

Nov. 18 2002: Lecture 25:

Symmetry and Equilibrium

Last Time

Classification of Equilibrium

Positive Definite Forms

Homogeneous Functions

Gibbs-Duhem Equation

Further Restrictions on Material Properties

The considerations above place restrictions on the properties of stable materials. These thermodynamic constraints are independent from, but combine with, any symmetry properties if the material in question. To remind you what you are probably learning in 3.13, restrictions on the symmetry of a material follow from Neumann's principle.

Neumann's Principle

Any observable symmetry of a physical property of a material must include the symmetry elements of the point group of the material.

Consider how this couples to the condition of a positive definite Hessian in a thermodynamic system. In particular, consider a linear elastic material:²⁶

$$\epsilon_{ij} = s_{ijkl}\sigma_{kl} \text{ or, equivalently } \sigma_{ij} = c_{ijkl}\epsilon_{kl} \quad (25-1)$$

or as a matrix equation

$$\begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix} = \begin{pmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \sigma_{23} \\ \sigma_{31} \\ \sigma_{12} \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\ c_{12} & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\ c_{13} & c_{23} & c_{33} & c_{34} & c_{35} & c_{36} \\ c_{14} & c_{24} & c_{34} & c_{44} & c_{45} & c_{46} \\ c_{15} & c_{25} & c_{35} & c_{45} & c_{55} & c_{56} \\ c_{16} & c_{26} & c_{36} & c_{46} & c_{56} & c_{66} \end{pmatrix} \begin{pmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \epsilon_4 \\ \epsilon_5 \\ \epsilon_6 \end{pmatrix} \quad (25-2)$$

Adding strains to the internal degrees of freedom,

$$\delta(U - T_0 S + \sigma_{ij}\epsilon_{ij}) > 0 \quad (25-3)$$



Therefore the second derivative will contain terms such as,

$$\delta\left(\frac{1}{2}c_{ijkl}\epsilon_{ij}\epsilon_{kl}\right) > 0 \quad (25-4)$$

or

$$\frac{1}{2}(d\epsilon_1, d\epsilon_2, d\epsilon_3, d\epsilon_4, d\epsilon_5, d\epsilon_6) \begin{pmatrix} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\ c_{12} & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\ c_{13} & c_{23} & c_{33} & c_{34} & c_{35} & c_{36} \\ c_{14} & c_{24} & c_{34} & c_{44} & c_{45} & c_{46} \\ c_{15} & c_{25} & c_{35} & c_{45} & c_{55} & c_{56} \\ c_{16} & c_{26} & c_{36} & c_{46} & c_{56} & c_{66} \end{pmatrix} \begin{pmatrix} d\epsilon_1 \\ d\epsilon_2 \\ d\epsilon_3 \\ d\epsilon_4 \\ d\epsilon_5 \\ d\epsilon_6 \end{pmatrix} > 0 \quad (25-5)$$

The stiffness matrix that must be positive definite for an isotropic material is:

$$\underline{c}_{\text{isotropic}} = \begin{pmatrix} (2\mu + \lambda) & \lambda & \lambda & 0 & 0 & 0 \\ \lambda & (2\mu + \lambda) & \lambda & 0 & 0 & 0 \\ \lambda & \lambda & (2\mu + \lambda) & 0 & 0 & 0 \\ 0 & 0 & 0 & \mu & 0 & 0 \\ 0 & 0 & 0 & 0 & \mu & 0 \\ 0 & 0 & 0 & 0 & 0 & \mu \end{pmatrix} \quad (25-6)$$

²⁶The summation convention is used. Any repeated index is summed over all possible values, i.e., $x_i x_i$ implies $x_1 x_1 + x_2 x_2 + x_3 x_3$.

Where λ and μ are the elastic Lamé coefficients and are related to the isotropic elastic coefficients:

$$\begin{aligned}
 \lambda_{el} &= \text{First Lamé coefficient} = \\
 &= \frac{2G_{el}\nu}{1-2\nu} = K_{el} - \frac{2G_{el}}{3} = \frac{E_{el}\nu}{(1+\nu)(1-2\nu)} \\
 G_{el} &= \text{Shear Modulus or Second Lamé coefficient} = \\
 &= \frac{E_{el}}{2(1+\nu)} = \frac{3}{2}(K_{el} - \lambda) = \frac{3K_{el}(1-2\nu)}{2(1+\nu)} \\
 E_{el} &= \text{Young's Modulus} = \\
 &= \frac{G_{el}(3\lambda_{el} + 2G_{el})}{\lambda_{el} + G_{el}} = 3K_{el}(1-2\nu) \\
 \nu &= \text{Poisson's ratio} = \frac{\text{lateral shrinkage}}{\text{linear extension}} = \\
 &= \frac{\lambda_{el}}{2(\lambda_{el} + G_{el})}
 \end{aligned} \tag{25-7}$$

The matrix in Equation 25-6 has three unique eigenvalues: $E_{el}/[2(1+\nu)]$, $E_{el}/(1+\nu)$, and $E_{el}/(1-2\nu)$.

Therefore for an isotropic elastic material to be thermodynamically stable, the following conditions must be satisfied, if $E > 0$ then $-1 < \nu < 1/2$ ²⁷ Therefore, ν can be negative. This is weird, but true. Cork has a small or almost negative Poisson's ratio, which makes it easy to push into a bottle and makes a good seal.

For a cubic material, the stiffness tensor is:

$$\underline{c}_{\text{cubic}} = \begin{pmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{pmatrix} \tag{25-8}$$

which has three eigenvalues, $c_{11} - c_{12}$, $c_{11} + 2c_{12}$, and c_{44} .

The positive definite condition for a cubic elastic material is, then

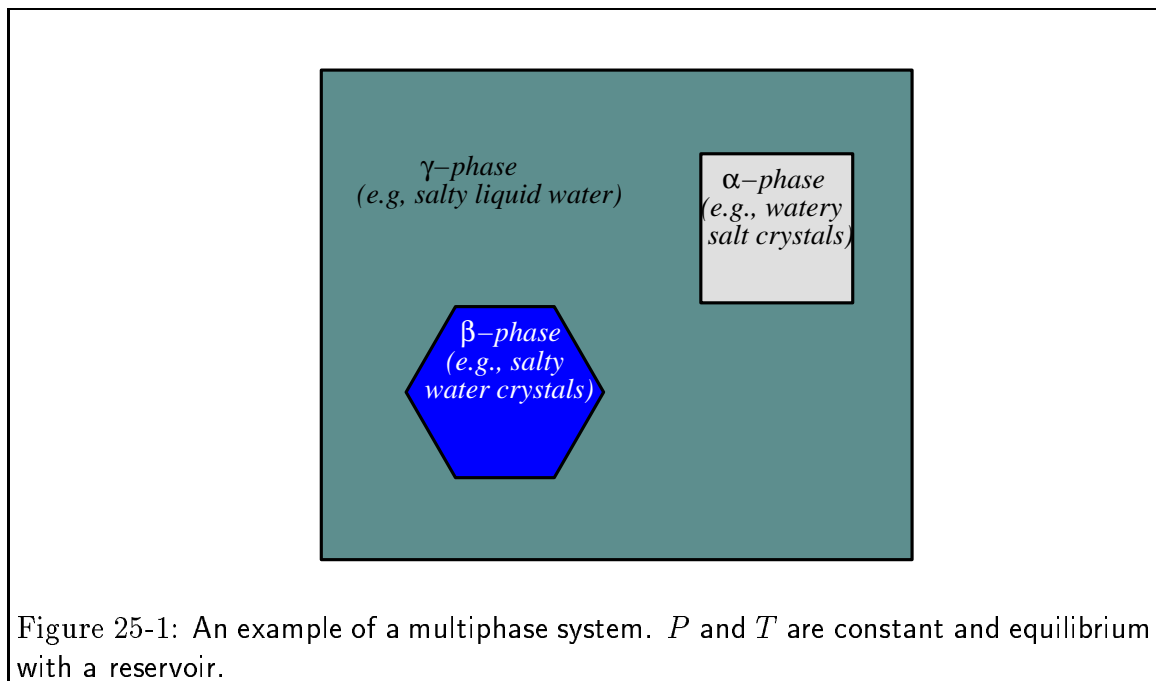
$$c_{44} > 0 \quad \text{and} \quad c_{11} > c_{12} \quad \text{and} \quad c_{11} + 2c_{12} > 0 \tag{25-9}$$

²⁷ While some materials do have a negative Poisson's ratio, like some cellular materials (see a nice review of this by Roderick Lakes, *Science*, 235, 1038-1040 (1987)), they are unusual. Our considerations do not imply that materials that have $E < 0$ and $\nu < -1$ or $E < 0$ and $\nu > 1/2$, but I have never heard of one that exists.

Conditions of Multiphase Equilibrium

Below it will be shown, for a multiphase system, that the chemical potential in each phase must be uniform and equal.

Consider the following simple multiphase system:



Application of the conditions of internal equilibrium to the entire system considering that

it is composed of f phases:

$$\begin{aligned}
 dG &= -SdT + VdP + \sum_{i=1}^C \mu_i dN_i = \sum_{j=1}^f \sum_{i=1}^C \mu_i^j dN_i^j \\
 &= -SdT + VdP \\
 &\quad + \mu_A^\alpha dN_A^\alpha + \mu_B^\alpha dN_B^\alpha + \dots + \mu_C^\alpha dN_C^\alpha \\
 &\quad + \mu_A^\beta dN_A^\beta + \mu_B^\beta dN_B^\beta + \dots + \mu_C^\beta dN_C^\beta \\
 &\quad \vdots \\
 &\quad + \mu_A^\zeta dN_A^\zeta + \mu_B^\zeta dN_B^\zeta + \dots + \mu_C^\zeta dN_C^\zeta
 \end{aligned} \tag{25-10}$$

μ_i^j is the chemical potential of chemical species i in phase j .

Write this out for a three ($f = 3$) phase system composed of two ($C = 2$) species W and B :

For a closed system,

$$dN_B^\alpha + dN_B^\beta + dN_B^\gamma = 0 \tag{25-11}$$

this follows for each possible species i , therefore:

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma \tag{25-12}$$

In other words, the chemical potentials of any chemical species is equal in all the present phases.

Or if we number the species $i = 1, 2, \dots, C$ and the number of phases $j = I, II, \dots, f$:

$$\begin{aligned}
 \mu_1^I &= \mu_1^{II} = \mu_1^{III} = \dots = \mu_1^f \\
 \mu_2^I &= \mu_2^{II} = \mu_2^{III} = \dots = \mu_2^f \\
 &\quad \vdots \\
 \mu_C^I &= \mu_C^{II} = \mu_C^{III} = \dots = \mu_C^f
 \end{aligned} \tag{25-13}$$

Each row has $f - 1$ equal signs; i.e. $f - 1$ equations. So in the above there are $C(f - 1)$ equations.

In addition we have, via the Gibbs-Duhem equation for each phase, another relation between the variables:

$$\begin{aligned}
 0 &= S^{\text{I}} dT - V^{\text{I}} dP + \sum_{i=1}^C N_i^{\text{I}} d\mu_i^{\text{I}} \\
 0 &= S^{\text{II}} dT - V^{\text{II}} dP + \sum_{i=1}^C N_i^{\text{II}} d\mu_i^{\text{II}} \\
 &\vdots \\
 0 &= S^{\text{f}} dT - V^{\text{f}} dP + \sum_{i=1}^C N_i^{\text{f}} d\mu_i^{\text{f}}
 \end{aligned}
 \tag{25-14}$$

that gives us another f equations. Therefore,

Let the number of free variables be D (degrees of freedom). Then,

$$D = (Cf + 2) - [C(f - 1) + f] \tag{25-15}$$

or:

$$D + f = C + 2 \tag{25-16}$$

This is a relation between the number of degrees of freedom in a system and the number of components. Commonly, one can think of the number of degrees of freedom in a system as the number of phases that can co-exist, or $D = P$.

And this brings to mind the following..... limerick:

*There was a recent graduate from MIT
 Who was forced to send back her course three degree
 she couldn't make a phase plot
 Because she had simply forgot
 that $P + F = 2 + C$*