Lecture 21

Mathematics of Thermodynamics

<u>Last Time</u>

When a chemical species can be transferred between two phasesthe chemical potential

Chemical Potential of an Ideal Gas

General Solutions

Reacting Mixtures of Ideal Gases

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───── Mathematics of Exact Differentials in Thermodynamics ─────

Our considerations of equilibrium have produced some useful results—these results are usually in the form of some differential expression between quantities.

We will now consider some the useful mathematical relations that follow from the combined form of first and second law.

First

$$dU = TdS - PdV + \sum_{i=1}^{C} \mu_i dN_i \tag{21-1}$$

This differential implies

$$\left(\frac{\partial U}{\partial S}\right)_{const\ V,N_i} = T(S, V, N_i)$$

$$\left(\frac{\partial U}{\partial V}\right)_{const\ S,N_i} = -P(S, V, N_i) \tag{21-2}$$

$$\left(\frac{\partial U}{\partial N_i}\right)_{const\ V,S,N_j \neq N_i} = \mu_i(S, V, N_i)$$

We can think of this equation as defining a "rolling tangent plane"

U

$$U - U(x_o) = \frac{\partial U}{\partial x}\Big|_{x=x_o} (x - x_o)$$

$$= F(x_o)\,(x - x_o)$$

$\Phi(F(x_o))=$
$U(x_o) - F(x_o)x_o$

x_o

$x=0$

Extensive Variable, x

Figure 21-1: Illustration of a rolling tangent plane in one dimension. Evaluated at some arbitrary point x_o, the slope of the plane is the conjugate force to that variable, $F(x_o)$. Using the equation of the tangent plane, we can define a new function. $\Phi(F)$, which is the the intercept of the tangent plane with slope F and the internal energy. The value of the slopes of the tangent surface to U are related to the conjugate forces—the values of these forces are in turn functions of where the tangent plane is placed. In other words, the conjugate forces are also functions of the extensive variables.

———— The Other Energy Functionals: The Legendre transformations

From Equation 21-1, the internal energy has the "natural variables" $U(S, V, N_i)$. To change to another set of natural variables, a new function is defined by subtracting off a particular conjugate pair:

For example: Enthalpy

$$H = U + PV \equiv H(S, P, N_i) \tag{21-3}$$

For example: Helmholtz Free Energy

$$F = U - TS \equiv F(T, V, N_i) \tag{21-4}$$

For example: Gibbs Free Energy

$$G = U + PV - TS = H - TS = F + PV \equiv G(T, P, N_i) \tag{21-5}$$

"The Legendre transformation" is defined as the procedure of subtracting off conjugate pair to change that particular variable.

To see how the new variables appear, consider the Helmholtz free energy:

$$
\begin{aligned}
dF = d(U - TS) &= dU - TdS - SdT \\
&= (TdS - PdV + \sum_{i=1}^{C} \mu_i dN_i) - TdS - SdT \\
&= -SdT - PdV + \sum_{i=1}^{C} \mu_i dN_i
\end{aligned}
\tag{21-6}
$$

implies

$$
\left(\frac{\partial F}{\partial T} \right)_{const\ V, N_i} = -S \qquad S(T, V, N_i)
\tag{21-7}
$$

Doing the same for $d(H) = d(U + PV)$

And for $d(G) = d(U - TS + PV)$

> ### Trivial Example of a Legendre Transform
>
> Suppose that the internal energy is composed of the thermal part plus a simple spring:
>
> $$U(S, x) = TS + Fx$$
> $$= TS + \frac{k}{2}x^2 \tag{21-8}$$
>
> where
>
> $$F(x) = \frac{\partial U}{\partial x} = kx \tag{21-9}$$
>
> The Legendre transform from the x-variable to the F variable is
>
> $$\Phi = U(S, x) - Fx$$
> $$= TS + \frac{k}{2}x^2 - kx^2$$
> $$= TS - \frac{k}{2}x^2 \tag{21-10}$$
> $$= TS - \frac{1}{2k}F^2$$
> $$= \Phi(S, F)$$
>
> It is fairly easy to show that the inverse Legendre transformation is simply $U = \Phi - (\partial \Phi / \partial F)F$.

LeChatelier's Principle

Another important set of thermodynamics concepts fall under the category of LeChatelier's principle. It is fundamentally an easy idea, but for some reason it is taught in fairly confusing ways.

The formal statement of LeChatelier's principle is something like this:

> "If a body at equilibrium is disturbed by changing one of its environment's variables, then the body's internal variables will change so as to mitigate the change in environment."

This is a pretty confusing statement for something that is fairly easy to understand. Perhaps, the following statement is easier? "If a stimulus would produce an effect of magnitude 1 in a material that is constrained not to change its internal degrees of freedom, then an unconstrained material would have a response that is less than or equal to magnitude 1." No, not

better? Oh, well.

Also, I've never found a good proof of this which leads to any additional physical enlighten-ment, so I won't disenlighten you by giving one (if you want to get confused, see the discussion by Landau and Lifshitz, Section 2.2; it is the best proof that I know of).

I think it best to give a few examples.

1. If the pressure is increased, the system will find an equilibrium that decreases its volume.

   Remember our friendly ideal gas reaction:

   $$H_{2(vapor)} + \frac{1}{2}O_{2(vapor)} \rightleftharpoons H_2O_{(vapor)} \tag{21-11}$$
   $$1.5\,\text{moles} \rightleftharpoons 1\text{moles}$$
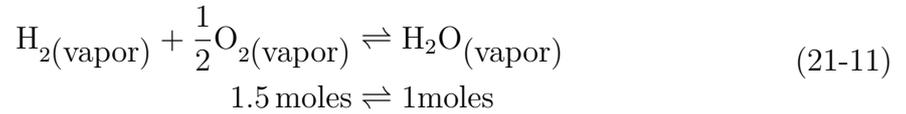
   If we increase pressure, will the composition favor the reactants or products?

   $$K_{eq} = \frac{P_{H_2O}/P_\circ}{P_{H_2}/P_\circ(P_{O_2}/P_\circ)^{\frac{1}{2}}} \tag{21-12}$$

   _____
   _____
   _____
   _____

   $$\left(\frac{P_{new}}{P_\circ}\right)^{\frac{1}{2}} K_{eq} = \frac{X_{H_2O}}{X_{H_2}X_{O_2}^{\frac{1}{2}}} \tag{21-13}$$

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2. A crack in a material:

Figure 21-2: A crack in a material—what is the response of the material to an increased load?
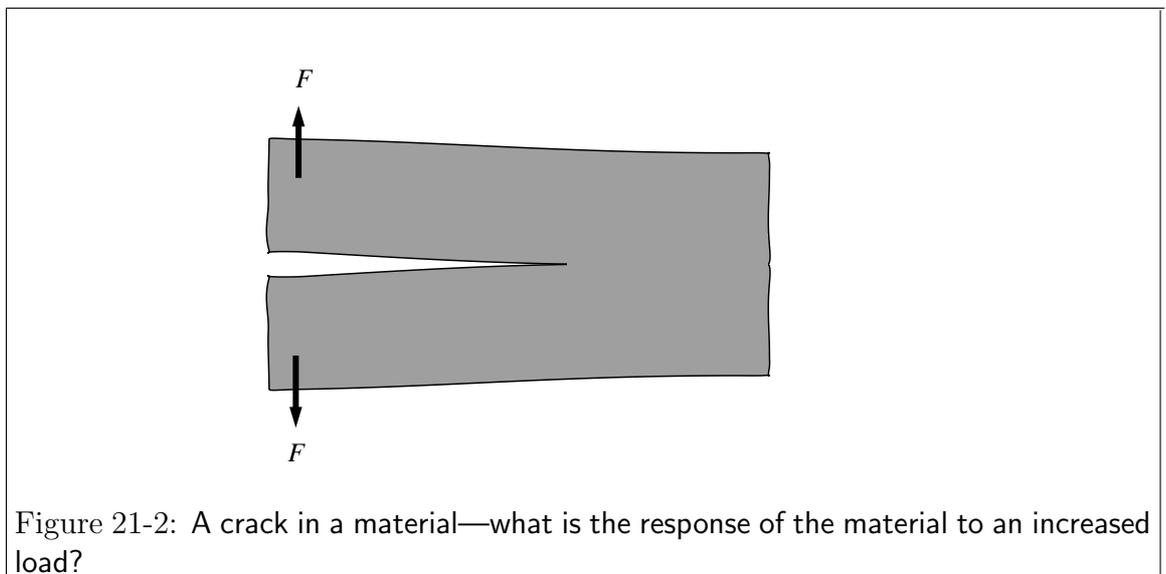
If the load is increased, the stiffness decreases by propagating the crack.

3. Suppose that each homework set I give you is about the same amount of work. You spend an average of $\langle h \rangle$ hours per problem. If I were to assign ten times as many problems this week $\langle h \rangle$ would tend to decrease.

One last note about LeChatelier's principle: it pertains only for small changes applied to an equilibrium system that is not near a condition of instability. If a system is not in equilibrium, or the change in the external conditions are very great, then we should not expect LeChatelier's principle to apply.

As an example, consider a house with the wind blowing past it. The wind blows the door shut which seems like a violation of LeChatelier's Principle.

Figure 21-3: The stupid door doesn't care about LeChatelier's principle.
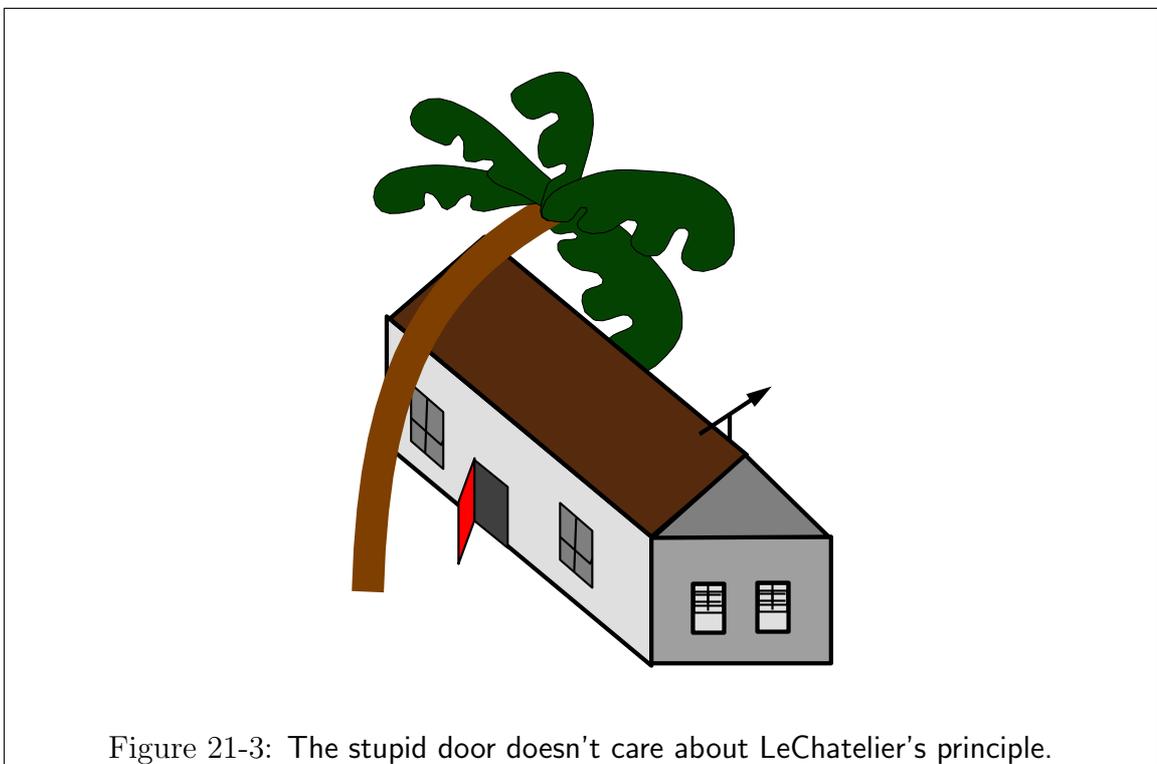
There is also the example of the "Stupid Crack:"