8.044 Lecture Notes
Chapter 3: Thermodynamics, first pass

Lecturer: McGreevy

Reading: CJ Adkins, *Equilibrium Thermodynamics*, Chapters 1, 2, 3.1-3.7.
Skip Adkins §3.5.4.
R Baierlein, *Thermal Physics*, Chapter 1.

The four laws of thermodynamics [according to Prof. Yosi Avron]:

0th Law: You have to play the game.

1st Law: You can't win.

2nd Law: You can't even break even.

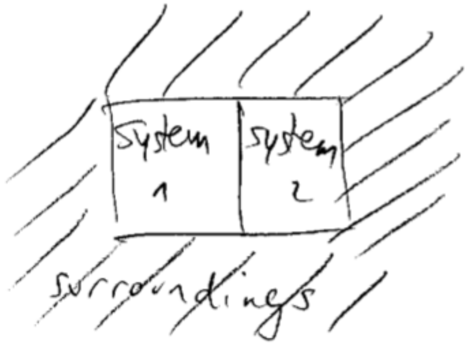
3rd Law: And you can't quit.

To counter your impatience to get to statistical mechanics, let me offer the following [from Prof. David Tong]:

> *...the weakness of thermodynamics is also its strength. Because the theory is ignorant of the underlying nature of matter, it is limited in what it can tell us. But this means that the results we deduce from thermodynamics are not restricted to any specific system. They will apply equally well in any circumstance, from biological systems and quantum gravity. And you cant say that about a lot of theories!*

3.1 Basic terminology

We will often refer to system(s) and surroundings.



Systems can be separated by boundaries of "walls" that can be either

- *adiabatic*: No heat can flow between them. Adiabatic walls keep the systems isolated.

system 1 T_1	system 2 T_2

... or ...

- *diathermal*: Heat can flow. (Particles cannot.) This means that after a little while $T_1 = T_2 = T$.

system 1 T	system 2 T

The macroscopic state of each system is described by thermodynamic varaibles.

These can be

- *extensive*: proportional to N, the number of particles
  ... or ...
- *intensive*: not proportional to N. Local in character.

The number of particles N is extensive. If I divide the room in half, (roughly) half the atoms will end up in each half. Similarly, energy is extensive. On the other hand, the temperature of each half of the room will be unchanged; temperature is intensive.

I claim that no other dependence on N will arise in the thermodynamic (large N) limit, at least in 8.044.

Examples:

Type of system	**Extensive Variable**	**Intensive Variable**
Gas or liquid in a cylinder	V volume	P pressure
2-dimensional film	A area	σ surface tension
filament or elastic rod	L length	f tension
electrically charged object	q charge	$\mathcal{E}$ voltage, EMF
dielectric material	$\vec{P}$ polarization	$\vec{E}$ electric field
paramagnetic material	$\vec{M}$ magnetization	$\vec{H}$ magnetic field
any system	S entropy	T temperature

The product of each pair has units of energy.

$$P\Delta V, \sigma\Delta A, f\Delta L, \mathcal{E}\Delta q, \vec{E}\cdot\Delta\vec{P}, \vec{M}\cdot\Delta\vec{H}$$

are all measures of *work*.

Such pairs of thermodynamic state variables and their associated generalized force are called *conjugate variables*.

T and S are also called conjugate variables, although $T\Delta S$ is related to heat, not work.

Thermodynamic, or Thermal, Equilibrium

When the surroundings of a system change, the system itself will change. After a time, no further macroscopically-detectable changes take place. Transients have died down. We say the system is in *equilibrium*.

The equilibrium state of a system is completely specified by a certain number (this number is called the number of (thermodynamic) degrees of freedom) of independent variables. In equilibriumhese specify the other variables via *equations of state*.

Classic example: ideal gas, with a fixed number of particles N.
Equation of state (EoS): $PV = Nk_BT$.
So, we can take P, V OR P, T OR V, T as the two independent varaibles. The third is the determined by the EoS.

An EoS is a functional relationship among thermodynamic variables that is satisfied *in equilibrium*.

Another example: Curie's Law for a paramagnet. $M = C_C \frac{H}{T}$. M is magnetization, H is an applied magnetic field, T is temperature. C_C is a constant. Valid for H/T not too large.

These examples above have two thermodynamic degrees of freedom (dofs). It's easy to generalize: *e.g.* consider a magnetic gas, where the atoms have spins. Then we need P, V *and* M, H.

We could also add more variables
(like say the compressibility κ of the gas),
but these would satisfy the same number of additional relations
(in this case, the new relation would be $\kappa = -V^{-1}\left(\frac{\partial V}{\partial p}\right)_T$).
In general there may be other variables of the system which are independent, but which we're not going to vary. In that case we can ignore them.

Thermodynamic Reversibility

A series of changes undergone by a system is *reversible* iff its direction can be reversed by an infinitesimal change in the condition. (*e.g.*: yanking the piston out of the cylinder is not reversible. Moving it out very slowly may be.)

Reversibility requires:

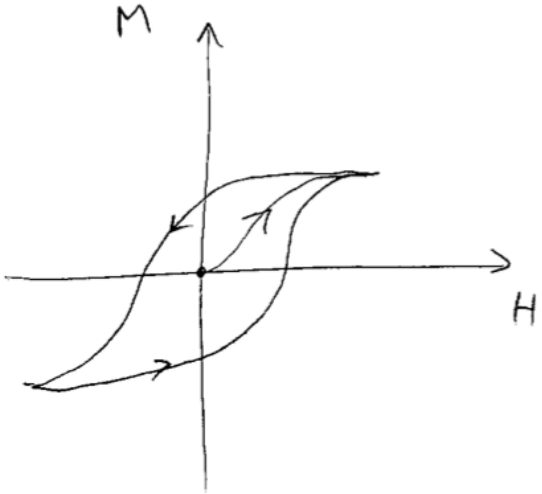
1. **Quasistatic processes**: (slowness) All changes must be made so slowly that every state through which the system passes may be considered an equilibrium state.
   In particular: $PV = NkT$ always satisfied
   no shock waves
   no energy dissipated due to friction: frictional forces $\propto v$.

   $$\Delta E_{\text{lost to friction}} \propto v \times \text{distance} \overset{v \to 0}{\to} 0.$$

   These are limits of real processes, performed arbitrarily slowly.

   Drawing lines on a PV diagram only makes sense for such quasistatic processes.

2. **No hysteresis** Even if all the stuff is done arbitrarily slowly, there are situations where what seemed like a closed loop in parameter space is not closed.



   e.g. bar of iron. Even if we quasistatically vary the applied field, the state of a ferromagnet depends on its history.

   e.g. rod under tension, when it deforms.

Having said this, in 8.044 we will only discuss systems for which quasistatic = reversible. That is, we will have no truck with hysteresis here. That's for 8.08.

[End of Lecture 7.]

3.2 0th Law of Thermodynamics and definition of temperature

Define: A is ”in equilibrium with” B if when we stick them next to each other, separated by a diathermal wall, nothing happens – no macroscopic change occurs.

Zeroth law: ”in equilibrium with” is a transitive property.

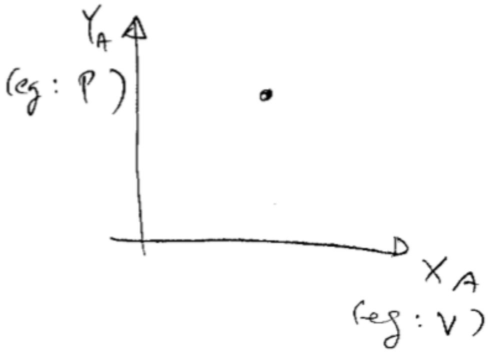
That is: If system A is in equilibrium with system B
and system B is in equilibrium with system C
then system A is in equilibrium with system C.

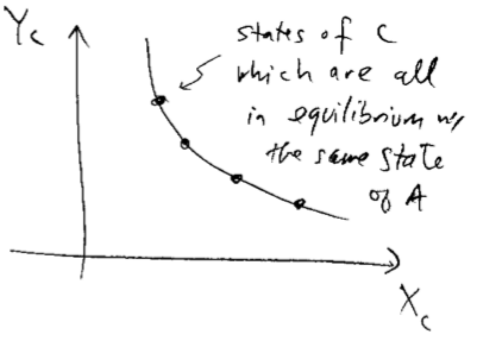
Once more, in symbols:

$$\underbrace{\boxed{A\,|\,B}}_{\text{in equilibrium}} \quad \text{and} \quad \underbrace{\boxed{B\,|\,C}}_{\text{in equilibrium}} \quad \Longrightarrow \quad \underbrace{\boxed{A\,|\,C}}_{\text{in equilibrium}}$$

Now, think of B as a thermometer! This fact makes thermometers possible.

Observation: many macroscopic states of C can be in equilibrium with a given state of A.





On the right, I've drawn the locus of states of C that are *all* in equilibrium with the same state of A. This is an isotherm.

Similarly, if I fix the state of C, there will be a locus (a curve in this case) of states of system A which are in equilibrium with it.

The property that these states have in common is called *temperature.*

We can use the 0th Law to define an "empirical temperature" called Θ by Adkins.

Idea: the temperature of a system is some function of the other state variables that determines whether or not the system is in equilibrium with other systems.

Two systems are in equilibrium if they have the same temperature.

Note the order of the logic here:

1. definition of equilbrium
2. statement of 0th Law
3. definition of isotherm
4. definition of temperature

A pedantic implementation of this definition

Consider two systems A, B which are initially isolated:

$$\boxed{P_A, V_A} \text{ isolated from } \boxed{P_B, V_B}$$

P_A, V_A, P_B, V_B are all unspecified here. We're not assuming that these are ideal gases, but as always that's a good example to keep in mind.

Now bring them in contact, and adjust V_B (move a piston) until they are in equilibrium.

$$\boxed{P_A, V_A}\boxed{P_B, V_B}$$

(If you like, it is some additional input from our experience of the world that it is possible to do this.) Demanding equilibrium imposes one relation among the four state variables:

$$e.g. \quad V_B|_{\text{equilibrium with A}} = f_1(P_A, V_A, P_B) \tag{1}$$

Now repeat for C and B, *i.e.* bring a second system C in contact with B.

$$\boxed{P_B, V_B}\boxed{P_C, V_C}$$

Hold fixed the parameters of B and adjust V_C to put $B + C$ in equilibrium. Again this gives one relation between the thermodynamic variables (this time of $B + C$), which I choose to express as:

$$e.g. \quad V_B|_{\text{equilibrium with C}} = f_2(P_C, V_C, P_B)$$

$$\text{Claim:} \quad f_1(P_A, V_A, P_B) = f_2(P_C, V_C, P_B) \tag{2}$$

by the 0th Law – if we got different values for V_B in these two cases, "equilibrium with" wouldn't be transitive. This equation (2) is one equation for 5 variables. Solve (2) for V_A:

$$V_A = g(P_A, P_C, V_C, P_B) \tag{3}$$

Now repeat the story for $A + C$ (adjust V_A to put it in equilibrium with C):

$$V_A = f_3(P_A, P_C, V_C) \tag{4}$$

Eqn. (4) determines V_A in terms of P_A, P_C, V_C.

But now combine the information in (3) and (4): if we plug the expression in (4) for V_A into (3) we discover that we can find g without knowing anything about P_B – g is independent of P_B. This is only possible if the equation (2) relating f_1 and f_2 is independent of P_B.[1] This allows us to rewrite equation (2) in a way that makes no reference to B:

$$f_1(P_A, V_A) = f_2(P_C, V_C) \equiv \Theta$$

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[1] Note that in fact $f_{1,2}$ themselves can depend on p_B in such a way that the dependence cancels. This is what happens *e.g.* for the ideal gas, where $P_A V_A = N k_B T$, so in this case $f_1(P_A, V_A, P_B) = \frac{P_A V_A}{P_B}$ and $f_2(P_C, V_C, P_B) = \frac{P_C V_C}{P_B}$. Equating these, we learn that $P_A V_A = P_C V_C$, each side of which is independent of system B (and is proportional to the temperature). Thanks to Sabrina Gonzalez Pasterski for correcting an error on this point.

We've found a function of state variables of system C which is equal to a function of the state variables of system A when they are in equilibrium.

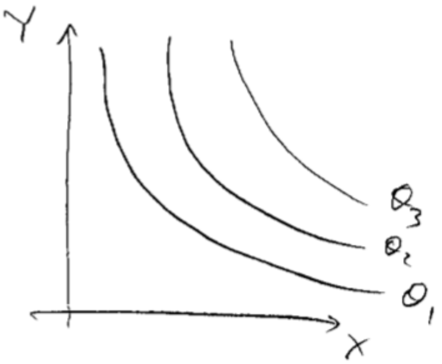
For each of the systems in equilibrium, there is a function of its state variables that takes on the same value:

$$\Theta = f_1(P_A, V_A) \text{ is EoS for A (gives shape of isotherm)}$$

$$\Theta = f_2(P_B, V_B) \text{ is EoS for C (gives shape of isotherm)}$$

Note that we could have called P, V here X, Y for some generic state variables. Details about gases are not relevant at all.

For any of the systems, we can now map out isotherms with varying Θ.



We can also determine that $\Theta_3 > \Theta_2 > \Theta_1$ by watching the *direction* of heat flow when we bring systems on the respective isotherms into contact. $\Theta_1 > \Theta_2$ if heat goes from 1 to 2.

Q: Suppose A, B have the same temperature. How do we know that the direction of heat flow is transitive – *i.e.* that it is the same between $A + C$ and between $B + C$?
A: We know because the states of A, B define *one* isotherm of C, by the 0th Law.

To choose units of temperature, we need to make some choices.

Thermodynamic temperature

... is a concept defined by Atkins, roughly Θ with units. It is measured in Kelvin (defined below). Based on the fact (we'll explain this later) that all gases *in the dilute limit* satisfy

$$PV = Nk_BT \quad .$$

The dilute limit is $P \to 0, V \to \infty$, with PV fixed. (Note that the curves I've been drawing are the hyperbolae in (P, V) specified by constant T in this ideal gas law.)

So we can use *any* gas to define a temperature scale, via

$$T = \text{const} \lim_{P\to 0, V\to\infty} PV \ .$$

This is is nice in that it doesn't depend on which gas we use.

The choice of constant is a convention:

$$T(\text{in Kelvin}) = 273.16 \frac{\lim_{P\to 0, V\to\infty} (PV \text{ of the gas whose } T \text{ we're defining})}{\lim_{P\to 0, V\to\infty} (PV)_{TP}}$$

where $(PV)_{TP}$ is the PV of the gas in question when it is in equilibrium with water at its Triple Point.
Definition of Triple Point: liquid water, solid water (ice), and gaseous water (vapor) are all in equilibrium with each other at

$$T_{TP} \equiv 273.16K = 0.01°C \text{ and } P_{TP}^{H_2O} = 611Pa = 0.006atm.$$

This is a useful convention because the triple-point of water is reproducible.

Then:

$$T(\text{water boils, at 1 atm}) = 373.15K = 100°C$$
$$T(\text{water freezes, at 1 atm}) = 273.15K = 0°C$$

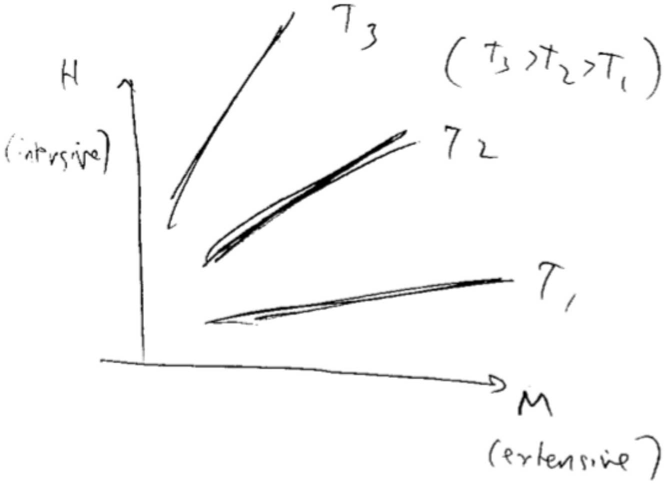
(The number 273.16 was chosen so that we get 100° between freezing and boiling of water.)

Although it's reproducible, this scale is not so practical. We can now use this dilute gas thermometer to calibrate other, more practical, thermometers. Any physically observable quantity which varies with temperature can be used. You can imagine therefore that lots of things have been tried. e.g.
expansion of liquids,
resistance (temperature dependence of resistance of metals and semiconductors),
thermocouples...
Different systems are useful for different temperature ranges and different sensitivities (there is generally a tradeoff between how sensitive a thermometer is and how large a range it can measure).

Combining all these together is something called the "International Practical Temperature Scale" which you can read more about in Adkins.

Then we can use these thermometers to map out isotherms of other systems. They are not always hyperbolae.

e.g. a paramagnet.



$$T = \text{const}\frac{H}{M} \quad .$$

Mapping isotherms ≡ empirical determination of equation of state.

3.3 Differential changes of state and exact differentials

Imagine an equation of state written as

$$V = f(P,T) \qquad \text{(think of } V = \frac{NkT}{P}\text{)} \tag{5}$$

An infinitesimal change from one state of equilibrium to another state of equilibrium involves tiny changes of of each of the state variables: dV, dT, dP. Since both states of equilibrium satisfy (5), we must have

$$dV = \left(\frac{\partial f}{\partial P}\right)_T dP + \left(\frac{\partial f}{\partial T}\right)_P dT$$

We can avoid the waste of an extra symbol by writing the EoS as $V = V(P,T)$ and therefore

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

I remind you that when we have several independent variables, we need to be careful in specifying what we mean by a derivative – we have to specify what is held fixed; this is indicated by the subscript: $\left(\frac{\partial x}{\partial y}\right)_z$ means the derivative of x with respect to y with z held fixed.

The coefficients above have names, because they can be measured.

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \quad \text{is called the } \textit{isothermal compressibility}$$

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \text{is called the } \textit{volume expansivity.}$$

Both are determined from the two independent variables (whichever two we pick) by the equation of state.

Similarly,

$$P = P(T,V) \quad \Longrightarrow \quad dP = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT$$

$$T = T(P,V) \quad \Longrightarrow \quad dT = \left(\frac{\partial T}{\partial V}\right)_P dV + \left(\frac{\partial T}{\partial P}\right)_V dP$$

These partial derivative quantities (like κ_T and α) of the form

$$\left(\frac{\partial \text{something}}{\partial \text{something else}}\right)_{\text{a third thing}}$$

are called *response functions*. How does the system's *something* respond when we make a perturbation of its *something else* under conditions where its *a third thing* is held fixed? This kind of thing is often what gets measured in experiments.

We've written six of them on the board. They are not all independent.

You can show (see Adkins and recitation and subsection 3.3.1) that if three variables x, y, z are related by one equation of the form

$$x = x(y, z) \text{ or } y = y(x, z) \text{ or } z = z(x, y)$$

then: $$\boxed{\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}}$$ ('Reciprocity Theorem')

and the two other equations related by permuting the varaibles. Note that the same quantity is held fixed on both sides.

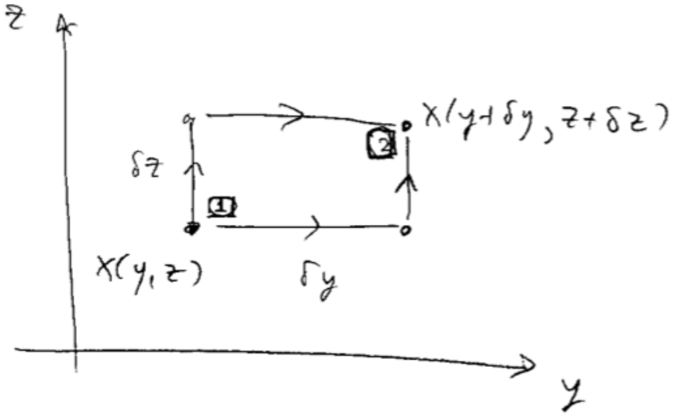
$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1}$$

These identities (just math, no physics) reduce six response functions to two independent ones. We'll use these over and over.

Exact differentials.

A third useful identity is

$$\boxed{\partial_z \left(\frac{\partial x}{\partial y}\right)_z = \partial_y \left(\frac{\partial x}{\partial z}\right)_y}$$



This identity says that it doesn't matter which path you take from the point $\boxed{1}$ to the point $\boxed{2}$. The end result, $x(\boxed{2})$, is the same no matter which path you take to get there. This is true as long as $x(y, z)$ is a smooth, single-valued function.

Terminology: If $x = x(y, z)$ is such a nice function then the expression

$$dx = \underbrace{A(y, z)}_{=\left(\frac{\partial x}{\partial y}\right)_z} dy + \underbrace{B(y, z)}_{=\left(\frac{\partial x}{\partial z}\right)_y} dz$$

is called an *exact differential*.

Integrating exact differentials.

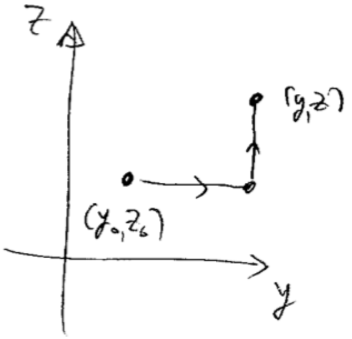
Suppose you know A, B (*e.g.* because you measured them), in $dx = Ady + Bdz$. How can you reconstruct the state variable $x(y, z)$?

First, in order for x to exist, it's necessary that its mixed partials be equal:

$$\left(\frac{\partial A}{\partial z}\right)_y = \left(\frac{\partial B}{\partial y}\right)_z$$

This is a necessary and sufficient condition for dx to be exact[2]

If your functions A, B pass this check, you can proceed as follows. The overall additive constant in x isn't fixed. Pick a random starting point y_0, z_0 and declare $x(y_0, z_0) = 0$. (Usually there will be some additional physical input that fixes this ambiguity.) To get x at some other point (y, z) we integrate along a path from (y_0, z_0) to (y, z); since the answer is path-independent, we can pick a convenient path. I pick this one:



Taking it in two steps, we have from the first horizontal leg:

$$x(y, z_0) = \int_{y_0}^{y} dy' A(y', z_0)$$

$$\text{Then:} \quad x(y, z) = \int_{y_0}^{y} dy' A(y', z_0) + \int_{z_0}^{z} dz' B(y, z')$$

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[2] Optional cultural comment for mathy people: This assumes that there is no interesting topology of the space of values of the thermodynamic variables. We'll assume this always.

An alternative procedure, which is a little slicker (but gives the same answer, of course, up to the additive constant), is:

1. $$x(y,z) = \int dy A(y,z) + f(z)$$

   The last term here is like an integration constant, except it can still depend on z. We need to figure it out. To do that consider:

2. $$B = \left(\frac{\partial x}{\partial z}\right)_y = \int dy \partial_z A + \frac{df}{dz}$$

3. $$f(z) = \int dz \left(B - \int dy \partial_z A\right)$$

$$\text{Result:} \quad x(y,z) = \int dy A(y,z) + \int dz B(y,z) - \int \int dy dz \left(\left(\frac{\partial A}{\partial z}\right)_y\right)$$

Example: a non-ideal gas

Suppose you have the following information (*e.g.* because you measured these things):

1. The system behaves like an ideal gas for large V.
2. $\left(\frac{\partial P}{\partial T}\right)_V = \frac{Nk}{V - Nb}$
3. $\left(\frac{\partial P}{\partial V}\right)_T = -\frac{NkT}{(V - Nb)^2} + \frac{2aN^2}{V^3}$

Find $P(V, T)$, the equation of state.

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

First check that it is an exact differential. I made sure that it is.

$$P = \int \frac{Nk}{V - Nb} dT + f(V) = \frac{NkT}{V - Nb} + f(V)$$

The additive constant is stuffed into $f(V)$ here.

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{NkT}{(V - Nb)^2} + f'(V) \overset{\text{fact 3}}{=} -\frac{NkT}{(V - Nb)^2} + \frac{2aN^2}{V^3}$$

Therefore:

$$f(V) = \int \frac{2aN^2}{V^3} dV = -\frac{aN^2}{V^2} + \text{const}$$

$$\Longrightarrow \boxed{P = \frac{NkT}{V - Nb} - a\frac{N^2}{V^2}} + \text{const}$$

The constant must be zero so that $PV = NkT$ at large V. (This is called the Van der Waals equation of state; it includes the leading corrections to a slightly non-ideal gas.)

3.3.1 Appendix: Reciprocity theorem, derivation

In case you are curious, here is the derivation of the 'Reciprocity Theorem' which applies also for N variables instead of 3 [Adkins, page 12 discusses the case of $n = 3$.]

Consider n variables satisfying one constraint

$$0 = F(x_1, ..., x_n), \tag{6}$$

so that $n - 1$ of them are independent. This specifies a locus in the n-dimensional space whose dimension is $n - 1$. We can write n different equations imposing the constraint

$$x_1 = x_1(x_2...x_n), x_2 = x_2(x_1, x_3...x_n), ..., x_n = x_n(x_1...x_{n-1}),$$

each of which encodes the same information about the shape of this $(n - 1)$-dimensional space. (In the case of $n = 3$, then, (6) specifies a surface in three dimensions.) Note that not all of these functions will be single-valued – a simple example is the case $x_1^2 = x_2$, in which there are two values of $x_1 = \pm\sqrt{x_2}$ for each value of x_2 (for $x_2 > 0$, or no real values if $x_2 < 0$). The relations we study below are true *locally*, *i.e.* pick a branch of solutions and stick with it.

The variation of any given variable as we move along the constraint surface can be expressed in terms of the variations of the others:

$$dx_1 = \sum_{j\neq 1} \frac{\partial x_1}{\partial x_j}|_{x_{l\neq 1,j}} dx^j \tag{7}$$

$$dx_2 = \sum_{j\neq 2} \frac{\partial x_2}{\partial x_j}|_{x_{l\neq 1,j}} dx^j \tag{8}$$

Note that you can actually ignore the annoying $|_{x_{l\neq 1,j}}$ bits here– they always express that all the other variables are fixed besides the two that are involved in the derivative. So I'm going to suppress them here to make the equations look better – you have to remember that they are there. Now substitute in (7) using (8) for dx_2:

$$dx_1 = \sum_{j\neq 1,2} \frac{\partial x_1}{\partial x_j} dx^j + \frac{\partial x_1}{\partial x_2} \left(\sum_{j\neq 1,2} \frac{\partial x_2}{\partial x_j} dx^j + \frac{\partial x_2}{\partial x_1} dx_1 \right)$$

Now we group terms together:

$$0 = dx_1 \left(-1 + \frac{\partial x_1}{\partial x_2} \frac{\partial x_2}{\partial x_1} \right) + \sum_{j\neq 1,2} \left(\frac{\partial x_1}{\partial x_j} + \frac{\partial x_1}{\partial x_2} \frac{\partial x_2}{\partial x_j} \right)$$

Now since we can vary x_1 and $x_3, x_4...x_n$ independently, this is actually $n - 1$ equations. Varying only x_1 we learn that:

$$-1 + \frac{\partial x_1}{\partial x_2} \frac{\partial x_2}{\partial x_1}$$

i.e.

$$\frac{\partial x_1}{\partial x_2}|_{\text{all others fixed}} = \frac{1}{\frac{\partial x_2}{\partial x_1}|_{\text{all others fixed}}}$$

Since $1, 2$ aren't special, we have

$$\frac{\partial x_i}{\partial x_j}|_{\text{all others fixed}} = \frac{1}{\frac{\partial x_j}{\partial x_i}|_{\text{all others fixed}}} \tag{9}$$

for any distinct i, j. This is sometimes called the "reciprocal theorem".

Varying any of the x_j with $j = 3..n$, we learn that:

$$\forall j \neq 1, 2, \quad -1 = \frac{\partial x_1}{\partial x_2}\frac{\partial x_2}{\partial x_j}\frac{\partial x_j}{\partial x_1}$$

Realizing that there isn't anything special about x_1, x_2, this says:

$$-1 = \frac{\partial x_i}{\partial x_j}\frac{\partial x_j}{\partial x_k}\frac{\partial x_k}{\partial x_i} \tag{10}$$

for any i, j, k distinct. Note that the RHS is dimensionless because each of $x_{i,j,k}$ appears once in the top and once in the bottom. This is sometimes called the "reciprocity theorem".

Comparison to 1d chain rule

Let's go back to the case of three variables for simplicity, and call them $(x_1, x_2, x_3) = (x, y, z)$ If we combine this last relation (10) with the reciprocal relation (9), we have

$$\frac{\partial y}{\partial x} = -\frac{\partial y}{\partial z}\frac{\partial z}{\partial x} \quad .$$

This way of writing (10) makes the minus sign seem to conflict with the chain rule in single-variable calculus, $\frac{dY}{dX} = \frac{dY}{dZ}\frac{dZ}{dX}$. There is actually no conflict, because the latter formula applies to a different situation, namely where X, Y, Z each determine each other, *i.e.* we have *two* independent relations $X = X(Y)$ AND $Y = Y(Z)$ among the three variables (which specifies a *curve* in space, rather than a surface).

But this makes the sign hard to remember.

An even simpler example

To check that this funny-seeming sign is really there, let's do a simple example. Take

$$0 = F(x, y, z) = x + y + z.$$

Then

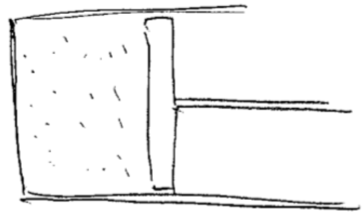
$$x(y, z) = -y - z, \quad y(x, z) = -x - z, \quad z(x, y) = -x - y$$
$$\frac{\partial x}{\partial y} = -1, \frac{\partial y}{\partial z} = -1, \frac{\partial z}{\partial x} = -1$$

So indeed their product is

$$\frac{\partial x}{\partial y}\frac{\partial y}{\partial z}\frac{\partial z}{\partial x} = -1.$$

3.4 Work in quasistatic processes

Consider the example of a hydrostatic system. This just means a fluid that exerts a constant pressure on its surroundings, for example, gas in a cylinder:

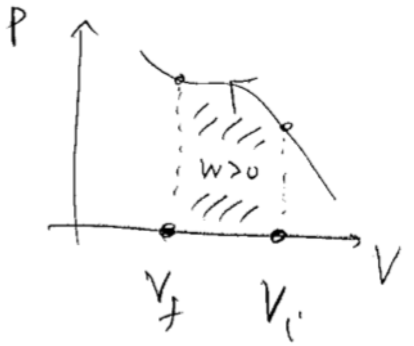


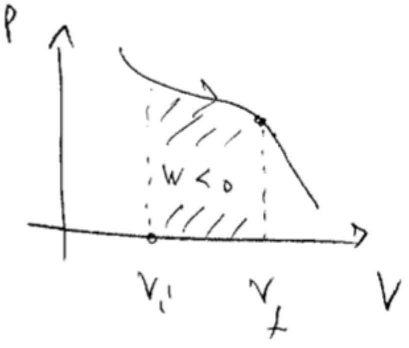
A is the cross-sectional area. In order for the piston to stay here it is, something must be exerting a force $F = PA$ to the left. If the piston is moved by some infinitesimal amount, Newton tells us that:

$$\text{đ}W = -\underbrace{P}_{\text{intensive}}\underbrace{dV}_{\text{extensive}} = \underbrace{(PA)}_{\text{force}}\underbrace{\left(\frac{-dV}{A}\right)}_{\text{displacement}}$$

for a quasistatic process.

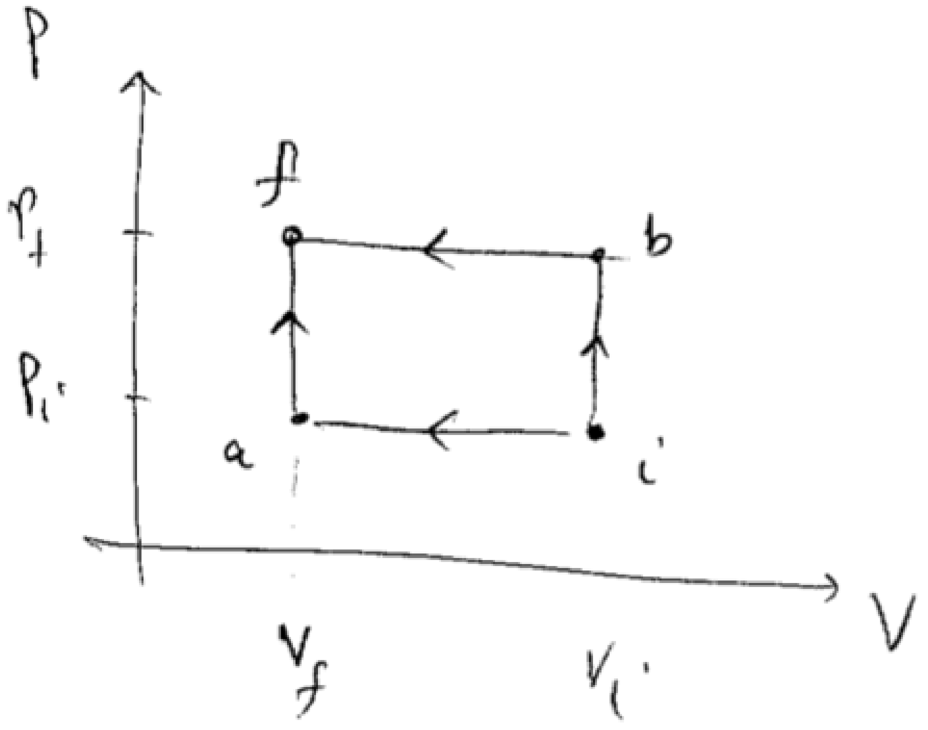
$$\text{work done ON system} = W = -\int_{V_i}^{V_f} P dV$$





Why $\text{đ}W$ and not dW?

Work done depends on the path:



$$W_{iaf} \neq W_{ibf}$$

$$\implies \quad đW \text{ is not an exact differential.}$$

$đW$ is NOT d of some single-valued function $W(P, V)$. That's the point of the little slash.

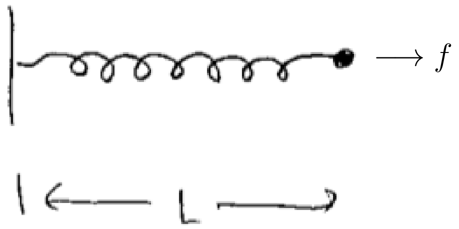
Work is not a state variable.

This is what I meant by “it's a verb”.

Note that $đW = -PdV$ is not exact, even though dV is exact.

Some other examples of how to do work on various systems. Most of the point here is the names and the signs.

Wire, rod, elastic, spring:

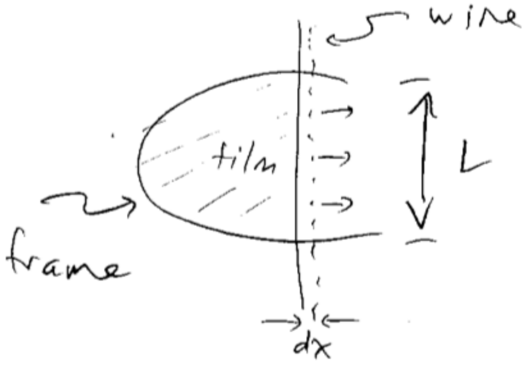


$$\text{đ}W = + \underbrace{f}_{\text{applied force}} \cdot \underbrace{dL}_{}$$

Note sign convention: assumes $f > 0$ means spring is under tension. $dL > 0 \implies \text{đ}W > 0$. If the spring is being compressed, $f < 0$. This is the opposite of the convention for pressure.

Surface film: (*e.g.* soap on a wire frame)

$$\text{đ}W = \underbrace{\sigma}_{\text{surface tension}} \cdot \underbrace{dA}_{=Ldx}$$



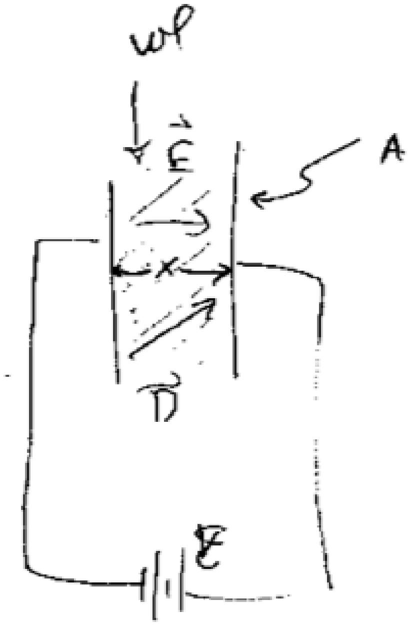
Capacitor:

$$\text{đ}W = \underbrace{\mathcal{E}}_{\text{voltage drop}} \cdot \underbrace{dq}_{\text{charge}}$$

Polarized dielectric:

$$đW = \underbrace{\vec{E}}_{\text{electric field}} \cdot \underbrace{d\vec{p}}_{\text{change in dipole moment}}$$

The total dipole moment is $\vec{p} = \vec{P}_e V$ where $\vec{P}_e$ is the electric polarization (the dipole moment per unit volume). To see this, imagine placing the dielectric between the plates of a capacitor:



The charge on the plates is $q = \vec{D} \cdot \hat{n} A$ where A is the area of the plates and $\vec{D}$ is the electric displacement; it is related to the electric field by

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P}_e \ .$$

So if $\mathcal{E} = Ex$ is the potential difference across the plates, and the separation between the plates is x,

$$đW = \mathcal{E} dq = x|E|dDA = VEdD$$

where $V = Ax$ is the volume of dielectric. Then

$$đW = \epsilon_0 \vec{E} \cdot d\vec{E} + \vec{E} \cdot d\vec{P} \ .$$

The first term is energy cost for making an electric field in vacuum and has nothing to do with the dielectric. The second term is what we want.

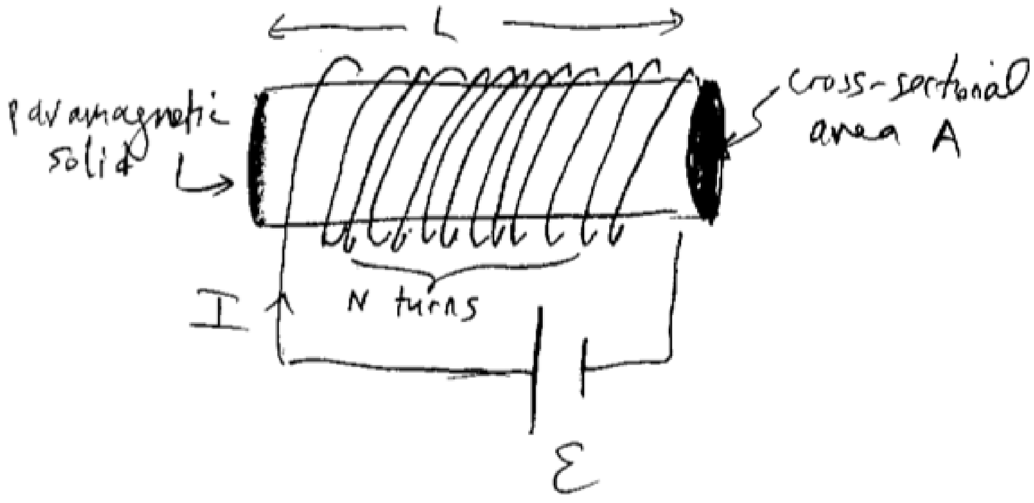
Magnetized paramagnet:

If we have a chunk of paramagnetic material, with magnetization $\vec{M}$, in an applied magnetic field $\vec{M}$, what's the work done in changing that magnetization?

$$\text{Claim:} \quad đW = \underbrace{\vec{H}}_{\text{appl. magn. field}} \cdot \underbrace{d\vec{M}}_{\text{magnetizat'n}}$$

[End of Lecture 8.]

Note: in all these examples, $đW = \text{intensive} \cdot d\,(\text{extensive})$.



Here is a derivation of the claim, using Ampere and Faraday. It's interesting, and confusingly treated in Adkins §3.5.4.

Q: how much work does it take to increase $\vec{M}$ by $d\vec{M}$? In practice, we have to do this by applying a field. How do we make the field? Let's do it by wrapping a coil around the paramagnet and hooking up a battery to it. The work is done by the battery, when charge dq moves across the EMF $\mathcal{E}$:

$$đW = \mathcal{E}dq = \mathcal{E}Idt \ . \tag{11}$$

Now we have to relate this to the field and the magnetization.

$$\text{Faraday:} \quad \text{EMF } \mathcal{E} = \frac{1}{c}N\frac{d}{dt}(BA)$$

N is the number of turns of coil, A is the cross-sectional area of the coil (which I assume equal to that of the chunk of paramagnet), and B is the "B-field", the magnetic induction, the actual field, which is related to the applied field H by:

$$B = H + \frac{4\pi M}{V} \ . \tag{12}$$

Therefore (11) becomes

$$đW = \frac{NAI}{c}\frac{dB}{dt}dt = \frac{NAI}{c}dB \ . \tag{13}$$

On the other hand, if we ask how much field is created by the coil, Ampere's law says

$$H = \frac{4\pi}{c}\frac{NI}{L}. \tag{14}$$

We recognize this quantity on the RHS of (13). Putting together (13) and (14), we have

$$đW = \frac{AL}{4\pi}HdB = \frac{V}{4\pi}HdB.$$

What's dB? Taking d of (12)

$$dB = dH + \frac{4\pi}{V}dM$$

$$đW = \underbrace{\frac{V}{4\pi}HdH}_{=d\left(V\frac{H^2}{8\pi}\right)} + \underbrace{HdM}_{\text{extra work done because of the presence of the paramagnet}}$$

The first term is the work needed to create H in vacuum. We don't care about this. The second term is the work done to magnetize the paramagnet. Therefore $đW = HdM$.

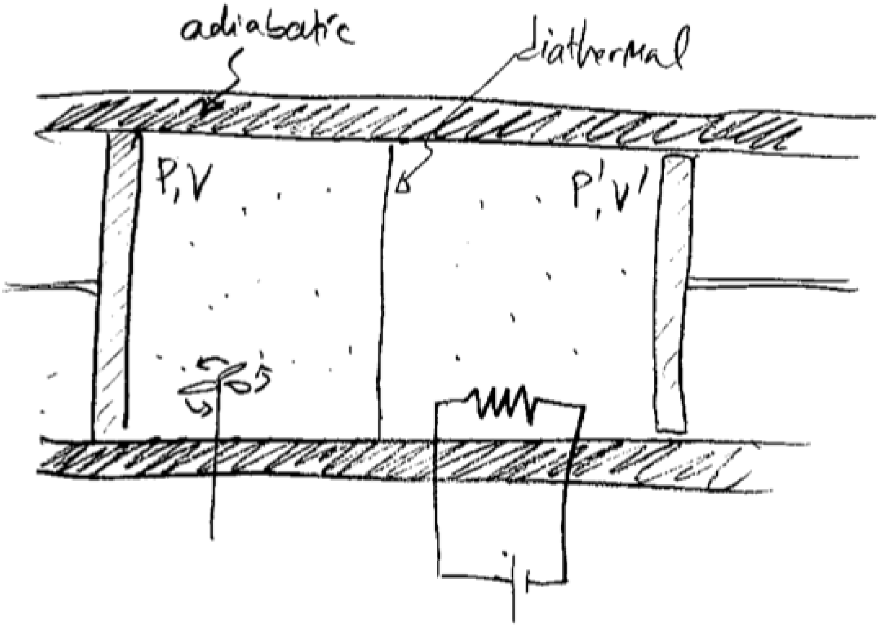
3.5 First law of thermodynamics; internal energy and heat

As usual, this Law is a statement of our experience of the world. This one we can prove microscopically: it's conservation of energy. Ultimately this follows (via Noether's theorem) from the fact that any time is the same as any other. That's a story for another time.

First Law: "If a system is changed from an initial state to a final state by adiabatic means only, the work done is the same for any path connecting the two states."

(Such an adiabatic path is called an *adiabat.*)

It applies to quasistatic processes *and* to sudden irreversible processes, as long as the system in question is thermally isolated.



In the figure: We can change the state quasistatically with the pistons.
We can change the state non-quasistatically with the pistons.
We can change the state by running current through the resistor.
We can change the state by stirring vigorously with the paddle wheel.
Heat can flow within the system.

No matter what combination of processes gets you from the initial state to the final state, the sum of the work done is the same.

Internal Energy.

This suggests to us that we should define a quantity whose differences give the work done:

$$W_{i\to f}(\text{adiabatic}) = U_f - U_i$$

U is called the internal energy. It's the thing that's *not* escaping through the adiabatic walls. (It's called U in thermodynamics, and E in stat mech. Get used to it.)

We can restate the 1st Law as:

$$\boxed{U \text{ is a state function.}}$$

That is, $U_f - U_i$ does not depend on the path we pick between i and f.

U is determined by the independent thermodynamic variables, whichever we pick those to be:

$$U = U(T,V) \text{ or } U(T,P) \text{ or } U(P,V) \text{ or } U(H,M) \text{ or } U(f,L)....$$

so *e.g.*

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

Now, suppose we take a system from state i to state f NON-adiabatically, *i.e.* while it's not isolated.
Then $U_f - U_i \neq W$. Define **heat** Q to be the quantity such that:

$$\boxed{U_f - U_i = \underbrace{W}_{\text{work done } \textbf{on} \text{ system}} + \underbrace{Q}_{\text{heat flowing } \textbf{into} \text{ system}}}$$

This is (a more general version of) the 1st Law of Thermodynamics which applies without restriction to adiabatic changes. It is less contentful in that it is really a definition of heat. It is more obviously the statement that energy is conserved.

Note the sign convention. It is important to be clear about this convention whenever we talk about heat or work. Also, don't forget that W and Q can be negative! A negative amount of heat flowing into the system is a positive amound of heat flowing out.

Differential form of 1st Law:

$$\underbrace{dU}_{\text{is an exact diff'l}} = \underbrace{đW + đQ}_{\text{are not exact diff'ls}}$$

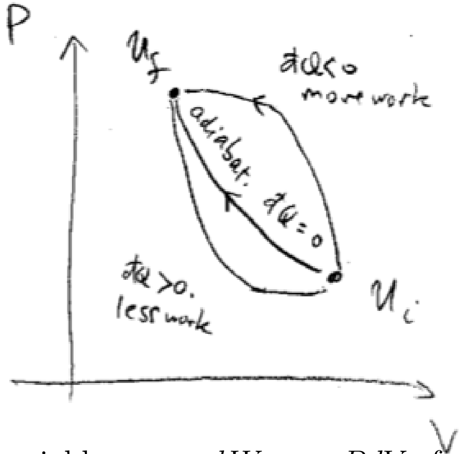
For a hydrostatic system, for quasistatic processes:

$$dU = đQ - PdV$$

(For non-quasistatic processes we can't make such an accurate account of the energy.)

Clearly $đQ$ depends on the path. Q is not a state variable.

Heat: U moving because of a temperature gradient.
Work: U moving in any other way (mechanically, electrically ...).
At this point, this seems like an unimportant distinction between $đW$ and $đQ$ – what we've shown so far is that they are both path-dependent. The difference comes to fruition in the 2nd Law: there are processes allowed by the 1st Law which don't occur, and there this distinction is crucial.



We have learned how to write $đW$ in terms of state variables: *e.g.* $đW = -PdV$, for quasistatic processes.
To do the same for $đQ$ we need a better statement of the 2nd Law. (Spoiler alert: $đQ = TdS$ for quasistatic processes.)

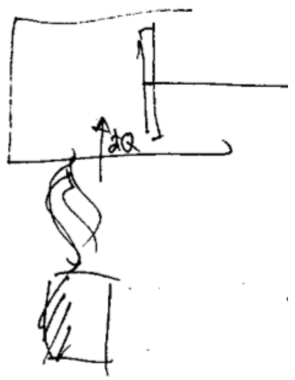
3.6 Heat Capacities

Now we begin our quantitative use of the 1st Law. Soon we will determine the shape of adiabats.

$$C_V \equiv \left(\frac{\text{đ}Q}{dT}\right)_V, \qquad C_P \equiv \left(\frac{\text{đ}Q}{dT}\right)_P$$

It is the answer to the natural question: how much heating $\text{đ}Q$ does it take to change the temperature of an object by dT? The answer depends on what we hold fixed when we shoot the heat gun (or do whatever we're doing to heat the object), *e.g.* whether we do this while fixing the volume V or fixing the pressure.

The difference arises because if we let the volume vary, the system can also change its internal energy by doing work $P\Delta V$ as we're heating it. This means that $C_P > C_V$, since if P is fixed (as in the figure at right), the volume varies; then some of the $\text{đ}Q$ goes into work (the gas expands), rather than into changing the temperature.



Don't be tricked by the name "heat capacity" into becoming a believer in the Caloric Theory – heat is not a conserved fluid that enters a body and stays there. The thing that stays is *energy*, which can also take many other forms.

For thermodynamic systems with other variables, we can hold other things fixed instead.
e.g. For a rod: C_L or C_f with $C_f > C_L$.
e.g. For a paramagnet: C_M or C_H with $C_H > C_M$.

3.7 C_V and C_P for a hydrostatic system; enthalpy; heat reservoirs

Let's find an expression for C_V in terms of other things we know for a hydrostatic system – a fluid in a cylinder.

$$dU = đQ - PdV \qquad \text{1st Law for quasistatic changes} \tag{15}$$

At constant volume: $dU = đQ$.
No work gets done. The heat all goes into internal energy.[3]

Consider U as a function of T, V. (We're going to set $dV = 0$.):

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{16}$$

Combining the 1st Law (15) and calculus (16), and specifying constant volume, $dV = 0$, we have:

$$đQ = \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$\implies \quad \boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V}.$$

That was easy, now what about C_P?
To figure that out we need to answer: what's dV during the heating process if we fix P? That's $dV|_P = \left(\frac{\partial V}{\partial T}\right)_P dT$.
So let's put back the dV terms in the 1st Law:

$$\begin{aligned} đQ &= dU + PdV \\ &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + PdV \end{aligned}$$

$$\implies \quad C_P \equiv \left(\frac{đQ}{dT}\right)_P = \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} + \left(\left(\frac{\partial U}{\partial V}\right)_T + P\right) \underbrace{\left(\frac{\partial V}{\partial T}\right)_P}_{V\alpha}$$

Recall that α is the "volume expansivity".

$$\boxed{C_P - C_V = V\alpha\left(\left(\frac{\partial U}{\partial V}\right)_T + P\right)}.$$

Soon, we'll specify further to an *ideal* gas.

---

[3] (By the way, how is this energy stored? For an ideal gas, it's stored in the kinetic energies of all the particles making up the fluid; but they are going all in random different directions and so can't be made to do any coherent work on macroscopic things. Like your brain when you drink too much coffee.)

Enthalpy

Wouldn't it be nice to be able to write

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

for some quantity H? Let's figure out what H has to be for this equality to be true (Spoilers: H stands for 'enthalpy').

$$đQ = dU + PdV \tag{17}$$

We're going to set $dP = 0$, so let's consider U as a function of T and P.

$$dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP \ . \tag{18}$$

Combining (17) and (18)

$$C_P \equiv \left(\frac{đQ}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \ .$$

Finally, notice that $\left(\frac{\partial(PV)}{\partial T}\right)_P = P\left(\frac{\partial V}{\partial T}\right)_P$. So

$$\boxed{C_P = \left(\frac{\partial H}{\partial T}\right)_P \quad \text{if we define } H \equiv U + PV}$$

H is called enthalpy. Since it's made from a simple combination of state functions it is clearly also a state function. (This particular way of assembling state variables is called a *Legendre transformation*. It will come up again.)

If we don't assume constant pressure

$$dH = \underbrace{dU + PdV}_{đQ} + VdP \ .$$

A sometimes useful relation, which can be shown using the same methods as above, is:

$$C_V - C_P = \left(\frac{\partial P}{\partial T}\right)_V \left(\left(\frac{\partial H}{\partial P}\right)_T - V\right) \quad .$$

H is most useful when $dP = 0$, in which case:

$$dH|_P = đQ|_P.$$

Chemical reactions involving gases usually take place at constant pressure, if *e.g.* they are exposed to the atmosphere. So, the heat released or absorbed in such a reaction ("heat of reaction") is $\Delta Q = \Delta H = \Delta(U + PV)$.

Heat reservoirs

This definition is most easily stated in terms of heat capacity, so it has waited until now.

Def: A *heat reservoir* is a system with such a large C_V and C_P (for whatever reason – usually this means it's made of lots of stuff and is very big and heavy) that it may absorb or give up "unlimited" quantities of heat (for purposes of discussion) without appreciable change in temperature or in any other intensive thermodynamic variable.

Note that this definition is meant to be flexible – the meaning of 'unlimited' depends on the system of interest; really we just want the reservoir to be have a C_V much bigger than that of the system of interest. For example, if we're doing a little chemistry experiment in a beaker, the air in the room is a useful heat reservoir, which is keeping the beaker at fixed T and P. This is to be contrasted with what happens if our little experiment blows up and creates a room-sized conflagration. Then the room can no longer be considered a heat reservoir.

3.8 C_V and C_P for ideal gas

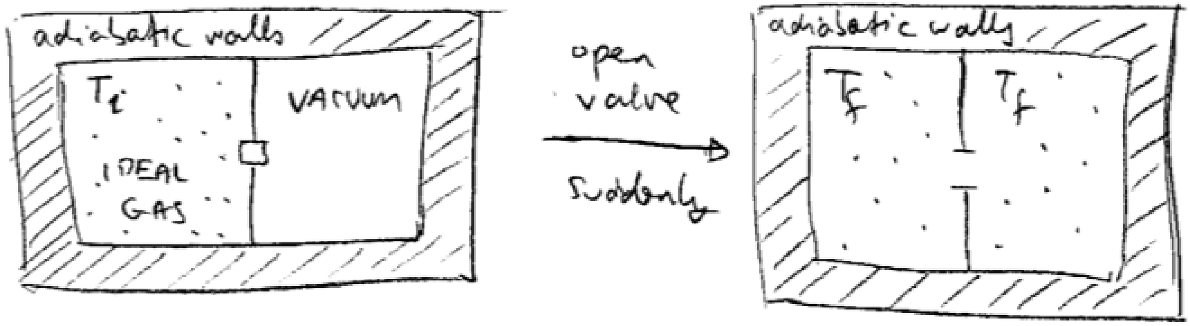
An *ideal gas* is a fluid where collisions between the constituents may be ignored. Mean free paths are infinite. How can it have a nonzero pressure? Only because of collisions with the walls of its container.

Any gas is ideal in the dilute limit.

For an ideal gas, the equation of state is $PV = NkT$. We'll derive this later. $k = k_B =$ Boltzmann's constant
$\simeq 10^{-16} \cdot 1.38$erg/Kelvin
$\simeq 10^{-5} \cdot 8.62$eV/Kelvin.
A useful statement about these to remember is:

$$kT \sim 1\text{eV when } T \sim 10^4 K \ .$$

What about U? Consider the following experiment: Free expansion of an ideal gas [Joule]:



Open the valve suddenly, then, as usual, wait until the system reaches a new equilibrium state.

What do you think happens? Is $T_f > T_i$? $T_f < T_i$? $T_f = T_i$? Experimental result: $T_f = T_i$.

[Microscopic explanation (later): speed of molecules is unchanged by letting them fill a bigger volume. Some of them go through the hole, but they don't do work on anything or slow down; their mean distance has just increased.]

$$\text{Conclusions:} \qquad \Delta Q = 0 \quad \text{(adiabatic walls)}$$

$$\Delta W = 0 \quad \text{(free expansion – no piston gets moved)}$$

$$\overset{\text{1st Law}}{\Longrightarrow} \Delta U = 0$$

In general, $U = U(V, T)$:

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

For a free expansion $dU = 0, dT = 0, dV \neq 0$

$$\Longrightarrow \left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$\Longrightarrow \boxed{U = U(T) \text{ for an ideal gas}}.$$

[End of Lecture 9.]

(A hard-to-resist comment about the microscopic picture: Particles in an ideal gas have no interactions. This means that microscopically U is made up of energies of the individual particles, and not interaction energies that depend on the separations between the particles – no dependence on the spacing between the particles means no dependence on V.)

$$\Longrightarrow dU = C_V dT$$

$$\Longrightarrow U(T) = \int_0^T dT' C_V(T') + \underbrace{\text{const}}_{\text{choose zero of energy to set this to zero}}$$

This formula is true for any system (not just ideal gas) *if* we heat it while holding its volume fixed. It's true for an ideal gas no matter how we do it.

Now, let's examine the formula we derived above for C_P in this case:

$$\begin{aligned} C_P - C_V &= V\alpha \left(\underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{=0} + P \right) \\ &= V\alpha P = P \left(\frac{\partial V}{\partial T}\right)_P \end{aligned}$$

Now use the equation of state: $V = NkT/P$:

$$\boxed{C_P - C_V = Nk} \text{ for any ideal gas.}$$

Different kinds of ideal gases are distinguished by the form of C_V. To go farther we will need more microphysical information[4]. For a *monatomic* ideal gas (*e.g.* He, Ne, Ar, Kr, Xe), *experiments show that* (in this chapter this phrase is almost always code for "we'll show this later using stat mech"):

$$C_V = \frac{3}{2} N k_B$$

This implies that $U = \frac{3}{2} N k_B T$ and $C_P = \frac{5}{2} N k_B$ and

$$\gamma \equiv \frac{C_P}{C_V} = \frac{5}{3} \text{ for a monatomic ideal gas.}$$

Note that $\gamma > 1$ for any gas since $C_P > C_V$.

Diatomic ideal gas

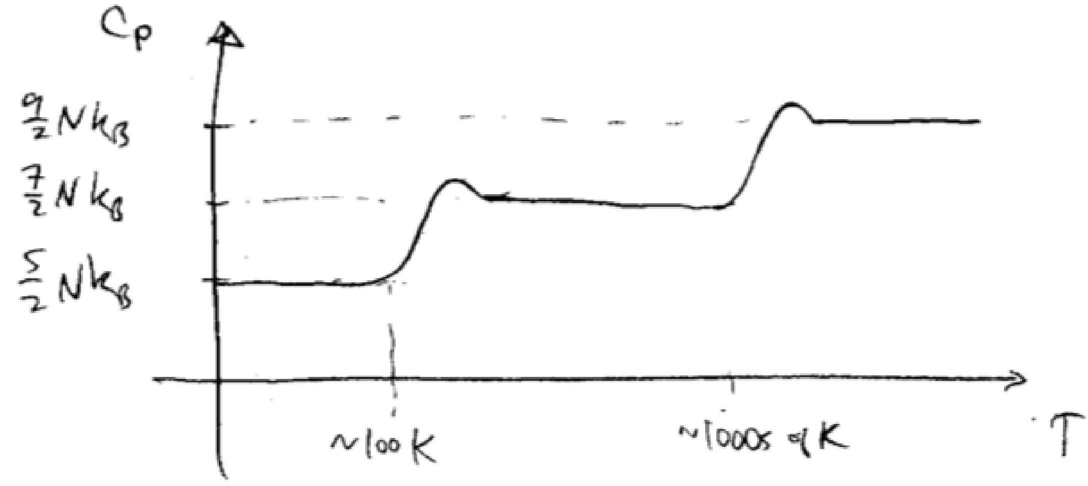
Microscopically, a monatomic gas molecule should be regarded as a featureless ball. For a *diatomic* ideal gas (such as the N_2, O_2 in air), the behavior is different, because the individual gas particles have some degrees of freedom, which can be excited when the system is heated. Think of them as made of two balls attached by a spring. The internal energy U of a system of diatomic ideal gas molecules must include the energies of vibration  and rotation  of the molecules, not just their translational motion. [5]

---

[4] I'm making a lot of promises here about what we're going to learn from statistical mechanics.

[5] (We'll see that the equation of state (*i.e.* the pressure P) doesn't care about this.)

For a typical diatomic gas:

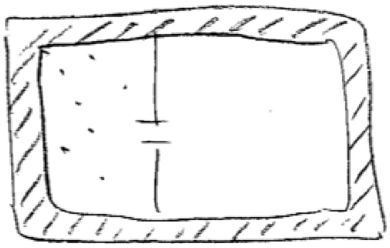


	just trans.	trans+vib	trans+vib+rot
C_V :	$\frac{3}{2}Nk_B$	$\frac{5}{2}Nk_B$	$\frac{7}{2}Nk_B$
U :	$\frac{3}{2}Nk_BT$	$\frac{5}{2}Nk_BT$	$\frac{7}{2}Nk_BT$
γ :	$\frac{5}{3}$	$\frac{7}{5}$	$\frac{9}{7}$

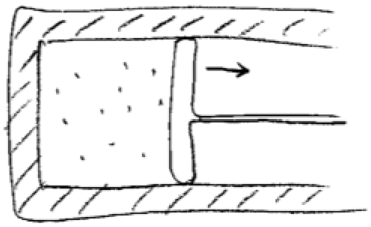
This picture (which you could imagine obtaining by a series of measurements involving adding a little heat and measuring temperature differences) is trying to tell about the internal structure of the constituents.

Two types of adiabatic expansion of an ideal gas:

1) Free expansion vs 2) Quasistatic adiabatic expansion (let piston expand slowly)



(1)



(2)

In case (2) it can be adiabatic and quasistatic – the piston moves slowly and the gas does work on it. All the energy is accounted for, and the process can be reversed.

Case (1), free expansion is *not* quasistatic. "sudden". We might want to write $\Delta W = -PdV$ but we can't – the pressure isn't even well-defined during the sudden escape of the gas.

case (1): free expansion		case (2): slow expansion
$\Delta Q = 0$	← (adiabatic) →	$\Delta Q = 0$
$\Delta W = 0 \neq -PdV$		$\Delta W = -PdV < 0$
$\Delta U = 0$		$\Delta U < 0 \implies T_f < T_i$.

We used this in Chapter I. Now we can be quantitative about the shapes of various curves describing reversible paths.

Isotherm: $T = \text{const} \implies PV = \text{const} \implies P \propto 1/V$ hyperbola.

Adiabat: $\text{đ}Q = 0$. What shape does this make on the PV diagram?

$$\text{recall: } \text{đ}Q = dU - \text{đ}W = dU + PdV$$

$$\text{đ}Q = \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} dT + \left(\underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{=0 \text{ for ideal gas}} + P\right) dV \overset{!}{=} 0$$

(More generally, $\left(\frac{\partial U}{\partial V}\right)_T + P = \frac{C_P - C_V}{V\alpha}$.)

$$\implies \left(\frac{\partial T}{\partial V}\right)_{\text{adiabatic}} = -\frac{P}{C_V} \text{ for adiabatic and quasistatic exp of ideal gas}$$

$$= -\frac{NkT}{C_V V}$$

$$= -\frac{C_P - C_V}{C_V}\frac{T}{V}$$

$\boxed{\frac{dT}{T} = -(\gamma - 1)\frac{dV}{V}}$ for adiabatic and quasistatic exp of ideal gas

The general result (not harder to show) is

$$\boxed{\frac{dT}{dV} = -\frac{\gamma - 1}{V\alpha}}$$

We can go further if we make the approximation that $\gamma =$ constant. You saw from the plots of C_P above that this is approximately true away from the special temperatures where new degrees of freedom appear. So this will be correct away from the steps.

$$\text{if } \gamma \text{ is constant:} \quad \ln T = -(\gamma - 1)\ln V + \text{const}$$

$$\Longrightarrow \quad \boxed{TV^{\gamma-1} = \text{const}}$$

If we use the equation of state $PV \propto T$:

$$\boxed{PV^{\gamma} = \text{const}}$$

or $P \propto V^{-\gamma}$. This is the shape of an adiabat. Since $\gamma > 1$ always, this is always a more steeply-falling curve than an isotherm. For a monatomic ideal gas, this is $P \sim V^{-5/3}$, which is plotted here: