8.044 Lecture Notes
Chapter 5: Thermodynamics, Part 2

Lecturer: McGreevy

**Reading:** Adkins, Chapters 4, 5.1-5.5, 7
(Chapters 8 and 9 are recommended but not required – they give examples.)
Baierlein, Chapters 3.1-3.4 and 10 (But: we'll come back to Chapter 10 when we discuss
chemical potential in 8.044 Chapter 8. Ignore chemical potential for now.)

5.1 Entropy is a state function

This is a fact we know from the microscopic discussion in Chapter 4. Here we will illustrate its thermodynamic consequences.

Example: Three different expansion processes for a hydrostatic system

1) Free   2) Quasistatic Isothermal   3) Quasistatic Adiabatic
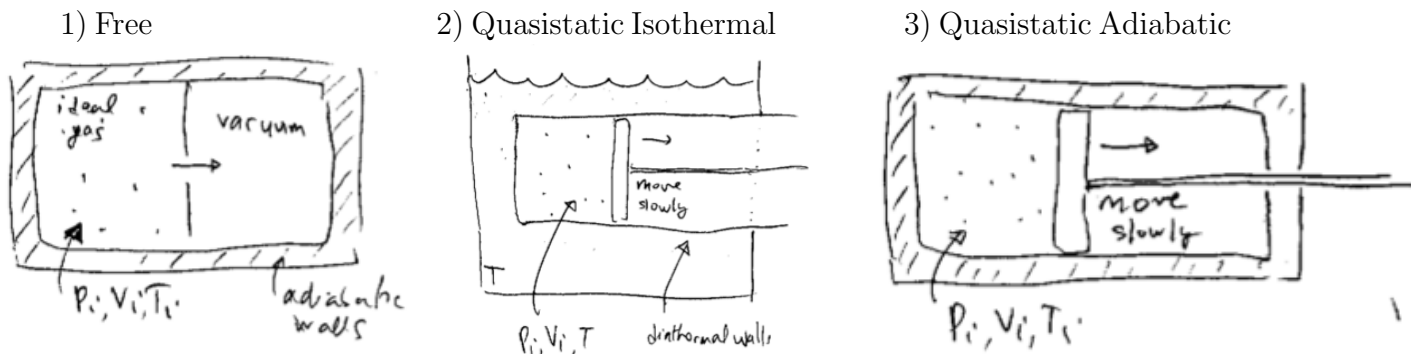
In each case, expand from *e.g.* V_i to $V_f = 2V_i$.

What is ΔS in each case?

1) Free expansion:

$dS > đQ/T$ since it is not quasistatic.

In particular, $\Delta S > 0$.

For an ideal gas,

$$S = k_B N \left(\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{E}{N}\right) + \text{const} \right)$$

Recall: E does not change. Neither does N or T.

$$\implies \quad \Delta S = k_B N \left(\ln\left(\frac{V_f}{N}\right) - \ln\left(\frac{V_i}{N}\right) \right) = k_B N \left(\ln \underbrace{\left(\frac{V_f}{V_i}\right)}_{=2} \right)$$

$$\boxed{\Delta S = k_B N \ln 2} \quad \text{for free expansion}$$

2) (Quasistatic) Isothermal expansion:

Isothermal means the temperature doesn't change. Since the temperature didn't change in protocol (1) above, this is another way to get to the *same* final state.

But this time we're getting there quasistatically, so $dS = đQ/T$.

Since T is constant and $E = E(T)$,

$$0 = dE = dQ + dW$$

$$\Longrightarrow \quad dQ = -dW = +PdV$$

$$\Longrightarrow \quad dS = \frac{P}{T}dV = \frac{Nk_B}{V}dV$$

$$\Longrightarrow \quad \Delta S = \int_i^f dS = Nk_B \int_{V_i}^{V_f} \frac{dV}{V} = Nk_B \ln\left(\frac{V_f}{V_i}\right)$$

Same answer:

$$\boxed{\Delta S = k_B N \ln 2} \quad \text{for isothermal expansion}$$

This had to be true in order for S to be a state function – it only depends on the endpoints, not on how we got there.
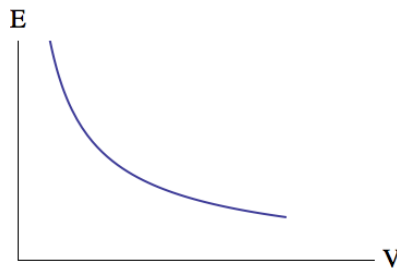
3) Quasistatic adiabatic expansion:

$$\text{quasistatic: } \Longrightarrow \quad dS = \frac{dQ}{T}$$

$$\text{adiabatic: } \Longrightarrow \quad dQ = 0 \Longrightarrow dS = 0.$$

$$\boxed{\Delta S = 0} \quad \text{for quasistatic adiabatic expansion}$$

Different final state means we can have a different ΔS.

$$S = k_B N \left(\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{E}{N}\right) + \text{const} \right)$$

$$\Delta S = 0 \quad \Longrightarrow \quad \ln V + \frac{3}{2}\ln E = \text{const}$$

$$\Longrightarrow \quad VE^{3/2} = \text{const}$$

So if V increases by a factor of 2, E decreases by a factor of $2^{2/3}$. (Since $E \propto T$, so does T.)

Aside:

$$E = \frac{3}{2}Nk_BT \Longrightarrow VT^{3/2} = \text{const}$$

$$PV = Nk_BT \Longrightarrow \text{const} = V(PV)^{3/2} = P^{3/2}V^{5/2}$$

$$\Longrightarrow PV^{5/3} = \text{const}$$

which is what we found before for the shape of an adiabat.

5-3

$C_P - C_V$ for a general hydrostatic system.

Recall from Chapter 3 that:

$$C_P - C_V = \underbrace{V\alpha}_{=\left(\frac{\partial V}{\partial T}\right)_P} \left(\underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{=0 \text{ for ideal gas}} + P \right)$$

The reason $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ has a name is that it is easy to measure. On the other hand, the term $\left(\frac{\partial U}{\partial V}\right)_T$ which was zero for ideal gas is not so easy to measure. (I guess we could imagine doing adiabatic free expansion lots of times into different size containers.) We can use the fact that entropy is a state function to find an alternate useful expression for it.

The fact that S is a state function means we can think of it as a function of any complete set of independent thermodynamic variables. It started its life in our discussion as a function of (E, V), but $S = S(T, V)$ would work just as well.

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \tag{1}$$

On the other hand, the 1st Law for quasistatic processes

$$dU = \underbrace{TdS}_{dQ} + \underbrace{-PdV}_{dW}$$

also gives an expression for dS:

$$dS = \frac{1}{T}dU + \frac{P}{T}dV$$

Use calculus on U: $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$ to get

$$dS = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T}\left(\left(\frac{\partial U}{\partial V}\right)_T + P\right) dV \tag{2}$$

Now we can equate the coefficients in the two expressions, (1) and (2), for dS.

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V \qquad\qquad \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left(\left(\frac{\partial U}{\partial V}\right)_T + P\right)$$

$$\implies \frac{\partial}{\partial V}(\quad\uparrow\quad) \qquad = \qquad \frac{\partial}{\partial T}(\quad\uparrow\quad)$$

The fact that S is a state variable means the mixed partials must be equal. This gives

$$\frac{1}{T}\frac{\partial^2 U}{\partial T \partial V} = \frac{1}{T}\frac{\partial^2 U}{\partial V \partial T} - \frac{1}{T^2}\left(\left(\frac{\partial U}{\partial V}\right)_T + P\right) + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V$$

$$\implies \left(\left(\frac{\partial U}{\partial V}\right)_T + P\right) = T\left(\frac{\partial P}{\partial T}\right)_V$$

We've rewritten $\left(\frac{\partial U}{\partial V}\right)_T$ in terms of things that are easier to measure – P and its derivatives. To see that this is something nicely measurable we do one more manipulation:

We've shown that
$$C_P - C_V = V\alpha\left(T\left(\frac{\partial P}{\partial T}\right)_V\right)$$

On the other hand, the reciprocity relation implies
$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{-1}{\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial T}{\partial V}\right)_P} = \frac{-1}{(-V\kappa_T)\frac{1}{V\alpha}} = \frac{\alpha}{\kappa_T}.$$

Since we can write it in terms of things that have historical names, it must be measurable.

$$\boxed{C_P - C_V = \frac{VT\alpha^2}{\kappa_T}}$$

This expression (or its derivation) involves basically everything we've learned so far.

A few things we can deduce from it:

- We know that $C_P - C_V \geq 0$. So consistency with this expression means $\kappa_T > 0$. (If this is not true, the system will explode or collapse.)

- $C_P - C_V = 0$ if $\alpha = 0$. That happens when $\left(\frac{\partial V}{\partial T}\right)_P = 0$.
  This happens for water at $4°C$.

Aside: we've shown along the way here that
$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V.$$

This is an example of a "Maxwell Relation". (A different kind of Maxwell relations are shown at right.) There are actually more of them, and we'll derive them systematically soon in §5.4.

5.2 Efficiency of heat engines

Recall:

1. A heat engine takes a system (some assembly of some substance) around a *closed cycle* over and over. It returns to the initial state after one cycle.

2. Heat is transferred into and out of the substance. Some part of the cycle involves a cold sink.

   Conventions:
   Q_H is the heat taken in from the hot reservoir.
   Q_C is the heat spat out to the cold sink.
 W_{OUT} is the work done *by* the system.

3. Work is performed.

4. Efficiency is a subjective thing, in that it is defined as the ratio of (what we want) to (what we use up) – it depends on our goals. For heat engines, efficiency is defined by

$$\eta \equiv \frac{\text{work out}}{\text{heat in from hot source}} = \frac{W_{\text{out}}}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

If all of Q_H enters from a reservoir at a single T_H, and
if all of Q_C exits to a reservoir at a single T_C, and
if the engine operates quasistatically
then this is called a *Carnot engine*.[1] Then the following is true:

$$\text{Carnot:} \quad \Delta S_H = \frac{Q_H}{T_H} \quad \Delta S_C = -\frac{Q_C}{T_C}$$

where ΔS_H is the change in entropy of the system during the heating stage of the cycle and ΔS_H is the change in entropy of the system during the cooling stage of the cycle. When we heat the system, we increase its entropy; when we extract heat, we decrease its entropy.

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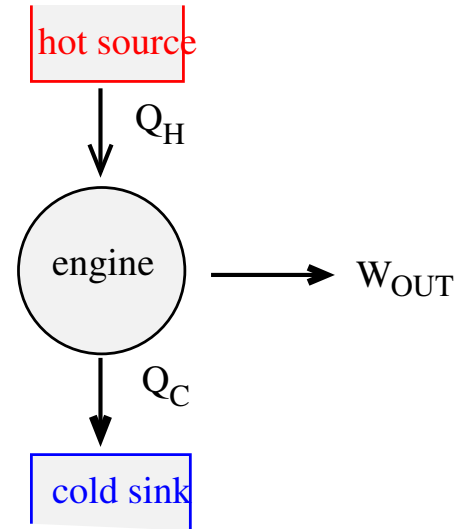
[1]Below we will consider more complicated things, *e.g.* more isothermal legs and more adiabatic legs. They will compare unfavorably with Carnot.

S is a state function, and we are going in a closed cycle, so during one whole cycle:

$$0 = \Delta S_{\text{TOT}}.$$

Finally, if we assume quasistatic operation, then the adiabatic legs involve no change in entropy:

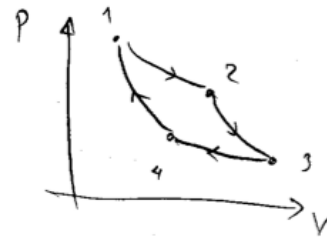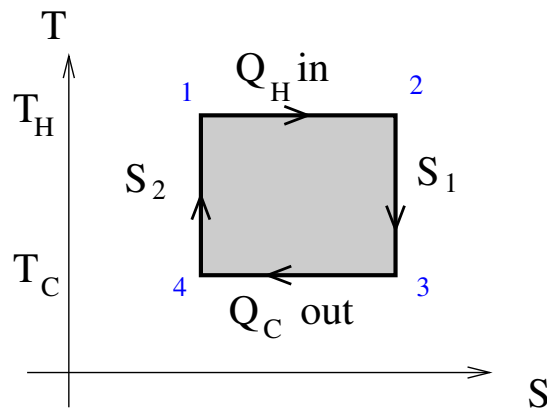$$0 = đQ = TdS \qquad \text{for adiabatic steps.}$$

So:

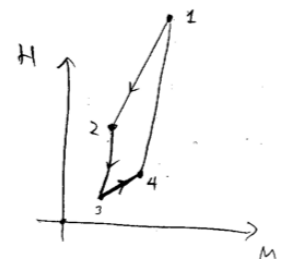$$0 = \Delta S_{TOT} = \frac{Q_C}{T_C} - \frac{Q_H}{T_H}$$

$$\implies \frac{Q_C}{T_C} = \frac{Q_H}{T_H}$$

$$\implies \boxed{\eta = 1 - \frac{T_C}{T_H}}.$$

There can be many implementations of such a Carnot engine: *e.g.* one where the substance in question was an ideal gas, or one involving a paramagnet. They all look the same on a T-S diagram:

The P-V diagram and the H-M diagram would look quite different from each other:

If everything is done quasistatically

$$\underbrace{\oint T\,dS}_{\text{=area enclosed in TS diagram}} = \oint đQ = Q_H - Q_C \overset{\text{1st Law}}{=} W_{OUT}$$

On the other hand, S is a state function means that

$$0 = \oint_{\text{any closed cycle}} dS \overset{\text{quasistatic}}{=} \oint \frac{đQ}{T}$$

If the cycle is *not* traversed quasistatically,

$$dS > \frac{đQ}{T} \qquad \Longrightarrow \qquad \oint \frac{đQ}{T} < 0$$

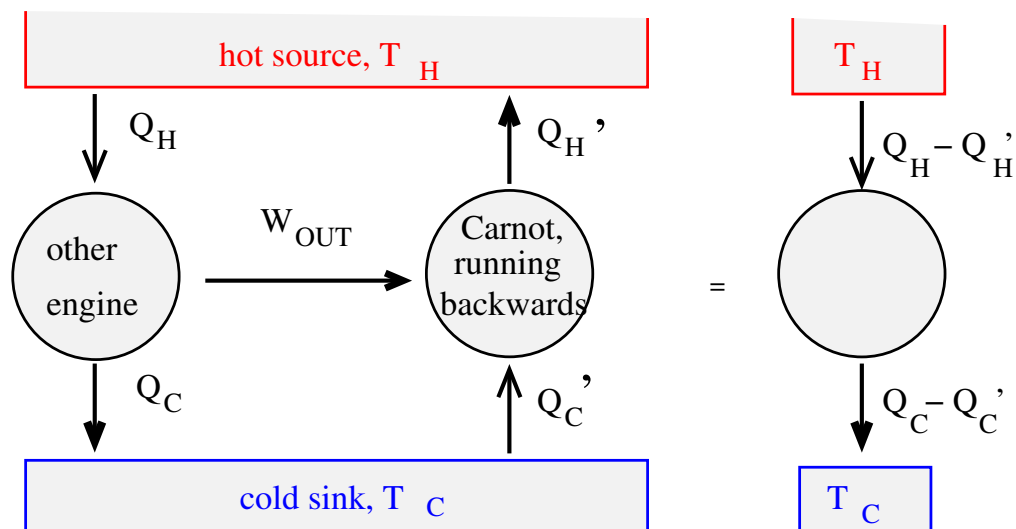$$\boxed{\oint \frac{đQ}{T} \leq 0} \qquad \text{Clausius' Theorem}$$

and the inequality is saturated for quasistatic cyclic processes (= Carnot engines).

Carnot is the best

Two arguments that Carnot efficiency is the maximum possible:

Consider a cyclic but *not* quasistatic engine which takes heat from some reservoir at T_H and dumping into a cold sink at T_C, just like the engine we just studied.

Clausius' Statement of 2nd Law: $Q_H - Q'_H \geq 0 \implies Q_H \geq Q'_H$. (Similarly for $Q_C \geq Q'_C$.)
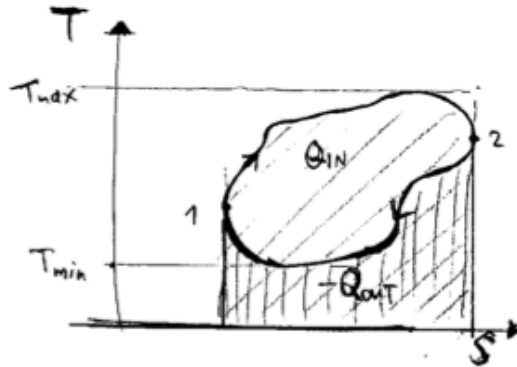
$$\implies \frac{W_{OUT}}{Q_H} \leq \frac{W_{OUT}}{Q'_H}$$

$$\implies \eta_{\text{other engine}} \leq \eta_{\text{carnot engine}}.$$

Carnot is the best, part 2

Q: Can we do better if we construct some complicated protocol involving reservoirs at different temperatures?

Consider the cycle of an arbitrary, quasistatic engine in the TS plane:

$$\eta = \frac{W}{Q_{IN}} = \frac{Q_{IN} - Q_{OUT}}{Q_{IN}} = 1 - \frac{Q_{OUT}}{Q_{IN}}.$$

$$Q_{IN} = \int_{\text{upper path from 1 to 2}} TdS \leq T_{\max} \int_1^2 dS = T_{\max}\left(S_2 - S_1\right).$$

$$Q_{OUT} = -\int_{\text{lower path from 2 to 1}} TdS = +\int_{\text{lower path from 1 to 2}} TdS \geq T_{\min} \int_1^2 dS = T_{\min}\left(S_2 - S_1\right).$$

These facts combine to imply that

$$\eta = 1 - \frac{Q_{OUT}}{Q_{IN}} \leq 1 - \frac{T_{\min}\left(S_2 - S_1\right)}{T_{\max}\left(S_2 - S_1\right)} = 1 - \frac{T_{\min}}{T_{\max}} = \eta_{\text{Carnot}}$$

It is less than the efficiency of a Carnot engine with just two reservoirs, one at $T_{\min}$ and one at $T_{\max}$.

A: No.

[End of Lecture 13.]

5.3 Refrigerators and heat pumps

Refrigerator: run the cycle backwards, extract heat at the cold end and dump heat into the hot reservoir. Accomplishing this requires that we do work on the system, $Q_H = W + Q_C$.

Assume that this is a Carnot refrigerator, *i.e.* everything is reversible, and there's just two temperatures involved T_H, T_C.

We know:
$$\frac{W}{Q_H} = 1 - \frac{T_C}{T_H}, \qquad \frac{Q_C}{Q_H} = \frac{T_C}{T_H}$$
but this isn't what we care about in judging whether this is a good refrigerator.
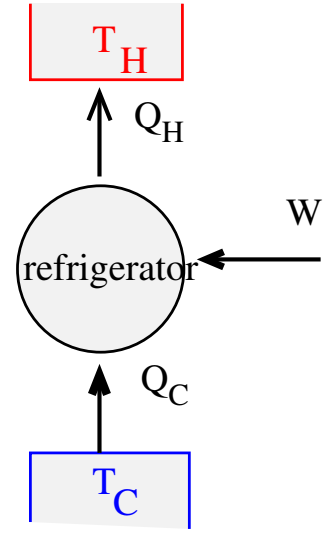
$$\eta_{\text{refrig}} = \frac{\text{what we want}}{\text{what we use up}} = \frac{\text{heat extracted from cold end}}{\text{work done on system}} = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C} = \frac{T_C}{T_H - T_C}$$

For $\frac{T_H}{T_C} = 1+$ a little, $\eta_{\text{refrig}} \gg 1$ – easy to cool without doing a lot of work, low power.

For $T_C \to 0, \eta_{\text{refrig}} \to 0$. It becomes increasingly difficult to cool something as $T \to 0$.

$T = 0$ is the point at which no further heat can be extracted.

Reaching $T = 0$ requires an infinite amount of work.

Heat Pump

Same setup, but with a different goal.

Suppose we want to heat the hot end, not cool the cold end.

$$\eta_{\text{heat pump}} \equiv \frac{Q_H}{W} = \frac{Q_H}{Q_H - Q_C} \overset{\text{if reversible}}{=} \frac{T_H}{T_H - T_C}$$

Now we have completed the rigorous version of Chapter 1.
Go back and read Chapter 1 again.

One more item in thermodynamics, however:

5.4 Legendre transforms, thermodynamic potentials, and Maxwell relations

A while back, we saw that we could start with[2]

$$E = E(S, V)$$

in terms of which the 1st Law for quasistatic processes is:

$$dE = T dS - P dV$$

and from this construct a new state variable:

$$H \equiv E + PV \qquad \text{enthalpy}$$

$$dH = dE + P dV + V dP \implies dH = T dS + V dP \tag{3}$$

Note then that the enthalpy H is most naturally $H(S, P)$. It is most useful in analyzing processes at constant pressure, in which case (3) reduces to

$$dH = \dbar Q$$

(this is true even if the process is not quasistatic).

E and H are two examples of *thermodynamic potentials.*

The step of going from $E(S, V)$ to $H(S, P)$ is an example of a *Legendre Transform.*

A place where you might have seen this operation is going between Lagrangian and Hamiltonian descriptions in classical mechanics.

As there, the same physics can be described using E or H. Sometimes one is more convenient than the other. For example:

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V \qquad\qquad\qquad C_P = \text{complicated expression with derivs of } E$$

$$C_V = \text{complicated expression with derivs of } H \qquad\qquad C_P = \left(\frac{\partial H}{\partial T}\right)_P$$
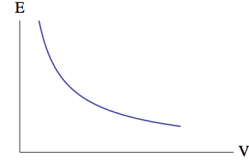
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[2]We wrote it as $U = U(S, V)$; if you like, this is the relation $S = S(U, V)$, rearranged by solving for the internal energy.
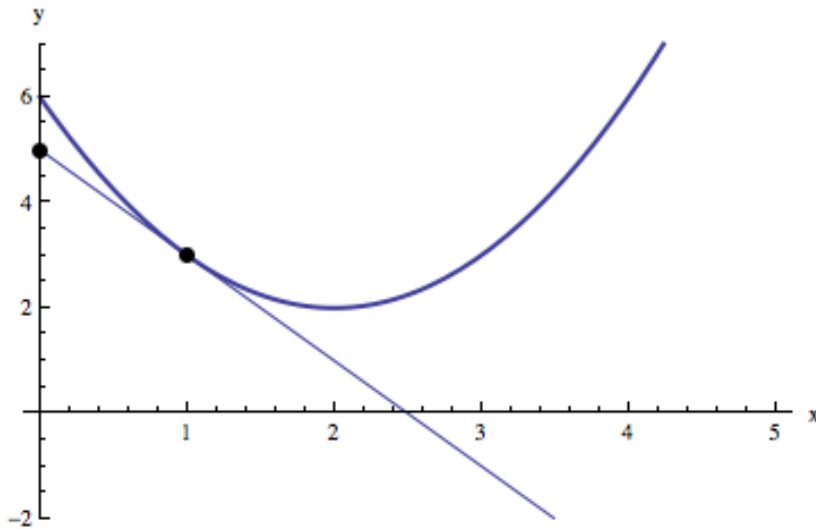
A mathematical interlude on Legendre Transform

Consider a function $y(x)$ whose second derivative $y''(x)$ is nowhere zero. (So it is everywhere concave, or everywhere convex.)

[Think of $E = E(V)$ at fixed S: $E = \frac{3}{2}Nk_BT, VT^{3/2} = $ const $\implies$ $E(V,S) \propto V^{-2/3}$.]

Geometric interpretation:

Consider the point $(x, y) = (x, y(x))$ along the curve $y(x)$; draw the tangent line through this point. It has slope $y' = y'(x)$. Its y-axis-intercept is at

$$I \equiv y - xy'.$$

We can represent the information about the same curve as either $y(x)$ or as $I(y')$. Here's the protocol for doing the latter:

Pick a y'. Draw a line with that slope. Slide it up and down until it is tangent to the curve $y(x)$; the resulting line has y-intercept $I(y')$. Repeat for however many values of y' you want.

This collection of straight lines (determined by $I(y')$) is the "envelope of tangents" of the curve of interest $y(x)$.

$$y(x) \leftrightarrow I(y')$$

Contain the same information, determine the same curve.

In the definition of $I \equiv y - xy'$, you recognize the formula for Legendre transformation. Rewrite in terms of thermo letters:

$$y(x) \rightarrow \underbrace{E}_{\text{think of this as } y} \quad (S, \quad \underbrace{V}_{\text{think of this as } x} \quad)$$
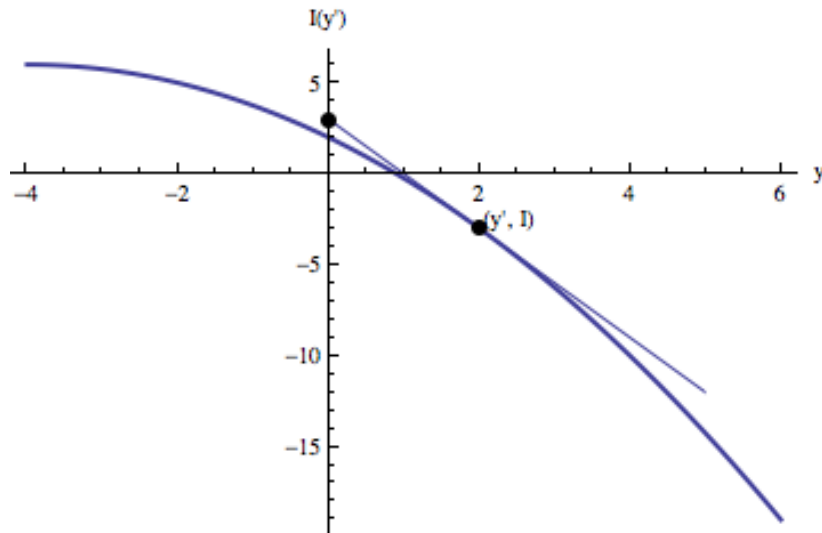
and S is just a spectator.

$$y' = \left(\frac{\partial E}{\partial V}\right)_S = -P.$$

$$\underbrace{I}_{H}(\underbrace{y'}_{-P}) = y - xy' = E + PV = H(S, P).$$

So $E(S, V)$ and $H(S, P)$ describe the same physics. [3]

Now we can Legendre transform back:

In the plot I have shown the curve $I(y')$.[4] Also indicated are the point (y', I) and the vertical-axis-intercept of the tangent through that point. Its height is

$$I - y'\frac{\partial I}{\partial y} \equiv \tilde{I}.$$

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[3] As long as E is a convex (or concave) function of V. This is in fact a requirement for stability.

[4] I'm using the $I(y')$ for the function I plotted above, which was $y(x) = (x - 2)^2 - 2$. This means

$$y'(x) = 2(x - 2) ;$$

I solved this for $x(y') = (4 + y')/2$ and plugged that into

$$I(y') = y(x) - xy' = 2 - 2y' - (y')^2/4.$$

We can represent the data in $I(y')$ just as well by $\tilde{I}(\frac{\partial I}{\partial y})$. But

$$\frac{\partial I}{\partial y'} = -x \quad \implies \quad \tilde{I} = I + xy' = y$$

That is, $\tilde{I} = y(x)$. So the Legendre transform squares to one, *i.e.* undoes itself.

Returning to physics variables again, start with $H(S, P)$ and $dH = TdS + VdP$. Construct $E = H - PV$.

$$dE = TdS - PdV$$

So this is $E(S, V)$.

So to go back and forth between E and H we Legendre transform, either way.

Maxwell Relations

$$dE = TdS - PdV \qquad\qquad dH = TdS + VdP$$

$$\implies \left(\frac{\partial E}{\partial S}\right)_V = T \qquad \left(\frac{\partial E}{\partial V}\right)_S = -P \qquad\qquad \implies \left(\frac{\partial H}{\partial S}\right)_P = T \qquad \left(\frac{\partial H}{\partial P}\right)_S = V$$

E is a state variable. $\qquad\qquad$ H is a state variable.

equate mixed partials of E: $\qquad\qquad$ equate mixed partials of H:

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

So: Maxwell Relations follow by equating mixed second derivatives of thermodynamic potentials. The second one is the one we encountered previously.

More thermodynamic potentials → more Maxwell relations

So far S has just gone along for the ride in our Legendre transforms: we haven't touched the TdS bit. We can Legendre transform that bit, too:

$$\text{Define} \quad \boxed{F = E - TS} \quad \text{``(Helmholtz) Free Energy''}$$

(Mnemonic: 'F' is for 'free'.)

$$dF = dE - TdS - SdT \quad \Longrightarrow \quad \boxed{dF = -SdT - PdV}$$

So $F = F(T, V)$.

[Preview: in the next Chapter, we will formulate statistical mechanics for a system which is *not* isolated, and in particular is held at constant temperature by a heat reservoir. F will play a key role.]

From this expression, we deduce:

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

Equating crossed derivatives gives our 3rd Maxwell relation:

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

The 4th Maxwell relation, by the Method of the Missing Box

$$
\begin{aligned}
E &= E(S,V), \\
dE &= TdS - PdV, \\
\left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V
\end{aligned}
$$

$\boxed{H = E + PV}$ ✓

↘ $\boxed{F = E - TS}$

$$
\begin{aligned}
H &= H(S,P), \\
dH &= TdS + VdP \\
\left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P
\end{aligned}
$$

$$
\begin{aligned}
F &= F(T,V), \\
dF &= -SdT - PdV, \\
-\left(\frac{\partial S}{\partial V}\right)_T &= -\left(\frac{\partial P}{\partial T}\right)_V
\end{aligned}
$$

$\boxed{G = H - ST}$ ↘

✓ $\boxed{G = F + PV}$

$$
\begin{aligned}
G &= G(T,P), \\
dG &= -SdT + VdP, \\
-\left(\frac{\partial S}{\partial P}\right)_T &= \left(\frac{\partial V}{\partial T}\right)_S
\end{aligned}
$$

G is for "Gibbs' Free Energy". The 4th and last thermodynamic potential (for a hydrostatic system): E, F, G, H.

You should be able to quickly recreate this derivation of the four Maxwell relations.
$\boxed{\text{DO NOT MEMORIZE THIS STUFF.}}$

Note that you can do this operation for *any* pair of conjugate variables. In systems with more thermodynamic variables, there are more thermodynamic potentials. For example in a system with a magnetization, $E = E(S,V,M)$ so

$$dE = TdS - PdV + HdM$$

and we can construct a new thermodynamic potential whose name is not standard:

$$I = I(S,V,H) \equiv E - HM$$

for which

$$dI = TdS - PdV - MdH.$$

Conditions for equilibrium (The point of F and G, and why they are called 'free' energies.)

1. Consider a system in contact with a bath at temperature T. Suppose the system is equilibrating at constant V.

   As it equilibrates, the 2nd Law tells us: $dS \geq \dfrac{dQ}{T_{\text{bath}}}$.

   Since V is constant, $dV = 0 \implies dW = 0$ so the 1st Law is: $dE = dQ$:

   $$dS \geq \frac{dE}{T_{\text{bath}}}$$

   $$\implies d\left(E - T_{\text{bath}}S\right) \leq 0$$

   $$\boxed{dF \leq 0} \qquad \text{at constant } V, T_{\text{bath}}$$

   So: at constant V, T, **the system evolves so as to minimize F.**

2. Suppose instead that work can be done, $dV \neq 0$, as the system equilibrates, but P is held constant.

   $$dS \geq \frac{dQ}{T_{\text{bath}}} = \frac{dE + PdV}{T_{\text{bath}}}$$

   $$\implies d\left(E - T_{\text{bath}}S + \underbrace{P}_{\text{assumed constant}} V\right)$$

   $$\implies \boxed{dG \leq 0} \qquad \text{at constant } P, T_{\text{bath}}$$

   So: at constant P, T, **the system evolves so as to minimize G.**

   Note also that at fixed P,

   $$d\left(E - TS\right) \leq -PdV$$

   $$\implies dF \leq +dW$$

   $$\implies \boxed{-dF \geq -dW}$$

   $-dW$ is the work done **by** the system.

   During relaxation to equilibrium at constant T and P, the work done *by* the system is less than or equal to the (magnitude of the) change in F, as F decreases.

   This is why F is called the 'Free Energy' or 'available energy'.

This is all the thermodynamics we're going to need, except for Chapter 8: Chemical Potential.

Next: the version of Stat Mech that we actually *use*.