3.23 Lecture 10

Last time we looked at the formal structure of Maxwell relations.

$$(\delta X / \delta Y)_{conj(x)} = +/-(\delta conj(y) / \delta conj(x))_y$$

In order to find the sign, look at the potential from which the relation can be derived. This can be done for simple systems with multiple work terms. Below is an example with a magnetic work term.

$$dU = TdS - pdV + \mu_o HdM$$

$$G^* = U - TS + PV - \mu_o HdM$$

$$dG^* = -SdT + VdP - \mu_o MdH$$

With three differentials, there are six Maxwell relations. Below is a Maxwell relation. There is the same structure as in previous relations but with an extra variable constant.

$$(\delta S / \delta P)_{T, H} = -(\delta V / \delta T)_{P, H}$$

Below is a Maxwell relation with the change in magnetization with respect to temperature.

$$(\delta \mu_o M / \delta T)_{H, P} = -(\delta S / \delta H)_{T,P}$$

From this relation, we see that the entropy is affected by a magnetic field and that this is measurable through $\delta \mu_o M / \delta T$.

Physical problem

Figure out the derivatives and use Maxwell relations. We know how to calculate the change in entropy at constant pressure. The expression can be written down instantaneously. Calculating the change in entropy with a pressure change is convoluted

$$dS = \delta Q / T$$
$$dS = C_p \, dT / T$$

$$(\delta S / \delta P)_T = -(\delta V / \delta T)_P$$

Evaluate the following expression.

$$V = nRT / P$$
$$(\delta V / \delta T)_P = nR / P$$
$$(\delta S / \delta P)_T = -nR / P$$

Write the general change of state

$$dS = (\delta S / \delta T)_P \, dT + (\delta S / \delta P)_T \, dP$$
$$= nC_P \, dT / T - nR \, dP / P$$

This is true for an ideal gas and could be useful for any material. From the thermodynamic expression, it is possible to learn about other properties.
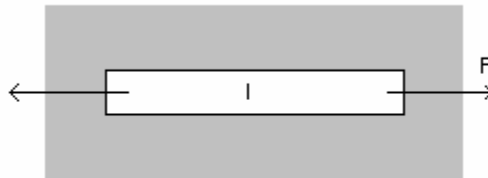
Useful relations

$$(\delta f / \delta x)_y = 1 / (\delta f / \delta x)_y$$

$$(\delta f / \delta x)_y = (\delta f / \delta u)_y \, (\delta u / \delta x)_y$$

$$(\delta f / \delta x)_y \, (\delta x / \delta y)_f (\delta y / \delta f)_x = -1$$

Variations with different things being kept constant

Pull on a material adiabatically. If there is an instantaneous response, there is not time for heat exchange. If the material is pulled adiabatically in the elastic region, does the temperature increase or decrease?

A first step is to put the question in mathematical form. Look at the temperature change with force.

$$(\delta T / \delta F)_S = (\delta l / \delta S)_F$$

This is at constant entropy due to the conditions of no heat flow and a reversible process. Can this be transformed by a Maxwell relation? Yes, it is the derivative of something with the conjugate constant. We need to know what to do with $(\delta l / \delta S)_F$

With S constant, it is possible to transform into derivatives of S. Heat capacity is given in terms of $\delta S / \delta T$. Useful expressions are of the form $\delta S / \delta(force)$

$$(\delta S / \delta P)_T = -(\delta V / \delta T)_P$$
$$(\delta S / \delta H) = (\delta M / \delta T)$$

In this case, transform between variables of what is being held constant using the expression below.

$$(\delta f / \delta x)_y \, (\delta x / \delta y)_f (\delta y / \delta f)_x = -1$$

$$(\delta T / \delta F)_S = (\delta S / \delta F)_T \, / \, (\delta S / \delta T)_F$$

The top form is a derivative in terms of force, which is good. Maxwell relations can be used. The bottom term is the heat capacity under constant force.

$$(\delta S / \delta T)_F = C_F / T$$
$$(\delta S / \delta F)_T = +/-(\delta l / \delta T)_F$$

The term $(\delta l / \delta T)_F$ is the linear thermal expansion. To find the sign look at the state function with F and T variables.

$$F^* = U - TS - Fl$$
$$dF = SdT - ldF$$

$$(\delta l / \delta T) = (\delta S / \delta F)$$

The term of thermal expansion is positive or negative depending on the material.

$$\Delta T = A \, l \, \alpha_L \, T \, \Delta\sigma \, / \, C_F$$

It's possible to turn C_F into a known heat capacity. In solids, this does not very much. Plug in a value of 25 J / mol K for C_F, $7 \; 10^{-6} \; m^3$ / mol for Al, and $12 \; 10^{-6}$ for α_L.

What is the physical explanation for why the temperature decreases? The entropy of the system goes up with the application of a force.

$$(\delta S / \delta F)_T = (\delta l / \delta T)_F > 0$$

At constant entropy, the system responds by lowering the temperature. There is an entropy exchange. This is where all the physics is.

General strategies of how to do derivative

1) Bring potentials to numerator

Substitute in differentials. The following differential was used in the problem with the bicycle tire.

$$(\delta P / \delta T)_H$$

Bring thermodynamic variable to the numerator.

$$(\delta T / \delta P)_H = -(\delta H / \delta P)_T / (\delta H / \delta T)_P$$
$$(\delta T / \delta P)_H = -(\,T\,(\delta S / \delta P)_T + V\,) / (T\,(\delta S / \delta P)_T\,)$$

Expressions from the differential form of the equation of a simple system are used to change terms in the above expression

$$dH = TdS + VdP$$

2) Bring S to the numerator and convert to heat capacity $(\delta S / \delta T)$ or eliminate Maxwell relations $(\delta S / \delta Y)$

The expression of $(\delta S / \delta T)_P$ can be converted to heat capacity. Use a Maxwell relation when there is a derivative of entropy with respect to an intensive force.

$$T\,(\delta S / \delta T)_P = C_P$$
$$(\delta S / \delta P)_T = -\,(\delta V / \delta T)_P$$
$$(\delta S / \delta P)_T = -V\,\alpha_v$$

$$(\delta T / \delta P)_H = V\,(T\,\alpha_v - 1) / C_P$$

Prove that this is zero for an ideal gas. Write out $(\delta U / \delta T)$ and see that all the terms cancel, resulting in zero.

After these two sets of substitutions, one is usually close to the end

3) Volumes in variables

Bring V or any extensive quantity to the numerator. Get the expression into derivatives of T and P.

4) Convert heat capacities

The expression of C_F can be turned into a term of C_P plus energy. For solids we don't see much difference. Bring extensive quantities to numerator. Turn into derivatives of extensive variables with respect to intensive. Usually get far with conversions.

Proof that $(\delta U / \delta V)_T = 0$ for an ideal gas

This is in the definition of an ideal gas. Substitute what dU is and take derivative.

$$dU = TdS - pdV$$

$$dU / dV = T(dS / dV)_T - P$$

Evaluate $(dP / dT)_V$ for an ideal gas

$$P = nRT / V$$
$$(dP / dT)_V = nR / V$$

$$TnR / V - P = 0$$

The energy of an ideal gas does not depend on volume.

U as a function of T, P

Write in terms of any variable.

$$dU = (\delta U / \delta T)_P \, dT + (\delta U / \delta P)_T \, dP$$

Get derivatives of *U* with respect to *T* and *P*. Put in differentials of *dU*.

$$(\delta U / \delta P)_T = ((TdS - pdV) / dP)_T$$
$$(\delta U / \delta P) = T(dS / dP)_T - p \, (dV / dP)_T$$

The term dS / dP can be turned into a derivative of volume with respect to temperature. The compressibility, βV, is a property and given by $(dV / dP)_T$.

$$(\delta U / \delta P) = -T(dV / dT)_P + \beta V$$
$$(dV / dT)_P = V\alpha_v$$
$$(dU / dT) = C_P - pV\alpha_v$$
$$dU = (C_p - pV\alpha_v) \, dT + V(RP - T\alpha_v)dP$$

This is how the internal energy changes with temperature and pressure. It depends on intensive variables.

Useful relation that can be used to convert heat capacities

$$f(x, y)$$
$$(\delta x / \delta f)_z = (\delta x / \delta f)_y + (\delta x / \delta y)_f (\delta y / \delta f)_z$$

This is used to transform what is being kept constant. The last two terms are a correction factor. This relation can be used to convert heat capacities.

$$C_p - C_v = T (\delta S / \delta T)_p - T (\delta S / \delta T)_v$$
$$C_p - C_v = (\delta S / \delta V)_T (\delta V / \delta T)_p$$

The thermal expansion term is $(\delta V / \delta T)_p$ and $(\delta S / \delta V)_T$ can be converted into $(\delta S / \delta P)$

Write in terms of intensive variables with the chain rule

$$(\delta S / \delta V)_T (\delta V / \delta T)_p = V\alpha_v^2 / \beta_T$$

The thermal expansion term is squared, which means that the sign doesn't matter. The greater quantity is always C_P.

Is a material stiffer under adiabatic or isothermal compression?

Data is usually from isothermal experiments. There are difference between a material being shock compressed, which as adiabatic, isentropic compression, or slowly compressed. A key is to evaluate the difference $(\delta U / \delta P)_S$ and $\delta U / \delta P)_T$. Work out the following expression on our own.

$$1/V[\beta_S - \beta_T]$$
$$1/V[(\delta U / \delta P)_S - \delta U / \delta P)_T]$$

Consider elongation with grain boundaries

Pull a material and the force varies with length. The relevant term to evaluate is $(\delta F / \delta l)_N$. If the material is an alloy, there may be segregation. If one pulls slowly and there is fast diffusion, the elastic constant may not be properly weighted. Material can reequilibrate at the grain boundary. Transition between $(\delta F / \delta l)_N$ and $(\delta F / \delta l)_{\mu i}$ with math shown here.
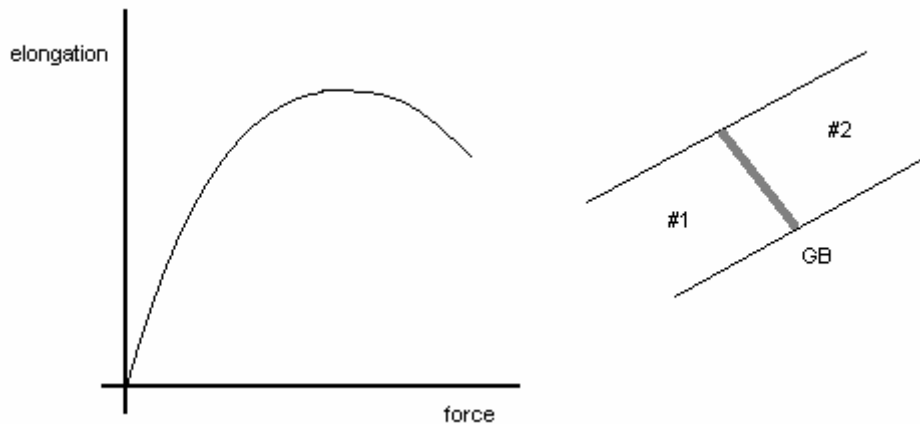
What kind of properties characterize a material?

From second derivatives of $G(T, P)$, there are three properties.

$$(\delta^2 G / \delta T^2) = -\delta S / \delta T$$
$$(\delta^2 G / \delta T^2) = -C_P / T$$

$$(\delta^2 G / \delta P^2) = \delta V / \delta P$$
$$(\delta^2 G / \delta P^2) = V\beta_T$$

$$(\delta^2 G / \delta T\, \delta P) = \delta V / \delta T$$
$$(\delta^2 G / \delta T\, \delta P) = \delta S / \delta P$$
$$(\delta^2 G / \delta T\, \delta P) = V\alpha_v$$

Look at the second derivatives schematically.

	T	P
T	$-C_P / T$	$V\alpha_v$
P	$V\alpha_v$	$V\beta_T$

Extend this to more terms

Magnetic work

$$dU = TdS - pdV + \mu_o HdM$$

The units of μ_o are lumped into H and the term dM contains volume.

$$G = U - TS + PV - HM$$
$$dG = -SdT + VdP - MdH$$

	T	P	H
T	$-C_{P,H} / T$	$V\alpha_v$	
P	$V\alpha_v$	$V\beta_T$	
H			

There are a few new properties. The matrix will be symmetric due to Maxwell relations.

$$(\delta^2 G / \delta T\, \delta H) = -(\delta S / \delta H)_{T,P}$$
$$(\delta^2 G / \delta T\, \delta H) = -(\delta M / \delta T)_{H,P}$$

There is not a classic name of this last term, but there are models to study this, such as $M \sim C/T$. More relations are below.

$$(\delta^2 G / \delta P\, \delta H) = -(\delta M / \delta P)_{H,\ T}$$
$$(\delta^2 G / \delta P\, \delta H) = -(\delta V / \delta H)_{P,\ T}$$

This relates how volume changes with an applied field. The definition of this effect of magnetostriction is complicated for solids.

$$\lambda = 1 / V\ (\delta U / \delta H)_{P,\ T}$$
$$(\delta^2 G / \delta H^2) = -(\delta M / \delta H)$$
$$(\delta^2 G / \delta H^2) = -\chi$$

The susceptibility, χ, describes how the magnetization changes with the applied field.

	T	P	H
T	$-C_{P,H}/T$	$V\alpha_v$	$(\delta M / \delta T)$
P	$V\alpha_v$	$V\beta_T$	$V\lambda$
H	$(\delta M / \delta T)$	$V\lambda$	$-\chi$

These are properties needed to fully characterize the material. Below is a listing of properties along the diagonal.

$-C_{P,H}/T$ thermodynamics, heat flow
$V\beta_T$ elasticity
χ magnetism, susceptibility

The properties in the bottom row and in the right column relate to the intersection between fields

λ how magnetic field and elasticity interact
$(\delta M / \delta T)$ magnetism and temperature
$V\lambda$

A formulism has been built that incorporates everything. The property matrix shows this best.

Looking at the term $(\delta M / \delta T)_H$

The term $(\delta M / \delta T)_H$ is negative, is a property, and is something known.

$$1 / V(\delta U / \delta M)_T = (\delta M / \delta T)_H$$

Use a chain rule and Maxwell relation

$$(\delta U / \delta M) = (\delta U / \delta H)_T (\delta H / \delta M)_T$$

The term $(\delta U / \delta H)_T$ is a magnetostriction term and is equal to $V\lambda$. The term $(\delta H / \delta M)_T$ includes an extensive and intensive variable. It is a diagonal term and is equal to $1 / \chi$.

$$\alpha_H = \alpha_M + \lambda / \chi \, (\delta M / \delta T)_H$$

Look at the sign of terms and what they represent.

α_H magnetized
α_M unmagnetized
χ > 0
$(\delta M / \delta T)_H$ < 0
λ magnestriction, either positive or negative

The correction term can be negative and the overall thermal expansion can be zero. It is often the case that the applied field is constant, such as the case when it is zero.

There is a particular material which at 30 % nickel demonstrates zero thermal expansion. The material is dimensionally stable around room temperature and is used in measurement tools and pendulums of clocks.

What is the physics behind this zero thermal expansion material? When raising the temperature, there is a counter force. When raising the temperature, M goes down. There are two competing effects that can balance: megnetostriction and the decrease of magnetization with temperature.