## Lecture 14: Introduction to Thermo and Stat. Mech. (continued)

## Free Energies and other forms of the fundamental relations.

Problem Set 2 due today.
In Tutorial Tuesday, I will do calculations related to S(E,V,N) for the ideal classical monatomic gas.
Midterm exam, Friday Oct. 29.

I have been sketching for you the structure of the relationships between the fundamental variables of thermodynamics. These differ for different systems but always include E,T and N,μ. For the case of the fluid (both ICMG and generally), the work related pair are V,P with $đW = PdV$.

At the end of last period, I stated for you the "fundamental relation" involving the extensive variables: $S(E,V,N)$ with first derivatives identified as $dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$ and with the property that, for any infinitesimal quasistatic process $đQ = TdS$.
S(E,V,N) packages efficiently all the information about the relations between the thermodynamic variables, including for fluids E(T,V,N) and the equation of state P(T,V,N).
Note that thermodynamics does not tell you what is the actual functional form S(E,V,N). We derived that for the ICMG. Whenever we measure in the lab, say, the equation of state and the energy, we can infer S from experimental data, just as we did (conceptually speaking) for the ideal classical gas.

There are a number of other "fundamental relations" involving other variables and based on other analogs of S, called "free energies." The one involving the variables (T,V,N) is based on the quantity, $F(T,V,N) \equiv E - TS$. "Helmholz free energy"

Note $dF = dE - SdT - TdS = \cancel{dE} - SdT - T\left(\frac{1}{T}\cancel{dE} + \frac{P}{T}dV - \frac{\mu}{T}dN\right)$, i.e.,

$F(T,V,N) \equiv E - TS$ with $dF = -SdT - PdV + \mu dN$, which means
$\frac{\partial F}{\partial T} = -S; \frac{\partial F}{\partial V} = -P; \frac{\partial F}{\partial T} = \mu$.
This is another "fundamental relation." It also stores E(T,V,N) , P(T,V,N), and μ(T,V,N).

These manipulations of "differentials" are just a convenient way of handling derivative relations when changing variables. Thus, e.g.,

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

### How does this work out for the ICMG?

$F_{ICMG}(T,V,N) = E - TS = \frac{3}{2}Nk_BT - T\left[Nk_B \ln\left(T^{3/2}\frac{V}{N}\right) + CNk_B\right]$ and check:

$\frac{\partial F}{\partial T} = -S$, which encodes $E = \frac{3}{2}Nk_BT$, and

$\frac{\partial F}{\partial V} = -P(T,V,N) = -\frac{Nk_BT}{V}$ checks

There are several more fundamental relations for different sets of variables.

Another that we may use is the "Grand Free Energy":
$\Psi(T,V,\mu) = E - TS - \mu N$ with derivatives given by $d\Psi = -SdT - PdV - Nd\mu$

All these are interconnected by a relationship which follows from extensivity.

Consider the relation S(E,V,N), satisfying $\lambda S(E,V,N) = S(\lambda E, \lambda V, \lambda N)$ **14.2**

This implies: $S = E\frac{\partial S}{\partial E} + V\frac{\partial S}{\partial V} + N\frac{\partial S}{\partial N}$ or, substituting from the differential relations for S,

$S = E\left(\frac{1}{T}\right) + V\left(\frac{P}{T}\right) + N\left(-\frac{\mu}{T}\right)$ which is the same as $\boxed{TS = E + PV - \mu N\text{, ("Euler relation")}}$

so, e.g.,

$F = E - TS = -PV + \mu N$ or $\Psi = E - TS - \mu N = -PV$

Finally, and following from the Euler relation (i.e., from extensivity), there is a relation between the intensive variables:

$TdS + SdT = dE + PdV + VdP - \mu dN - Nd\mu$ differentials of the Euler relation

But, $TdS = dE + PdV - \mu dN$.

Subtracting gives, $\boxed{VdP = SdT + Nd\mu \quad \text{("Gibbs-Duhem relation")}}$

which can be regarded as giving the derivatives of the relation between the intensive variables,

$P(T,\mu)$ with $dP = \frac{S}{V}dT + \frac{N}{V}d\mu$.

Each one of these "free energies" (I include the entropy) comes with:

- It's own connection to statistical mechanics, including its own equilibrium ensemble. Of course, for large systems, all these ensembles are equivalent. (for small systems, they are not)
- It's own maximum/minimum principle.

I will start with the first of these.

Claims:

1. $S(E,V,T) = k_B \ln W(E,V,N,\Delta E)$ where W is the number of microstates of specified V,N and with E lying in the range E to E+ΔE.

The corresponding equilibrium ensemble is the energy "shell". We say that in describing equilibrium every microstate specified in this way is equally likely. This is called the hypothesis of "equal a priori probability."

Comments:

- It will turn out that for a large system ΔE is irrelevant. However, the reason I have to put it in here is because the microstate energies $E_n$ are discrete at the quantum level (as I have emphasized).
- The hypothesis of equal a priori probability is a guess—an assumption—just like the hypothesis that all the coin-toss microstates were equally likely.
- Q: Might equal a priori be wrong? A: In principle, yes, but, as in the coin-toss example, it would take a systematic and massive error to affect the outcome. If this hypothesis gets wrong the probability of a small number of unlikely states (like (+++++…), it won't make any detectable difference, and we would never know. This hypothesis is well tested in experiment; but, not at the "micro" level.

2. $F(T,V,N) = -k_B T \ln Z(T,V,N)$, where Z is the partition function $Z(T,V,N) = \sum_n e^{-\frac{E_n(V,N)}{k_B T}}$.

The corresponding equilibrium ensemble is the canonical distribution. This is subject to the same kind of caveats as the equal-a-priori-probability distribution.

Comments:

- These connections allow us—if we are good enough at calculating—to calculate thermodynamic quantities from the “mechanical” properties $\{E_n\}$.
- If I were going to “prove” thermodynamics—which I am not—I would simply have to show you that these quantities, when you calculate them, have the properties postulated by thermodynamics.

connections between ensembles, why they are equivalent

To illustrate what these formulas mean, I am going to calculate S(E,V,N) and F(T,V,N) for the ICMG:

**Let’s do F first, since it’s easier:**

$Z = \sum_n e^{\beta E_n}$, where n runs over discrete microstates and $E_n$ is the energy of the n<sup>th</sup> microstate.

Classically, the microstates are labeled by the 6N variables $\{\vec{r}_k, \vec{p}_k\}_{k=1}^{N}$, with $E(\{\vec{r}_k, \vec{p}_k\}) = \sum_{k=1}^{N} \frac{\vec{p}_k^{\,2}}{2m}$.

You might imagine that the sum over microstates n is just replaced by $\sum_n \overset{?}{\rightarrow} \int_V \prod_{k=1}^{N} (d^3 p_k)(d^3 r_k)$.

This is basically correct, except that quantum mechanics provides two changes:

- Quantum state for each particle occupies a small “volume” in phase space $(2\pi\hbar)^3$ where $\hbar$ is called Planck’s constant and has a value $1.05 \times 10^{-34}\ J \cdot s$. Planck’s constant has no analog in classical physics. It is very small. The discreteness it introduces is so fine that you do not see it in classical phenomena.
- Quantum mechanics incorporates the indistinguishability of the N particles by not counting as distinct states which differ only by interchanging the labels of the N particles. Thus, if you want to integrate over all the particles separately, you need to divide the result by N!

The upshot is that $\boxed{\sum_n \rightarrow \frac{1}{N!} \int_V \prod_{k=1}^{N} \frac{(d^3 p_k)(d^3 r_k)}{(2\pi\hbar)^{3N}}}$

Notice that $J \cdot s = m \times kg \cdot \frac{m}{s}$, so that the quantity on the right is dimensionless, as it should be, since we are just counting the number of microstates.

Now, calculate:

$$Z(T,V,N) = \frac{1}{N!} \int_V \prod_{k=1}^{N} \frac{(d^3 p_k)(d^3 r_k)}{(2\pi\hbar)^{3N}} e^{-\beta \sum_{k=1}^{N} \frac{\vec{p}^{\,2}}{2m}} = \frac{1}{N!}\left[V \int_{-\infty}^{\infty} \left(\frac{d^3 p}{(2\pi\hbar)^3}\right) e^{-\beta \frac{\vec{p}^{\,2}}{2m}}\right]^N .$$

The remaining integral is Gaussian:

$$\int_{-\infty}^{\infty} (d^3 p)\, e^{-\beta \frac{\vec{p}^{\,2}}{2m}} = \left[\int_{-\infty}^{\infty} dp\, e^{-\frac{p^2}{2mk_B T}}\right]^3 = \left[2 I_0\left(\frac{1}{2mk_B T}\right)\right]^3 = (2\pi m k_B T)^{3/2}$$, so

$$Z(T,V,N)=\frac{1}{N!}\left[\frac{V}{\lambda_t^3}\right]^N$$ where $$\lambda_t=\left(\frac{2\pi\hbar^2}{mk_BT}\right)^{1/2}$$ is called the "thermal wavelength." **14.4**

Note the explicit dependences on T,V,N and where they came from.

The upshot is $F(T,V,N)=-k_BT\ln Z=-k_BT\left[N\ln\left(VT^{3/2}\right)+\frac{3}{2}N\ln\left(\frac{mk_B}{2\pi\hbar^2}\right)-\ln N!\right]$

But $N!=\sqrt{2\pi N}\,N^Ne^{-N}\left(1+O\left(\frac{1}{N}\right)\right)$, so $\ln N!=N\ln N-N+\frac{1}{2}\ln(2\pi N)+\text{small}$, and

$$\boxed{F(T,V,N)=-k_BT\ln Z=-Nk_BT\left[\ln\left(\frac{T^{3/2}V}{N}\right)+\frac{3}{2}\ln\left(\frac{mk_B}{2\pi\hbar^2}\right)+1\right]},$$

where I have dropped small (i.e., sub-extensive) terms.

This has exactly the form I derived earlier only now the extra $CNk_B$ terms are evaluated.

I showed you earlier that this gave all the rest of the thermodynamic information via $dF=-SdT-PdV+\mu dN$ .