Module 1 :: Lecture 6

6.1 Of Entropy, Dice and Pegs

[Bellan 2.4.1, Howard 2.5]

Assume that someone is throwing a pair of labeled die (i.e. the die are individually distinguishable) and reporting the sum, denoted $S$, of the outcome. If we are only given the sum corresponding to any given throw, what can we say about the numbers on the each individual dice? *The answer to this question depends on the sum!* Indeed, the table below lists the possible configurations of the die corresponding to any $S$:

<table>
<thead>
<tr>
<th>$S$</th>
<th>Die configurations</th>
<th># of configurations</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>(1,1)</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>(1,2),(2,1)</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>(1,3),(3,1),(2,2)</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>(1,4),(4,1),(2,3),(3,2)</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>(1,5),(5,1),(2,4),(4,2),(3,3)</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>(1,6),(6,1),(2,5),(5,2),(3,4),(4,3)</td>
<td>6</td>
</tr>
<tr>
<td>8</td>
<td>(2,6),(6,2),(3,5),(5,3),(4,4)</td>
<td>5</td>
</tr>
<tr>
<td>9</td>
<td>(3,6),(6,3),(4,5),(5,4)</td>
<td>4</td>
</tr>
<tr>
<td>10</td>
<td>(4,6),(6,4),(5,5)</td>
<td>3</td>
</tr>
<tr>
<td>11</td>
<td>(5,6),(6,5)</td>
<td>2</td>
</tr>
<tr>
<td>12</td>
<td>(6,6)</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 6.1: Sums of a pair of dice and the individual configurations that generate them.

So, if you were only given the information that $S = 2$, you would automatically know that each dice must have a face value of one (i.e. only one configuration can generate a sum of two). On the other hand, we know
much less, if only given the information that $S = 7$, as there are six possible configurations of dice that can generate such an outcome.

In terms stat. therm., the Sum of the die would be called a **macrostate**, with each specific configuration of die a **microstate**. For example, there are six possible microstates that could generate the macrostate $S = 7$. In Stat. Therm. the macrostates are normally values that are measured from a collections of many many particles. The number of corresponding microstates to these measured variables is huge due to their being so many particles in systems normally analysed via Stat. Therm.

Formally, what is meant by a system being in thermal equilibrium is that the Boltzmann postulate holds true for the system, i.e. a system is in thermal equilibrium when the system is equally likely to be in any accessible microstate. It is possible to relax this notion via the fluctuation theorem, but that is beyond the scope of this course.

With this, the **entropy of a system is defined to be the natural logarithm of the number of microstates corresponding to a given macro state**. Note that a collection of macrostates can be collectively considered as a single, unified macrostate in this definition.

Now, consider a pegboards with $N$ holes, labeled $h_1, h_2, \ldots, h_N$ with $N$ pegs labeled $p_1, p_2, \ldots, p_N$. How many ways can we arrange the pegs into the holes? Starting with hole $h_1$, there are $N$ possible pegs we can place there, but once this choice is made, there are only $N - 1$ pegs to choose from for $h_2$, and so forth. Iterating through all the holes in this manner leads to the conclusion that there are $N!$ ways to arrange $N$ pegs in $N$ holes.

Next, we extend this example by dividing the holes in the pegboard into $M$ groups of various size with an associated, integer mapping (labelled $f$) that takes the group index to the number of holes associated with that group. For example if group 1 had 3 holes, group 2 had 5 holes, etc. then $f(1) = 3, f(2) = 5$ and so forth. By the argument in the previous paragraph, the number of ways to arrange the pegs within a given group is just $f(j)!$ for the group indexed by $j$. Here, we are assuming the pegs associated with that group are selected and fixed.

Consider $C$ as being the number of ways of arranging $N$ pegs in $M$ groups, without caring about the internal arrangement of pegs within each group. With this, the number of ways of arranging the pegs in these groups,
while caring about the internal configuration of pegs within each group is

\[ C \times \prod_{j=1}^{M} f(j) = N! . \]  

(6.1)

Thus, the entropy associated with the macrostate corresponding to the selection of groups (or full determination of \( f \)) is

\[
S = \ln C \\
= \ln \left( \frac{N!}{\prod_{j=1}^{M} f(j)} \right) \\
= \ln N! - \sum_{j=1}^{M} \ln f(j).
\]  

(6.2)

To proceed, we use Stirling’s formula to approximate the log-factorials:

\[
\lim_{k \to \infty} \ln k! = k \ln k - k,
\]  

(6.3)

to approximate Eq. (6.2) as

\[
S = N \ln N - \sum_{j=1}^{M} f(j) \ln f(j),
\]  

(6.4)

where we have used the fact that \( N = \sum_{j=1}^{M} f(j) \). Often the \( N \ln N \) term is dropped in the definition (as we care about relative values of entropy for the most part):

\[
S = - \sum_{j=1}^{M} f(j) \ln f(j),
\]  

(6.5)

Generalising this notion to entropy encapsulates various subtleties that are beyond the scope of this course; but to put it simply, Eq. (6.5) looks very close to a discrete expectation value of \(- \ln(f)\):

\[
\frac{S}{N} = - \sum_{i=1}^{N} \frac{f(i)}{N} \ln f(i) \\
= E[- \ln f],
\]  

(6.6)

where \( E \) just indicates a functional that maps the argument function to its expectation value. With Eq. (6.6), we write the continuous analogy of the
expectation value of $-\ln f$ and take this to be the definition of entropy for a continuous mapping $f$:

$$\frac{S(t)}{\int f(\vec{x}, \vec{v}, t) \ d\vec{x} d\vec{v}} = -\int \frac{f(\vec{x}, \vec{v}, t)}{\int f(\vec{x}, \vec{v}, t) \ d\vec{x} d\vec{v}} \ln f(\vec{x}, \vec{v}, t) \ d\vec{x} d\vec{v}$$

$$\Rightarrow S(t) = -\int f(\vec{x}, \vec{v}, t) \ln f(\vec{x}, \vec{v}, t) \ d\vec{x} d\vec{v}. \quad (6.7)$$

### 6.2 Entropy, collisions and the Maxwellian

If a system is in thermodynamic equilibrium, it is *by far* most likely to be seen in a state of highest entropy, as the state with the highest entropy has the most number of microstates associated with it (and the system shows no statistical preference for being in any particular microstate over another). How thermodynamic equilibrium is achieved (i.e. where all microstates gain equal probability) is through any genuine randomisation process. In our case, this randomisation process are the collisions between plasma particles. Indeed, a random process is *defined* here as being any process that randomly (in a uniform distribution sense) “scrambles” the plasma configuration into any physically accessible microstate with equal probability.

With this the stage is set to gain a deeper understanding about our distribution function when the plasma is in thermal equilibrium. That is, we know the distribution function must maximise entropy; but the caveat being that it is also constrained by the conservation of mass and energy. In particular, we assume that our plasma is neither gaining nor losing energy nor particles. That is $N$, the number of particles, and $N\langle E \rangle$, the number of particles times the average energy of the particles, is fixed. We can now solve a variational problem for $f$ that maximises $S$ under the constraints of fixed $N$ and $N\langle E \rangle$, via the method of Lagrange multiplies (see the module assignment for a detailed problem walking you through a detailed calculus of variations calculation):

$$\delta S - \lambda_1 \delta N - \lambda_2 \delta (N\langle E \rangle) = 0, \quad (6.8)$$

where

$$N = V \int f(\vec{v}) \ d\vec{v}, \quad (6.9)$$

with $V$ being a given fixed volume. As $E = \frac{mv^2}{2}$ in the centre of mass frame of the entire collection of particles, the total kinetic energy is

$$N\langle E \rangle = V \int \frac{mv^2}{2} f(\vec{v}) \ d\vec{v}. \quad (6.10)$$
6.3. THE MAXWELLIAN AND THE PRESSURE

With this the variational problem becomes

$$\delta \int \left( f \ln f - \lambda_1 V f - \lambda_2 V \frac{m v^2}{2} f \right) d\vec{v} = 0.$$  \hspace{1cm} (6.11)

Using the chain-rule we can write

$$\delta g = \frac{dg}{df} \delta f,$$  \hspace{1cm} (6.12)

for any arbitrary \( g(f) \). Thus, we can reduce Eq. (6.11) to

$$\int \left( 1 + \ln f - \lambda_1 - \lambda_2 \frac{m v^2}{2} \right) \delta f d\vec{v} = 0,$$  \hspace{1cm} (6.13)

where \( V \) has been absorbed into \( \lambda_1 \) and \( \lambda_2 \). Since \( \delta f \) is arbitrary, the integrand must vanish:

$$\ln f = \lambda_1 + \lambda_2 \frac{m v^2}{2},$$  \hspace{1cm} (6.14)

where the 1 has been absorbed into \( \lambda_1 \). From this, the distribution function for an isolated system in thermal equilibrium is

$$f = \lambda_1 \exp \left( -\lambda_2 \frac{m v^2}{2} \right),$$  \hspace{1cm} (6.15)

where we have again manipulated constants to absorb and simplify the expression. Equation (6.15) is called the Maxwellian distribution, and the constants are determined by using the knowledge that \( N \) and \( N\langle E \rangle \) are fixed. Ultimately, using \( \vec{u}_\sigma \) to denote the lab frame for the centre of mass of species \( \sigma \), we get

$$f_\sigma(\vec{x}, \vec{v}, t) = n_\sigma \left( \frac{m_\sigma}{2 \pi \kappa T_\sigma} \right)^{N/2} \exp \left( -m_\sigma (\vec{v} - \vec{u}_\sigma)^2 / 2 \kappa T_\sigma \right).$$  \hspace{1cm} (6.16)

6.3 The Maxwellian and the pressure

Without loss of generality we can assume that we can assume that \( \vec{u}_\sigma = 0 \) and calculate the second velocity moment (i.e. the pressure) of the species:

$$P_\sigma = \frac{m_\sigma}{3} \int v^2 n_\sigma \left( \frac{m_\sigma}{2 \pi \kappa T_\sigma} \right)^{N/2} \exp \left( -m_\sigma v^2 / 2 \kappa T_\sigma \right) d\vec{v}$$

$$= n_\sigma \kappa T_\sigma,$$  \hspace{1cm} (6.17)

which is just the ideal gas law. This confirms that our notion of the Maxwellian corresponding to thermal equilibrium is consistent with our intuition.