Notes for Chapter 6

Consider a gas or liquid of $N$ molecules and of total energy $E$ in a volume $V$. Suppose the volume $V$ is isolated — surrounded by a fixed, hard wall that lets no heat or energy in or out of $V$. If we let this system sit for a long while, then it will eventually come to equilibrium. Due to the constant stream of collisions between pairs of molecules and between the molecules and the wall, the precise velocities $\vec{v}_i$ and locations $\vec{r}_i$ of the $N$ molecules keep changing. In fact, the microstate $E, \vec{v}_i, \vec{r}_i$ changes from nanosecond to nanosecond.
The sum of the energies
\[ \sum_{i=1}^{N} \frac{1}{2} m \tilde{v}_i^2 = E \]
in each microstate is the total energy \( E \).
All of the \( \tilde{v}_i \) are within the volume \( V \).

How many microstates are there?

Suppose there are \( \Omega \) of them. Then
the entropy \( S \) is defined as
\[ S = k \ln \Omega . \quad (6.5) \]

We shall assume that all the \( \Omega \) microstates at equilibrium are equally likely. The entropy \( S \) is a measure of our lack of knowledge of the exact microstate of the system.

Why the logarithm?
To see why our uncertainty should be measured by a logarithm of the total number \( \Omega \) of microstates, let us consider two independent, isolated systems with \( \Omega_1 \) and \( \Omega_2 \) microstates. The total number \( \Omega \) of microstates for the combined system is

\[ \Omega = \Omega_1 \Omega_2. \]

Thus the entropy of the combined system is

\[ S = k \ln \Omega = k \ln \Omega_1 \Omega_2 = k \ln \Omega_1 + k \ln \Omega_2 = S_1 + S_2. \]

The logarithm makes entropy additive.
Additive physical quantities are called extensive. The logarithm makes entropy extensive.

Let's estimate $R$ and $S$ for an ideal gas of $N$ molecules and total energy $E$ isolated and in equilibrium in a volume $V$. For each microstate $\Sigma \vec{v}_i^2, \vec{v}_j^2, \vec{v}_k^2$, the energy $E$ is the sum of the kinetic energies of the $N$ molecules

$$E = \sum_{i=1}^{N} \frac{1}{2} m \vec{v}_i^2 = \sum_{i=1}^{N} \sum_{j=1}^{3} \frac{1}{2} m v_{ij}^2$$

Since $\vec{v}_i^2 = v_{i1}^2 + v_{i2}^2 + v_{i3}^2$. (Here $x, y, z$ have morphed into $1, 2, 3$.) Thus, the momenta $p_{ij}$ are the $3N$ components of a vector of length $R$. 
\[ \frac{1}{2m} \sum_{i=1}^{N} \sum_{j=1}^{3} p_{ij}^2 = E = \frac{R^2}{2m} \]

\[ R = \sqrt{2mE} = \sqrt{\sum_{i=1}^{N} \sum_{j=1}^{3} p_{ij}^2} \]

This 3N-dimensional vector lies on the surface of a sphere. Different points on that sphere of radius \( R = \sqrt{2mE} \) correspond to different microstates.

In a space of 3 dimensions, the area of a sphere of radius \( R \) is \( 4\pi R^2 \).

In a space of 3N dimensions, the area of a sphere of radius \( R = \sqrt{2mE} \) is

\[ A_{\text{vol}} = \frac{2}{3N} \frac{3N-1}{\pi^\frac{3N}{2}} \left( \frac{3N}{2} \right)^{\frac{3N-1}{2}} \]

\[ = \frac{2}{(3N^2 - 1)!} \pi^\frac{(3N)}{2} (2mE)^{\frac{3N-1}{2}} \]
Each molecule can be anywhere in the box $V$. So the number $\Omega$ of microstates for one molecule must be proportional to $V$, or $\Omega \propto V^2$, and for $N$ molecules

$$\Omega \propto V^N.$$ 

So

$$\frac{3N-1}{2} \frac{N}{2} \propto \text{constant} \times (2mE)^{\frac{3N-1}{2}} \times V^N.$$ 

Thus the entropy $S$ is with constant $= c'$

$$S = k \ln \Omega = k \ln (c' \times (2mE)^{\frac{3N-1}{2}} \times V^N) = k \left[ \ln c' + \frac{3N-1}{2} \ln 2mE + N \ln V \right],$$

When $N=10$, the $-1$ in $3N-1$ is important, but when $N$ is more than a few thousand, let alone $6 \times 10^2$, the $-1$
can be dropped. Now \( S \) looks nice:

\[
S = k \ln \left( c' \left( \frac{3N}{2} \right)^{\frac{3N}{2}} V^N \right) \\
= k \ln \left( c'' \left( \frac{3N}{2} \right)^{\frac{3N}{2}} V^N \right) \\
= k \left[ \ln c'' + N \ln \left( \frac{3N}{2} \right)^{\frac{3N}{2}} + N \ln V \right]
\]

or

\[
S = kN \left( \frac{3}{2} \ln \frac{\xi}{\ln V} + \ln V \right) + \text{constant}
\]

The Sackur-Tetrode formula is:

\[
S = k \ln \left[ \frac{2}{(3N/2 - 1)!} \left( \frac{3N}{2} \right)^{\frac{3N}{2}} \sqrt{\frac{N}{N! (2\pi h)^{\frac{3N}{2}}}} \right].
\]

The two new things here are the \( N! \) and \( h = h/2\pi \) where \( h \) is Planck's constant.

The \( N! \) is there because the molecules are indistinguishable: if you've seen one nitrogen molecule \( \text{N}_2 \), you've seen them all.
\[ S = k \ln \Omega = k \ln \Omega_A \Omega_B \]
\[ = k \ln \Omega_A + k \ln \Omega_B \]
\[ = k \left[ N_A \left( \frac{3}{2} \ln E_A + \ln V_A \right) + N_B \left( \frac{3}{2} \ln E_B + k \ln V_B \right) \right] + \text{constant} \]

But \[ E = E_A + E_B, \] so
\[ S = k \left[ N_A \left( \frac{3}{2} \ln E_A + \ln V_A \right) + N_B \left( \frac{3}{2} \ln (E - E_A) + k \ln V_B \right) \right] + C, \]

The most probable \( S \) is
\[ 0 = \frac{dS}{dE_0} = \frac{3}{2} \frac{N_A}{E_A} - \frac{3}{2} \frac{N_B}{E_B} \]

or
\[ \frac{E_A}{N_A} = \frac{E_B}{N_B} \]

so the two systems have the same \( \langle \frac{1}{2} m \dot{v}^2 \rangle \) per molecule.
This is the zeroth law of thermodynamics: two systems in thermal contact come to
the same temperature.

\[ \frac{3}{2} k T_A = \frac{\mathcal{E}_A}{N_A} = \frac{3}{2} k T_B = \frac{\mathcal{E}_B}{N_B} . \]

We define temperature \( T \) as

\[ T = \left( \frac{dS}{dE} \right)^{-1} = \left( \frac{dS}{dQ} \right)^{-1} . \quad (6.9) \]

\[ \boxed{6 A} \]

(a) Do the units work in (6.9)?

\[ [S] = [k] = E \text{ K}^{-1} \quad \text{so} \quad [\frac{dS}{dE}] = \frac{E}{E} \text{ K}^{-1} \]

\[ \left[ \left( \frac{dS}{dE} \right)^{-1} \right] = \text{ K}, \text{ degrees Kelvin.} \]

(b) \( S = k \frac{3N}{2} \ln E + kN \ln V \)

\[ T = \left( \frac{dS}{dE} \right)^{-1} = \left( \frac{k \frac{3N}{2E}}{2E} \right)^{-1} = \frac{2E}{3kN} \]
\[ \frac{E}{N} = \frac{3}{2} kT \text{ as expected.} \]

(There's a typo in the 1st & 2d printings.)

(c)

\[ S = S_A + S_B \text{ is maximal when} \]

\[ 0 = \frac{dS}{dE_A} = \frac{dS_A}{dE_A} + \frac{dS_B}{dE_A} \]

But \[ E = E_A + E_B, \text{ so } E_B = E - E_A, \]

so \[ \frac{d}{dE_A} = \frac{dE_B}{dE_A} \frac{d}{dE_B} = -\frac{d}{dE_B} \]

Thus, the condition \[ 0 = dS/dE_A \text{ gives} \]

\[ 0 = \frac{dS_A}{dE_A} - \frac{dS_B}{dE_B} = \frac{1}{T_A} - \frac{1}{T_B} \]

So \[ T_A = T_B \]

(6.10)

as follows from the 0th law of thermodynamics.
We add $dE$ to the combined system with entropy

$S = S_1 + S_2 = 2S_1$

We put $\alpha dE$ in $\square_1$ and $(1-\alpha)dE$ in $\square_2$.

$S(E + dE) = S_1(E + \alpha dE) + S_2(E + (1-\alpha)dE)$

$= S_1(E) + \frac{dS_1}{dE} \alpha dE + S_2(E) + \frac{dS_2}{dE} (1-\alpha)dE$

$= S_1(E) + \frac{\alpha dE}{T_1} + S_2(E) + \frac{(1-\alpha)dE}{T_2}$

$= 2S_1(E) + \frac{\alpha dE + (1-\alpha)dE}{T_1}$

$= 2S_1(E) + \frac{dE}{T_1}$

Now $T$ is given by

$\frac{1}{T} = \frac{dS}{dE} = \frac{1}{T_1} = \frac{1}{T_2}$

So $T = T_1 = T_2$ as long as $dE \ll E$. 
Thus when a system is duplicated, 
$S$ doubles, but $T$ stays constant.
$S$ is extensive, $T$ is intensive.
Two systems brought into contact will
assume the same $T$ eventually; the
total energy & entropy will be the sum
of those of the two systems after equilibration.

The first law of thermodynamics
is the conservation of energy, including heat.

The second law of thermodynamics:
If we release a constraint on an
isolated system, then some states become
accessible, and the number $S_2$ of states
increases, and so $S = k \ln S_2$ goes up.
Example:

Suppose we remove a baffle that keeps \( N \) Argon atoms on one side of a volume \( 2V \). By removing this constraint, we make many more microstates accessible.

The change \( \Delta S \) in the entropy \( S \) is

\[
\Delta S = k \left[ \ln \left( \frac{2^N}{E^2} \cdot 2V \right) - \ln \left( \frac{E^2}{V^N} \right) \right]
\]

in which the final and initial energies are both \( E \), since we did no work on the gas as we allowed it to expand into the volume \( 2V \). So

\[
\Delta S = k \left( \ln(2V)^N - \ln V^N \right)
\]

\[
= kN \ln 2.
\]

Our uncertainty about the system —
a) its disorder—has increased by
\[ \Delta I = \frac{\Delta S}{k \ln 2} = N \]

bits of information because we once knew that all \( N \) atoms were in the left \( V \) and not merely in the whole \( 2V \).

To restore this system to its original state, we could compress the gas again to the left \( V \) by pushing a piston from the right.

The gas would get hotter. We then could cool the gas by replacing
some of the insulation by a conductor and allowing the extra heat to escape until the temperature and energy of the gas returned to their initial values. The cost of releasing the constraint (removing the baffle) would be the transformation of some ordered energy (mechanical work) into disordered energy (heat).
Example:

We release two stop (\(\bullet\))s and the spring pushes the piston a distance \(S\) compressing the gas with force \(f\). The work \(\Delta W = fS\) done by the spring increases the kinetic energy \(E\) of the gas by the same amount

\[
\Delta E = fS, 
\]

The change \(\Delta S\) in the entropy of the gas is

\[
\Delta S = k \left( \Delta \ln \frac{E}{2N} + \Delta \ln \frac{V^N}{N} \right)
\]

\[
= \frac{3Nk}{2} \frac{\Delta E}{E} + N k \frac{\Delta V}{V}.
\]