

# Lesson 18

## Maxwell's Relations

### Review of Yesterday

(2 min)

- Quick summary of what we did
- Re-explain anything that was particularly tricky

### Learning Goals

(2 min)

Upon successful completion of this lesson, students should be able to:

- Identify conjugate forces
- Determine the appropriate free energy for when a selection of forces is held constant
- Derive a desired Maxwell's relation
- Calculate thermodynamic properties based on other known properties

### Conjugate Forces

(10 min)

Each extensive degree of freedom in the energy equation has a conjugate force:

$$\begin{aligned} -P &\longleftrightarrow V \\ T &\longleftrightarrow S \\ \underbrace{\mu_i}_{\text{chemical potential for species } i} &\longleftrightarrow N_i \end{aligned}$$

Other forms of work include:

$f \longleftrightarrow L$	force–length
$\gamma \longleftrightarrow A$	surface tension–area
$\phi \longleftrightarrow Q$	electric potential–charge
$B \longleftrightarrow I$	magnetic field–magnetic moment

In general, the value for a force can be expressed as the partial derivative of the appropriate energy with respect to the force's conjugate extensive degree of freedom:

$$\mathcal{F}_j = \left( \frac{\partial U}{\partial x_j} \right)_{S, V, \vec{N}, x_{i \neq j}}$$

$\mathcal{F}_j$  = generalized force  
 $x$  = generalized extensive variable

We can derive the partial differential expression for any force by using a fundamental energy equation. An example of a fundamental energy equation:

$$dU = TdS - pdV + \sum_k \mu_k dN_k + fdL + \gamma dA + \phi dQ + BdI + \sum_j \mathcal{F}_j dx_j$$

In the general equation, we multiply the extensive variable by the derivative of the conjugate force. So, what is the appropriate free energy when  $T$ ,  $p$ ,  $N$ , and  $A$  are independent? Since these are the only variables that we care about, we keep the terms that involve those variables, and we can discard all of the extra terms:

$$dU = TdS - pdV + \mu dN + \gamma dA$$

If we're interested in knowing the surface tension of this system, we can write a partial differential equation, holding all of our other variables constant:

$$\gamma = \left( \frac{\partial U}{\partial A} \right)_{S,N,V}$$

As a math review, the natural variables for  $U$  in this case would be  $S$ ,  $V$ ,  $N$ , and  $A$  (the variables that we are taking the derivatives of.) But these don't match up with what we've specified above, that is that  $T$  and  $p$  are independent. In this formula of surface tension, neither  $T$  nor  $p$  are being held constant, so are not independent. We have to transform to a free energy which makes this so. Starting with the fundamental energy equation

$$U - TS + pV = G$$

Differentiating:

$$dU - TdS - SdT + pdV + Vdp = dG$$

Substituting in for  $dU$ :

$$\cancel{TdS} - \cancel{pdV} + \mu dN + \gamma dA - \cancel{TdS} - SdT + \cancel{pdV} + Vdp = dG$$

Rearranging:

$$dG = -SdT + Vdp + \mu dN + \gamma dA$$

The natural variables here are  $T$ ,  $p$ ,  $N$ , and  $A$ , and also defines:

$$\gamma = \left( \frac{\partial G}{\partial A} \right)_{T,p,N}$$

### Think/Clicker/Pair/Share

(8 min)

The energy of a magnetic material is dependent on  $S$ ,  $V$ ,  $N$ , and  $I$ , giving the differential form:

$$dU = TdS - pdV + \mu dN + BdI$$

What is the partial differential expression for entropy at constant  $N$ ,  $p$ , and  $T$ ?

A.  $S = \left(\frac{\partial G}{\partial T}\right)_{N,p,B}$

B.  $S = -\left(\frac{\partial G}{\partial T}\right)_{N,p,B}$

C.  $S = -\left(\frac{\partial G}{\partial B}\right)_{N,p,T}$

D.  $S = \left(\frac{\partial G}{\partial B}\right)_{N,p,T}$

### Maxwell Relations and Partial Derivatives

(15 min)

The Maxwell relations interrelate partial derivatives, which is helpful so that we can measure desired quantities in lab. Some variables are difficult to measure, and this allows us to replace them with more easily measured variables. Let's use this free energy:

$$dF = -SdT - pdV + \mu dN$$

For state functions, cross derivatives are equal:

$$\begin{aligned} \frac{\partial^2 F}{\partial T \partial V} &= \frac{\partial^2 F}{\partial V \partial T} \\ \left( \frac{\partial}{\partial T} \underbrace{\left( \frac{\partial F}{\partial V} \right)_T}_{-p} \right)_V &= \left( \frac{\partial}{\partial V} \underbrace{\left( \frac{\partial F}{\partial T} \right)_V}_{-S} \right)_T \\ \therefore - \left( \frac{\partial p}{\partial T} \right)_V &= - \left( \frac{\partial S}{\partial V} \right)_T \\ \left( \frac{\partial p}{\partial T} \right)_V &= \left( \frac{\partial S}{\partial V} \right)_T \end{aligned}$$

The definitions of  $-S$  and  $-p$  come from looking at the  $dF$  expression

## Recipe for Finding Maxwell's Relations

Let's suppose you want to know how the entropy of a material changes when it is squeezed and we have a fixed quantity of that material that remains at a given temperature. We're looking for:

$$\left(\frac{\partial S}{\partial p}\right)_{T,N}$$

Entropy changes are extremely difficult to measure, so can we use an equivalent Maxwell relation that is easy to measure and is equivalent to the solution that we are looking for?

*(This is the step-by-step guide to finding the relations. While going through the questions, ask the students for the answers to this particular problem. If there is disagreement, ask for explanations from the students, and possibly poll the class for agreement.)*

- What are the independent variables?  
 $T, p, N$
- Which free energy is a natural function of these variables?  
 $G(T, p, N)$
- What's the differential form of the free energy expression?  
 $dG = -SdT + Vdp + \mu dN$
- Identify the partial derivative that you want. This should involve the free energy variable, the variable that you want to replace, and the conjugate variable

$$-S = \frac{\partial G}{\partial T}$$

The differential that we're looking for is with respect to  $p$ , so we need to differentiate what we have and use cross-derivatives to simplify:

$$-\frac{\partial S}{\partial p} = \frac{\partial^2 G}{\partial p \partial T} = \frac{\partial^2 G}{\partial T \partial p} = \frac{\partial}{\partial T} \left( \frac{\partial G}{\partial p} \right) = \frac{\partial V}{\partial T}$$

## Susceptibilities

*(15 min)*

Where can we use the differential expressions? In susceptibilities. A susceptibility of a material describes a response to an applied force to that material. It shows how an extensive property changes with a change in an intensive property.

$$\alpha \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$$

where  $\alpha$  is the thermal expansion coefficient and has intensive units of  $[K^{-1}]$  The Maxwell relations tells us:

$$\left(\frac{\partial S}{\partial p}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_p = -V\alpha$$

This means that if  $\alpha > 0$ , then increasing the pressure *orders* the material. If  $\alpha < 0$ , then increasing the pressure *disorders* the material

Most materials have  $\alpha < 0$

Ideal gas:

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$$

$$V = \frac{NkT}{p}$$

$$\frac{\partial V}{\partial T} = \frac{Nk}{p}$$

$$\alpha = \frac{p}{NkT} \frac{Nk}{p} = \frac{1}{T}$$

which means  $\alpha$  is always  $> 0$ .

Cold water, though is anomalous. It has  $\alpha < 0$ . Applying pressure *disorders* it. (Cold H<sub>2</sub>O is cage-like, and applying pressure distorts and disorders the cages.)

We can use  $\alpha$  to find  $S(P)$

$$dS = \left( \frac{\partial S}{\partial p} \right)_{T,N} dp$$

$$= \left( \frac{\partial V}{\partial T} \right)_{p,N} dp = -\alpha V dp$$

So:

$$\Delta S = - \int_{p_1}^{p_2} \alpha(p) V(p) dp$$

Another easily-measured susceptibility is isothermal compressibility

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T$$

For an ideal gas:

$$\frac{\partial V}{\partial p} = \frac{\partial}{\partial p} \left( \frac{NkT}{p} \right) = -\frac{NkT}{p^2}$$

$$\therefore \kappa_T = -\frac{p}{NkT} \left( -\frac{NkT}{p^2} \right) = \frac{1}{p}$$

Water also has an anomalous  $\kappa_T$ . It is less compressible between 0 °C–46 °C.

An example: How does  $U$  change with volume? This will tell us about cohesive forces in the materials. How could we get this information from experiments?

Start with  $U(T, V)$  and  $S(T, V)$

**Think/Share**

What are the differential forms of  $U(T, V)$  and  $S(T, V)$ ?

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT$$

Fundamental energy equation, followed by substitution:

Fundamental energy equation:

$$dU = TdS - pdV$$

$$\left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT = T \left[ \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT \right] - pdV$$

When  $T$  is constant:

$$\left(\frac{\partial U}{\partial V}\right)_T dV = \left( T \left(\frac{\partial S}{\partial V}\right)_T - p \right) dV$$

**Think/Share**

Is this differential easily found in the lab? *No*

How might we fix that? *Use a Maxwell relation*

What is the appropriate Maxwell relation to use?

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V, \text{ thermal pressure coefficient}$$

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

For an ideal gas:

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{Nk}{V}$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = \frac{NkT}{V} - p = 0$$

For typical *liquids*, however  $T\left(\frac{\partial p}{\partial T}\right)_V - p < 0$  at low densities and  $> 0$  at high densities.

<p style="margin: 0;">high <math>\rho</math></p> <p style="margin: 0;"><math>V \downarrow U \uparrow</math></p> <p style="margin: 0;">Pushing against repulsive forces</p>	<p style="margin: 0;">low <math>\rho</math></p> <p style="margin: 0;"><math>V \uparrow U \uparrow</math></p> <p style="margin: 0;">Pulling apart attractive forces</p>
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