

Elements of Thermodynamics

Indispensable link between
seismology and mineral physics

Physical quantities are needed to describe the state of a system:

- Scalars: Volume, pressure, number of moles
- Vectors: Electric or magnetic field
- Tensors: Stress, strain

We distinguish extensive (size dependent) and intensive (size independent) quantities.

Conjugate quantities: product has the dimension of energy or energy per unit volume.

intensive	extensive
Temperature T	Entropy S
Pressure P	Volume V
Chemical potential μ	Number of moles n
Electrical field \mathbf{E}	Displacement \mathbf{D}
Stress σ	Strain ϵ

By analogy with the expression for mechanical work as the product of **force** times **displacement**,

Intensive quantities \rightarrow generalized forces

Extensive quantities \rightarrow generalized displacements

Consider a system of n extensive quantities e_k and n intensive quantities i_k , the differential increase in energy for a variation of e_k is:

$$dE = \sum_{k=1,n} i_k de_k$$

The intensive quantities can thus be defined as the partial derivative of the energy with respect their conjugate quantities:

$$i_k = \partial E / \partial e_k$$

To define the extensive quantities we have to introduce the Gibbs potential:

$$G = E - \sum i_k e_k$$

$$dG = - \sum e_k di_k$$

The intensive quantities can thus be defined as the partial derivative of the Gibbs potential with respect their conjugate quantities:

$$e_k = - \partial G / \partial i_k$$

Conjugate quantities are related by **constitutive relations** that describe the response of the system in terms of one quantity, when its conjugate is varied. The relation is usually taken to be linear (approximation) and the coefficient is a **material constant**. An example are the elastic moduli in Hooke's law.

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl} \text{ (} C_{ijkl} \text{ are called stiffnesses)}$$

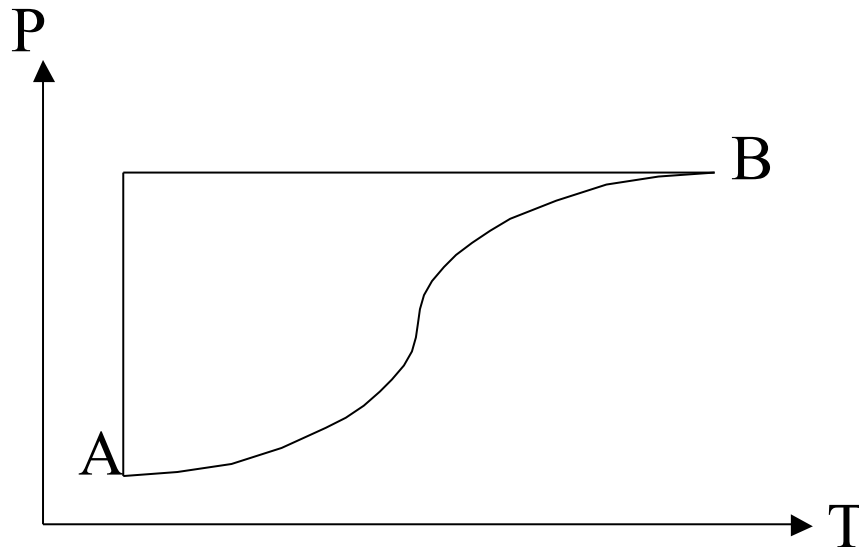
$$\varepsilon_{ij} = c_{ijkl} \sigma_{kl} \text{ (} c_{ijkl} \text{ are called compliances)}$$

!!! In general $C_{ijkl} \neq 1/c_{ijkl}$

The linear approximation only holds for small variations around a reference state. In the Earth, this is a problem for the relation between pressure and volume at increasing depths. Very high pressures create finite strains and the linear relation (Hooke's law) is not valid over such a wide pressure range. We will have to introduce more sophisticated **equations of state**.

Thermodynamic potentials

The energy of a thermodynamic system is a state function. The variation of such a function depends only on the initial and final state.



1st law

$$\begin{aligned}dU &= dQ + dW \\ &= TdS - PdV\end{aligned}$$

Internal energy = heat + mechanical work

Internal energy is the most physically understandable expressed with the variables entropy and volume. They are not the most convenient in general \rightarrow other potentials H, F and G by Legendre transform

Energy can be expressed using various potentials according to which conjugate quantities are chosen to describe the system.

Internal energy	U
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Enthalpie	$H=U+PV$
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Helmholtz free energy	$F=U-TS$
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Gibbs free energy	$G=H-TS$
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In differential form

Internal energy (1st law) $dU = TdS - PdV$

Enthalpie $dH = TdS + VdP$

Helmholtz free energy $dF = -SdT - PdV$

Gibbs free energy $dG = -SdT + VdP$

These expressions allow us to define various extrinsic and intrinsic quantities.

$$T = \left(\frac{\partial U}{\partial S} \right)_V = \left(\frac{\partial H}{\partial S} \right)_P$$

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = - \left(\frac{\partial G}{\partial T} \right)_P$$

$$P = - \left(\frac{\partial U}{\partial V} \right)_S = - \left(\frac{\partial F}{\partial V} \right)_T$$

$$V = \left(\frac{\partial H}{\partial P} \right)_S = \left(\frac{\partial G}{\partial P} \right)_T$$

Maxwell's relations

Potentials are functions of state and their differentials are total and exact. Thus, the second derivative of the potentials with respect to the independent variables does not depend on the order of derivation.

if $f(x, y)$

and $df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy$

then $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$

$$dU = TdS - PdV$$

$$dU = \left(\frac{\partial U}{\partial S} \right) dS + \left(\frac{\partial U}{\partial V} \right) dV$$

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}$$

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V$$

Similar relations using the other potentials. Try it!!!

Maxwell's relations are for conjugate quantities.
 Relations between non-conjugate quantities are possible

$$dX = \left(\frac{\partial X}{\partial Y} \right)_Z dY + \left(\frac{\partial X}{\partial Z} \right)_Y dZ$$

$$dY = \left(\frac{\partial Y}{\partial X} \right)_Z dX + \left(\frac{\partial Y}{\partial Z} \right)_X dZ$$

$$dX = \left(\frac{\partial X}{\partial Y} \right)_Z \left(\left(\frac{\partial Y}{\partial X} \right)_Z dX + \left(\frac{\partial Y}{\partial Z} \right)_X dZ \right) + \left(\frac{\partial X}{\partial Z} \right)_Y dZ$$

$$dX \left(1 - \left(\frac{\partial X}{\partial Y} \right)_Z \left(\frac{\partial Y}{\partial X} \right)_Z \right) - dZ \left(\left(\frac{\partial X}{\partial Y} \right)_Z \left(\frac{\partial Y}{\partial Z} \right)_X + \left(\frac{\partial X}{\partial Z} \right)_Y \right) = 0$$

$$\left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial X}\right)_Z = 1$$

useful
relations

$$\left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial Z}\right)_X \left(\frac{\partial Z}{\partial X}\right)_Y = -1$$

If $f(P,V,T)=0$ then

example

$$\left(\frac{\partial V}{\partial T}\right)_P = - \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V$$

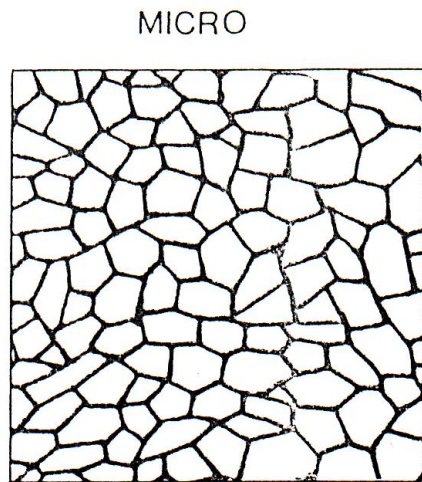
1 Background of thermodynamics of solids

Table 1.2. *Derivatives of extensive (S, V) and intensive (T, P) quantities*

$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$	$\left(\frac{\partial S}{\partial V}\right)_T = \alpha K_T$	$\left(\frac{\partial S}{\partial P}\right)_V = \frac{C_P}{\alpha K_S T}$
$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$	$\left(\frac{\partial S}{\partial V}\right)_P = \frac{C_P}{\alpha V T}$	$\left(\frac{\partial S}{\partial P}\right)_T = -\alpha V$
$\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}$	$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{\alpha K_S T}{C_P}$	$\left(\frac{\partial T}{\partial P}\right)_V = \frac{1}{\beta P}$
$\left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_P}$	$\left(\frac{\partial T}{\partial V}\right)_P = \frac{1}{\alpha V}$	$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\alpha V T}{C_P}$
$\left(\frac{\partial P}{\partial T}\right)_V = \alpha K_T$	$\left(\frac{\partial P}{\partial V}\right)_S = -\frac{K_S}{V}$	$\left(\frac{\partial P}{\partial S}\right)_T = -\frac{1}{\alpha V}$
$\left(\frac{\partial P}{\partial T}\right)_S = \frac{C_P}{\alpha V T}$	$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{K_T}{V}$	$\left(\frac{\partial P}{\partial S}\right)_V = \frac{\alpha K_S T}{C_P}$
$\left(\frac{\partial V}{\partial T}\right)_S = -\frac{C_P}{\alpha K_S T}$	$\left(\frac{\partial V}{\partial P}\right)_S = -\frac{V}{K_S}$	$\left(\frac{\partial V}{\partial S}\right)_T = \frac{1}{\alpha K_T}$
$\left(\frac{\partial V}{\partial T}\right)_P = \alpha V$	$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{V}{K_T}$	$\left(\frac{\partial V}{\partial S}\right)_P = \frac{\alpha V T}{C_P}$

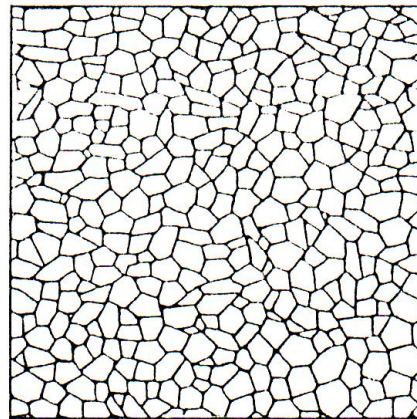
Dealing with heterogeneous rocks

In general, the heterogeneity depends on the scale



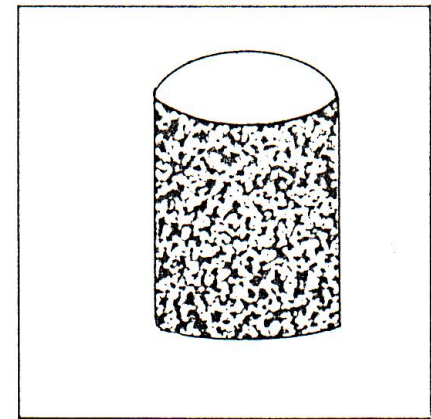
(a)

0.1mm



(b)

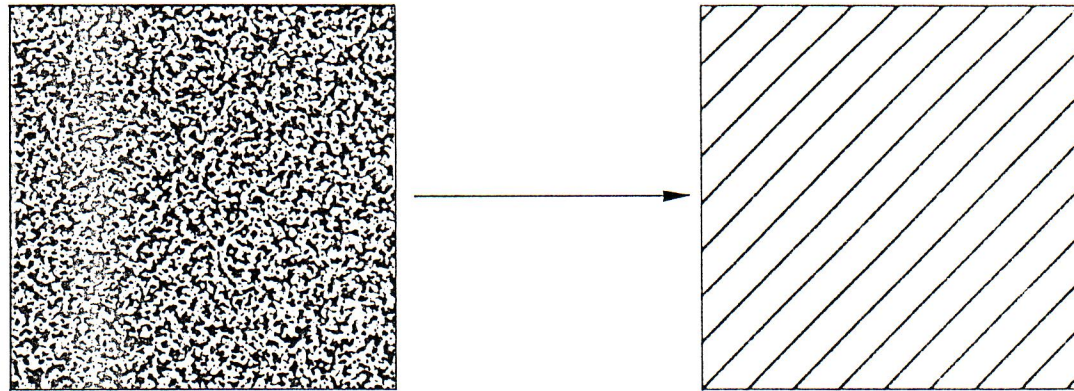
1mm



(c)

1cm

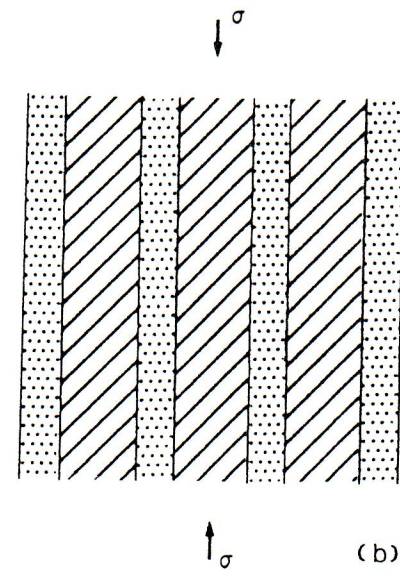
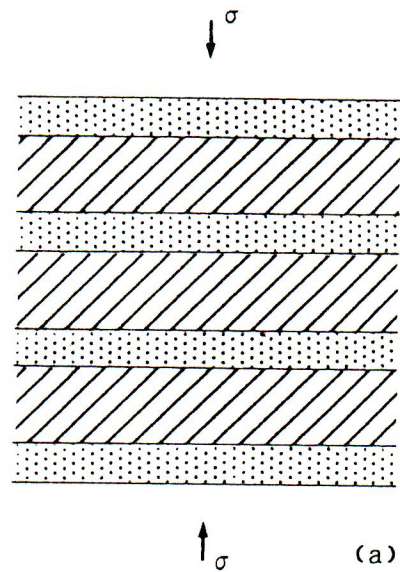
If at the small scale, the heterogeneity is random, it is useful to define an effective homogeneous medium over a large scale



$$\langle u \rangle = \frac{1}{V} \int_V u(x, y, z) dx dy dz$$

In general, of course, rocks are not statistically homogeneous. There is some kind of organization. In the classical approximation this is usually ignored, however.

In the direct calculation, the evaluation of $\langle u \rangle = \frac{1}{V} \int_V u(x, y, z) dx dy dz$ requires the knowledge of the exact quantities and geometry of all constituents. This is often not known, but we can calculate reliable bounds.



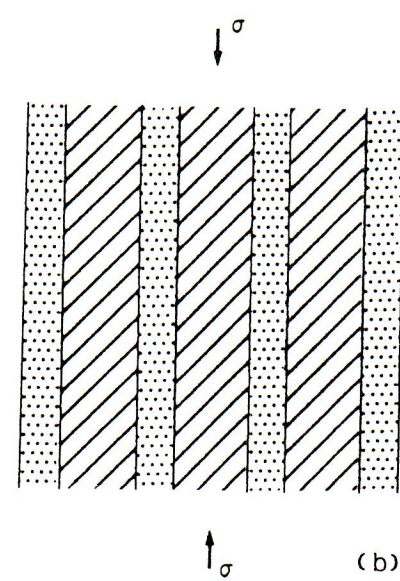
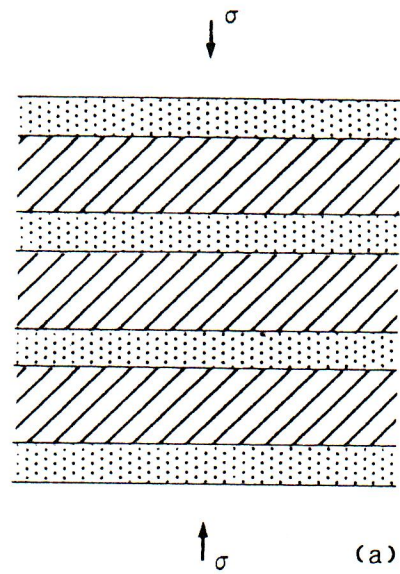
(a) Deformation is perpendicular to layers.

We define $M_a = (\sigma/\epsilon)_a$

We have $\sigma = \sigma_1 = \sigma_2$ homogeneous stress (Reuss)

And $\epsilon = \epsilon_1 V_1 + \epsilon_2 V_2$

Thus $1/M_a = V_1/M_1 + V_2/M_2$



(b) Deformation is parallel to layers.

We define $M_b = (\sigma/\epsilon)_b$

We have $\sigma = \sigma_1 V_1 + \sigma_2 V_2$

And $\epsilon = \epsilon_1 = \epsilon_2$ homogeneous strain (Voigt)

Thus $M_b = V_1 M_1 + V_2 M_2$

The effective medium constant has the property

$$M_a < M < M_b$$

Hill proposed to average M_a and M_b which is known as the Voigt-Reuss-Hill average

$$M = (M_a + M_b) / 2$$

In general, $1/M_a = \sum V_i / M_i$ and $M_b = \sum V_i M_i$

Tighter bounds are possible, but require the knowledge of the geometry (Hashin-Shtrikman)