Lecture 13: Introduction to Thermo and Stat. Mech. (continued)

Reading Assignment for Lectures 10-12: PKT Chapter 6
Problem Set 2 due Friday.

An application of our discussion of extensivity:

Energy Fluctuations in the canonical ensemble:

You will recall (Lecture 11.1) that we showed for any system in contact with a heat bath that

$$\langle E\rangle_c = \frac{1}{Z}\sum_n E_n e^{-\beta E_n} = \frac{\sum_n E_n e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} = -\frac{d}{d\beta}\ln Z.$$

This is true for any canonically distributed system, large or small. When the system is thermodynamically large, then $E = \langle E\rangle$ is extensive, β is intensive, and lnZ is extensive.

What happens when we differentiate again w.r.t. β?

$$-\frac{\partial E}{\partial \beta} = \frac{\partial^2 \ln Z}{\partial \beta^2} = \frac{1}{Z}\sum_n E_n^2 e^{-\beta E_n} - \langle E\rangle_c^2 = \left\langle \left(E - \langle E\rangle_c\right)^2 \right\rangle_c$$

At the left is the extensive quantity $-\frac{\partial E}{\partial \beta}$; at the right are the energy fluctuations in the canonical ensemble. Recall that $E(N,V,T) = Nf(n,T)$ where $n \equiv \frac{N}{V}$ is the number density (intensive).

Thus, rms energy fluctuations scale with system size as $\sqrt{N}$.

Note the parallel with the coin-toss problem.

We can also write, $\left.\frac{\partial E}{\partial T}\right|_{N,V} \equiv C_V = \left.\frac{\partial E}{\partial \beta}\right|_{N,V} \cdot \frac{\partial \beta}{\partial T} = \frac{1}{k_B T^2}\left\langle \left(E - \langle E\rangle_c\right)^2 \right\rangle_c$, which shows that the "heat capacity" C_v of the sample (extensive) is intrinsically positive and related to the canonical energy fluctuations.

We turn now to thermodynamics:

Thermodynamics gives you information about relationships between the thermodynamic variables (and the other quantities which can be derived from them).
In general, thermodynamics does NOT tell you what these functional relations are: For that you need to appeal to experiment or theory (e.g., statistical mechanics).

So, what is thermodynamics good for?
1. It is a framework for packaging information.
2. It sets certain limits on the outcome of certain processes.

I will give you examples of these features.

First Law of Thermodynamics:

Energy conservation applied to thermodynamic macrostate *THE SYSTEM* during some "process."
ΔQ = ΔE + ΔW, which I am going to write as $đQ = dE + đW$, where
$đQ$ is an increment of heat flowing *into* the system,
dE is the incremental change in the internal energy of the (thermodynamic) system, and
$đW$ is the incremental work done *by* the system on the external world.

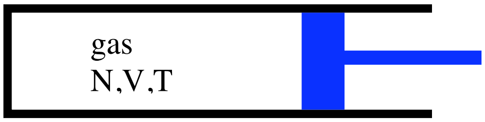
Notes:

1. ΔQ = ΔE + ΔW is in itself just a statement about mechanics with E the mechanical energy. It becomes a thermodynamic statement when the initial and final states are equilibium macrostates, so that

the energy difference ΔE becomes the difference between, e.g., the functions E(T,V,N) for these different states.

2. $\text{đ}W$ depends on how the system does work and what the "process" is.

Example: For a gas or liquid, work may (or may not!) be done if the volume of the system increases.



Work can be done by the gas if the pressure of the gas pushes the piston back (to the right) against some external agency.
If the piston is pushed back slowly, so that the gas remains in equilibrium and the pressure P of the gas on the piston is well-defined, then (and only then) $\text{đ}W = PdV$. This is called a "quasistatic" process. All the intermediate state are equilibrium states. For such a process, the first law states
$\text{đ}Q = dE + PdV$.
Note, however, that, if the piston is withdrawn very rapidly, so that no gas molecules actually contact the piston during its motion, then $\text{đ}W = 0$. Intermadiate states are not equilibrium states but the final state is (else we cannot define an internal thermodynamic energy E). For this process, the first law still holds but $\text{đ}Q = dE$.

Q: What does the "slash" mean?
A: I am using the slash to indicate that the quantity is just an increment and NOT the differential of some function. (more below)

At this point, I want to illustrate some thermodynamic ideas by going through in some detail the example of the ideal classical monatomic gas (ICMG). In this very specific context I will derive some results which turn out to be general.
Take care in what follows to distinguish what is special and what is general.
The ICMG is defined by the two (thermodynamic) relations:

$P = \dfrac{Nk_BT}{V}$ (true for all classical gases, not just monatomic)

$E = \dfrac{3}{2}Nk_BT$ (this is special to the monatomic gas, so there are only three degrees of freedom)

These relations are of the form P(N,V,T) intensive, E(N,V,T) extensive treating N,VT as the independent variables.
Note how extensivity/intensivity come about.
For the energy, it is an "accident" that V does not show up.
The general form of these two relations is P(n,T) and E=Nf(n,T), which holds for non-ideal gases and fluids.
Consider a process in which $\text{đ}Q$ is slowly ("quasistatically") added to the gas in the cylinder and the piston is pushed back against some external force F=PA so the gas does work. According to the first law, $\text{đ}Q = dE + PdV = \dfrac{3}{2}Nk_BdT + \dfrac{Nk_BT}{V}dV$
Note that there are well-defined differentials on the right but $\text{đ}Q$ remains simply and increment.

It is not the differential of some function: Suppose Q(T,V), with $dQ = \dfrac{\partial Q}{\partial T}dT + \dfrac{\partial Q}{\partial V}dV$.

For this to be so for $\text{đ}Q$ we would have from the dT part that $Q(T,V) = \dfrac{3}{2}Nk_BT + fcn(V)$

and from the dV part that $Q(T,V) = Nk_BT\ln V + fcn(T)$. These are not consistent.

Comment:

Q: Generally, for a function of two variables, if you are given two quantities f(x,y) and g(x,y) what is the criterion that there exists a function h(x,y) such that $\frac{\partial h}{\partial x} = f$ and $\frac{\partial h}{\partial y} = g$?

A: If such an h(x,y) existed, then the cross derivatives must be equal, $\frac{\partial^2 h}{\partial x \partial y} = \frac{\partial^2 h}{\partial y \partial x}$, i.e., $\frac{\partial f}{\partial y} = \frac{\partial g}{\partial x}$.

Is this criterion satisfied in the example above?:

$\frac{\partial}{\partial V}\left(\frac{3}{2}Nk_B\right) \overset{?}{=} \frac{\partial}{\partial T}\left(\frac{Nk_BT}{V}\right)$. Clearly fails.

But, now divide by T: $\frac{đQ}{T} = \frac{3}{2}Nk_B\frac{dT}{T} + Nk_B\frac{dV}{V}$.

Q: Can the quantity on the right be the differential of some function S?

A: Yes, with any S of the form,

$$S(N,V,T) = \frac{3}{2}Nk_B \ln T + Nk_B \ln V + fcn(N) = Nk_B \ln\left(T^{3/2}V\right) + fcn(N).$$

If we require that S be an *extensive* (thermodynamic) quantity, then the form is further narrowed down:

$S(N,V,T) = S_{ICMG}(N,V,T) = Nk_B \ln\left(T^{3/2}\frac{V}{N}\right) + Ck_BN$ for the ideal monatomic classical gas.

The constant C has a well-defined value which we will derive below from a different point of view.

General statements (not restricted to the ICMG):

There exists an extensive function S(E,V,T), called the "entropy" such that for any infinitesimal quasistatic process $đQ = TdS$.

(differential form of what is called the "Second Law of Therodynamics")

For a fluid system (gas or liquid) the thermodynamic variables are N,V,T (or N,V, E or…) and $đW = PdV$, so combining with First Law: $TdS = dE + PdV$. (N fixed)

Note: This relation has as a consequence that, if we choose to regard S as a function of (N,V,E) instead of N,V,T, then $dS = \frac{1}{T}dE + \frac{P}{T}dV + (?)dN$, so

$$\left.\frac{\partial S}{\partial E}\right|_{N,V} = \frac{1}{T}$$

$$\left.\frac{\partial S}{\partial V}\right|_{E,N} = \frac{P}{T}$$

Furthermore, the derivative of S wrt to N at fixed E,V defines the "chemical potential" μ according to

$$\left.\frac{\partial S}{\partial N}\right|_{E,V} = -\frac{\mu}{T}$$

The extensive function $S(E,V,N)$ along with the identification of derivatives

$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$ is called a "fundamental relation."

Check this for the special case of the ICMG:

Note $E = \frac{3}{2} N k_B T \quad \Rightarrow \quad T = \text{const} \times \frac{E}{N}$. Thus,

$$S_{ICMG}(N,V,E) = N k_B \ln\left(E^{3/2} \frac{V}{N^{5/2}} \right) + \bar{C} k_B N$$ and

$$\frac{\partial S}{\partial E} = \frac{3}{2} \frac{N k_B}{E} = \frac{1}{T}$$

$$\frac{\partial S}{\partial V} = \frac{N k_B}{V} \cdot \frac{T}{T} = \frac{P}{T}$$

(checks)

Note how S(E,V,N) stores both the relations E(T,V,N) and P(T,V,N) in a single function.
For a quasistatic process which is "adiabatic" (i.e., no heat gain or loss, system insulated)

$\bar{d}Q = TdS = 0$, so for the ideal gas $E^{3/2} V = \text{const}$, i.e., $T^{3/2} V = \text{constant}$ (which you may recall from Phys. 101).

Furthermore,

$$-\frac{\mu}{T} \equiv \frac{\partial S}{\partial N} = k_B \ln\left(\frac{E^{3/2} V}{N^{5/2}} \right) + \text{const} \cdot k_B = k_B \ln\left(\frac{T^{3/2} V}{N} \right) + \text{const} \cdot k_B$$, so

$$n \equiv \frac{N}{V} = const \cdot T^{3/2} e^{\mu / k_B T}.$$

(All this for the IMCG only)

We will fill in the constants later.