions.

All the ways that a force can be applied to small element of material is illustrated below. A force divided by an area is a stress—think of it the area density of force.

\[
\sigma_{ij} = \frac{F_i}{A_j} \quad \text{(i.e., } \sigma_{xz} = \frac{F_x}{A_z} = \sigma_{xz} = \frac{\vec{F} \cdot \hat{i}}{\vec{A} \cdot \hat{k}} \text{)} \quad (7-1)
\]

\( A_j \) is a plane with normal in \( \hat{j} \)-direction (or the projection of the area of a plane \( \vec{A} \) in the direction parallel to the \( \hat{j} \)).

Figure 7-2: Illustration of stress on an oriented volume element.

\[
\sigma_{ij} = \begin{bmatrix}
\sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\
\sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\
\sigma_{zx} & \sigma_{zy} & \sigma_{zz}
\end{bmatrix}
\quad (7-2)
\]

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13Consider a blob modeling clay—you can deform it by placing between one of your opposable thumbs and a finger; you can deform it by simultaneously squeezing with two sets of opposable digits; you can “smear” it by pushing and pulling in opposite directions. These are examples of uniaxial, biaxial, and shear stress.
There is one special and very simple case of elastic stress, and that is called the hydrostatic stress. It is the case of pure pressure and there are no shear (off-diagonal) stresses. (i.e., all \( \sigma_{ij} = 0 \) for \( i \neq j \), and \( \sigma_{11} = \sigma_{22} = \sigma_{33} \)). An equilibrium system composed of a body in a fluid environment is always in hydrostatic stress:

\[
\sigma_{ij} = \begin{bmatrix}
-P & 0 & 0 \\
0 & -P & 0 \\
0 & 0 & -P
\end{bmatrix}
\]  \hspace{1cm} (7-3)

And the pure hydrostatic pressure is given by \( P \)

\[
\Delta = \frac{dV}{V}
\]  \hspace{1cm} (7-5)

If the body that is being stressed hydrostatically is isotropic, then its response is pure dilation (in other words, it expands or shrinks uniformly and without shear):

\[
\epsilon_{ij} = \begin{bmatrix}
\Delta/3 & 0 & 0 \\
0 & \Delta/3 & 0 \\
0 & 0 & \Delta/3
\end{bmatrix}
\]  \hspace{1cm} (7-4)

So, for the case of hydrostatic stress, the work term has a particularly simple form:

\[
V \sum_{i=1}^{3} \sum_{j=1}^{3} \sigma_{ij} \epsilon_{ij} = -PdV
\]  \hspace{1cm} (7-6)

This expression is the same as the rate of work performed on a compressible fluid, such as an ideal gas.
### Models for Anisotropic materials

As part of our discussion of different ways that the internal energy of a body $U$ could be changed, we considered what would happen to a material if it is held in an electric field. In an electric field, charges of opposite sign move in opposite directions, so one side of the material takes on a different charge than another side—in other words, it becomes polarized.

**Question:** Do you think the internal energy of the material increases or decreases as it gets polarized? What about the energy associated with the device that creates the electric field?

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**Models for Anisotropic Polarizable Materials**

We discussed a model for isotropic polarizable materials—we wrote down an expression for the work of polarizing a material in an electric field and then assumed linear isotropic behavior to find an expression for the polarization energy in such an idealized material. We introduced a material parameter $\chi$ that quantifies how much internal polarization develops for an applied electric field: $\vec{P} = \kappa_0 \chi \vec{E}$.

In an isotropic material, therefore, the underlying material cannot influence the material response and the induced polarization, total polarization, and applied field are all parallel.

![Diagram](image)

*Figure 7-3: For an isotropic material, the vectors $\vec{E}$, $\vec{P}$, and $\vec{D}$ are parallel; in an anisotropic material the ions or electron clouds may be constrained to move in particular directions due to the underlying lattice or symmetry.*

In an anisotropic material, the material response depends on the relative direction of the applied field and the crystal orientation—physically, the internal dipoles are constrained to lie in particular directions with respect to the underlying material.
Figure 7-4: Model of an internal dipole in a crystalline material

The polarization is not necessarily in the direction of the field. The polarization is linearly related to the field direction.

Such linear relationships can be written as follows:

\[
\begin{pmatrix}
P_x \\
P_y \\
P_z
\end{pmatrix} = \kappa \chi \begin{pmatrix}
\chi_{xx} & \chi_{xy} & \chi_{xz} \\
\chi_{yx} & \chi_{yy} & \chi_{yz} \\
\chi_{zx} & \chi_{zy} & \chi_{zz}
\end{pmatrix} \begin{pmatrix}
E_x \\
E_y \\
E_z
\end{pmatrix}
\]

\[\vec{P} = \kappa \chi \vec{E} \]

\[P_i = \sum_{j=1}^{3} \kappa \chi_{ij} E_j \]

where \( \chi \) is called the dielectric susceptibility tensor.

You won’t be tested or otherwise asked whether you understand what a tensor is in this course, but I will tell you what they are because they are important. They are representations
of materials properties that may depend on the underlying symmetry of the material—or any measurable quantity that can depend on the orientation of the measuring device with respect to some laboratory coordinate system.

<table>
<thead>
<tr>
<th>Tensors</th>
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<tbody>
<tr>
<td>Extraneous but Potentially Instructive Material</td>
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<tr>
<td>A tensor expresses the relation between material response or force with respect to the axes of its underlying symmetry to the axes of response or force in a laboratory frame.</td>
</tr>
<tr>
<td>A first rank tensor is a spatial vector: its three components refer to the axes of some reference frame.</td>
</tr>
<tr>
<td>A second rank tensor has 9 components, like a matrix. Each component is associated with two axes: one from the set of the reference frame axes and one from the material frame axes. You can think of the second rank tensor as a linear relationship between two vectors (or equivalently, two first rank tensors).</td>
</tr>
<tr>
<td>A third rank tensor is a relationship between a first rank tensor and a second rank tensor, and so on.</td>
</tr>
<tr>
<td>An $N$-rank tensor will have $3^N$ components, but there may be symmetry relations that reduce the number of independent components considerably.</td>
</tr>
</tbody>
</table>

When a material property is a tensor, there are constraints on the form of the tensor that follow from the symmetry of the underlying material. We will discuss this constraint, called Neumann’s Principle, in a later lecture.

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Models for Diamagnetic and Paramagnetic Anisotropic Materials

Because the equations for magnetization and polarization are so similar, it is not surprising that the anisotropic material properties will have a similar form.

The general (anisotropic) relationship between the induced magnetization density and the applied field is

\[
\begin{pmatrix}
I_x \\
I_y \\
I_z
\end{pmatrix} = \mu_o \begin{pmatrix}
\psi_{xx} & \psi_{xy} & \psi_{xz} \\
\psi_{yx} & \psi_{yy} & \psi_{yz} \\
\psi_{zx} & \psi_{zy} & \psi_{zz}
\end{pmatrix} \begin{pmatrix}
H_x \\
H_y \\
H_z
\end{pmatrix}
\]

\[\vec{I} = \mu_o \vec{\psi} \vec{H}\]

\[I_i = \sum_{j=1}^{3} \mu_o \psi_{ij} H_j \]

\[I_i = \mu_o \psi_{ij} H_j \quad \text{summation convention}\]
where $\psi$ is the magnetic susceptibility tensor.

Therefore Eq. 6-11 becomes:

$$\begin{pmatrix} B_x \\ B_y \\ B_z \end{pmatrix} = \begin{pmatrix} \mu_{xx} & \mu_{xy} & \mu_{xz} \\ \mu_{yx} & \mu_{yy} & \mu_{yz} \\ \mu_{zx} & \mu_{zy} & \mu_{zz} \end{pmatrix} \begin{pmatrix} H_x \\ H_y \\ H_z \end{pmatrix}$$

$$\vec{B} = \mu \vec{H}$$

$$B_i = \sum_{j=1}^{3} \mu_{ij} H_j$$

where $\mu_{ij} = \mu_0 (\delta_{ij} + \psi_{ij})$ is the magnetic permeability tensor. $\delta_{ij}$ is the identity matrix and is also called Kronecker-delta tensor which is 1 if $i = j$ and zero otherwise.

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**Models for Anisotropic Elastic Materials: Advanced Material**

An elastic material is one that responds to an applied stress by deforming—and then “pops” back to its original shape when the stress is returned to its original value.

The resistance to deformation—or material stiffness—is ultimately related to the bonds between the atoms or molecules that comprise a solid. Weak bonds in a particular direction would result in a material that is not very stiff—in other words, highly compliant—when a force is applied in the direction of the weak bonds.

![Figure 7-5: Illustration of the effect of applying a stress in two different directions in graphite. Because the deformation will depend on the direction that a particular stress is applied, the elasticity properties will be anisotropic.](image)
Because the stress is a rank-2 tensor (i.e., it has two components $i$ and $j$) and the strain $\epsilon_{ij}$ is also a rank-2 tensor, the most general linear relationship between the two is:

\[
\epsilon_{ij} = \sum_{l=1}^{3} \sum_{l=1}^{3} S_{ijkl} \sigma_{kl}
\]

(7-10)

where $S$ is the elastic compliance tensor—a rank-4 tensor. The inverse of $S$ is related to the elastic modulus or stiffness tensor. For example, the shear strain associated with twisting around the $y$-axis is:

\[
\epsilon_{xz} = S_{xx} \sigma_{xx} + S_{xxy} \sigma_{xy} + S_{xxz} \sigma_{xz} \\
S_{xzy} \sigma_{yx} + \ldots \\
\vdots \\
\ldots + S_{zz} \sigma_{zz}
\]

(7-11)

and is related to all nine possible applied stresses.\(^{14}\)

\(^{14}\) There are actually only six independent stresses in elastic equilibrium—it can be shown that $\sigma_{ij} = \sigma_{ji}$, i.e., the stress is symmetric.