Equipment

Administrative

- Exam – Graded, folks did fairly well. I’ll hand back at the end.
  - You’ll see: Exam grade, course grade, missing grades
  - Mistakes – “2nd Law” Meant “1st Law” (I’d been teaching Newton’s 2nd Law all week in my other class)
  - no, I hadn’t set my watch to the clock that morning.
- Collect homework & Deep Thoughts

Last Time

Basic background of Thermodynamics. We’d introduced the concepts, used them on the Macroscopic, Thermodynamic, level; and hinted at their microscopic origins. This was worthwhile in its own right, these tools and concepts are powerful and applicable to a wide range of Macroscopic (many particle) systems, (which, on some level, almost all real systems are). This was also necessary to set the context for where we’re going now.

This Time

Chapter 1

- Outline
  - This was a real hodge-podge of a chapter; a lot of different goals were set for it: introducing you to the subject, recapping some basic Thermodynamic properties and principles (hopefully familiar from last month), introducing the 1st Law, and (as a supplement) introducing magnetic work.

- Introduction
  - Statistical mechanics is the meeting of familiar classical (or quantum) mechanics of individual particles, and the mathematics of statistics. Statistics are used to scale our understanding of individual particles up to an understanding of a system of, say $10^{23}$ particles. It bridges the gap between Microscopic and Macroscopic. We use statistics because it would be unnecessarily unwieldy, at best, or downright impossible, at worst, to consider the positions and momenta of all $10^{23}$ particles. What is practical and possible is to consider statistical distribution of positions and momenta, and from that to determine the macroscopic properties of the system: Volume, Temperature, and Pressure.
  - While Thermodynamics is historically rooted in empirical observation of macroscopic systems and was developed in the early 19th Century, statistical mechanics is rooted in the atomic theory, and was developed near the end of that century, when the atomic theory was beginning to take hold. There are many systems that are far too complicated for a rigorous, analytical, statistical mechanics approach, and thus require a thermodynamics approach; however, there are some very illuminating ones that are tractable.

- Terminology:
- **State Variables:** variables, that characterize a macroscopic state: Pressure, Temperature, Volume, Number of particles,…

- **Equation of State:** a relationship between the state variables, in general form, say solved for \( T, T(P, V, N,...) \).
  - Generally speaking, the relationship between the state variables won’t be simple, unique, and analytical – ex. anything with a hysteresis curve has, say two possible values of Magnetization, associated with the same external field. In that example, can’t write \( M(B) \).

- **Equilibrium:** (or quasi-equilibrium) the condition that the state variables are constant over the length and distance scales relevant to your experiment / application. In contrast, say you suddenly pull up the head of a piston. Momentarily, there is a local rarefaction right under the head – the pressure there is much less than at other locations in the piston, and the system’s pressure (and other state variables) adjust over time until it is equilibrated.

- **Temperature:** In thermodynamics, temperature is a tough property to define, relative to other properties; however, it is easy to observe its effects on the other state variables, \( P, V \). As we get into the book, what becomes more relevant than temperature is the product \( kT \).
  - \( eV \): Since we’ll be looking at the atomic scale, it’s convenient to talk in energy units on scale with atomic processes. Fundamentally, atomic energies have to do with the behavior of their charged particles, and the charges are on the order of \( e = 1.6\times10^{-19} \) Coul. The convenient energy scale then is \( 1e \times 1\) Volt = 1eV(multiplying this out: \( 1.6\times10^{-19} \) Coul\( \times 1\) Volt = \( 1.6\times10^{-19} \) J. In terms of this scale, chemical / atomic processes usually involve energies in the range of 0.1 to 24 eV.
  - \( kT \): For comparison, a typical thermal energy, at a typical temperature is \( kT \), say, \( T = 290 \) K (around room temperature) \( \frac{1}{40} eV \).

- **1st Law**
  - \( \Delta E_{\text{int}} = Q_{\rightarrow s} + W_{\rightarrow s} \)
  - \( E_{\text{int}} \) = sum of energies of individual particles in the system, not responsible for bulk motion of the system.
  - \( E_{\text{int}} \) is a state variable, speaks only to the condition of the system, not how it got there. So, it can be written as a function of the state variables, but given an equation of state, you have one less independent variables, say \( T = T(P,V,N) \), and \( E = E(T, P, V, N) = E(T(P,V,N),P,V,N) = E(P,V,N) \) or \( E(T,P,V) \), or...
  - **Work:**
    - We won’t make serious use of it, but Mandl points out the technicality that \( dW \geq PdV \). We have an inequality because the average pressure in the system, \( P \), needn’t be the exact pressure moving, say, the piston. You can imagine such a scenario:
      - The piston moves suddenly, much faster than the system can equilibrate – it can leave a local rarefaction or
compression immediately below the piston head, which is not at all equal to the average pressure of the rest of the gas.

- Such a case is irreversible because, when you suddenly compress the head – it is working against a locally exaggerated pressure, \( P_\text{e} \) but suddenly pulling up the head has it working against a locally dropped pressure \( P_\text{d} \). So the ‘reverse’ process doesn’t run like a movie in reverse. The movie in reverse is unachievable – it’s an irreversible process.

**Heat Capacity**

- Mandl goes about this in a nice, no-nonsense, kind of way, so it’s worth retracing this:

  - For a reversible process, \( dQ = dE + PdV \)

  - \( C_V = \left( \frac{dQ}{dT} \right)_V = \left( \frac{dE}{dT} \right)_V \) note the partial derivatives

  - \( C_p = \left( \frac{dQ}{dT} \right)_p = \left( \frac{dE}{dT} \right)_p + P \left( \frac{dV}{dT} \right)_p \)

  - \( C_p - C_V = \left( \frac{dE}{dT} \right)_p + P \left( \frac{dV}{dT} \right)_p - \left( \frac{dE}{dT} \right)_V \)

**Ideal Gas:**

- However, as we’ve seen for an ideal gas, \( E \) only depends directly on \( T \), \( E = E(T) \), so it’s partial derivatives with \( P \) and \( V \) held constant are the same. \( \left( \frac{dE}{dT} \right)_p = \left( \frac{dE}{dT} \right)_V \)

- Also, \( PV = RT \) (here I follow the book in suppressing \( n \))

  - \( C_p - C_V = P \left( \frac{dV}{dT} \right)_p = P \left( \frac{\partial}{\partial T} \frac{RT}{P} \right)_p = \frac{P}{P} R \left( \frac{\partial T}{\partial P} \right)_p = R \)

  - \( C_p - C_V = R \)

**Magnetic Work**

- A little over the top for our application: We won’t bother with.

---

**Ch 2 2nd Law**

- **Introduction**

  - This is where the statistics comes in.

  - Thermodynamically, the second Law says that a macro system tends toward the macrostate with the highest entropy. (\( \Delta S \geq 0 \)). We’re also familiar with the notion that entropy some how measures disorder, and so the second law says that macro systems tend toward the most disordered state.

  - Statistically, complicated systems tend toward the most probable state.

  - It follows that entropy, disorder, and probability are close kin. We will start with probability and disorder and work our way to a definition of entropy in terms of them.

- **Disorder**
We’ll call the disorder of a macroscopic state the number of combinations of microscopic states that yield the macroscopic state (as defined by its state variables).

- **Example: Dice**
  - Your macroscopic system has one macrostate variable: value. It is built of two dice, each of which have one variable: value (1-6), the microstate of the system is the information of the state of each particle (dice).
  - Individually, each microstate is equally probable. However, the macrostates are not.
  - Work out the macrostates and the microstates that make them up.
  - The Macrostate with the most microstates associated with it (Value = 7) is the most probable
    - Probability = (number of microstates satisfying) / (total number of microstates)
  - We’d say that the most probable roll is a 7. In terms of thermodynamics, we’d say that 7 was the most disordered macrostate (most microstates make it up), it’s the state with the greatest entropy.

<table>
<thead>
<tr>
<th>Macro State Value</th>
<th>Micro State Value pairs</th>
<th># of Microstates</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Impossible</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>Impossible</td>
<td>0</td>
</tr>
<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) (2,2) (3,1)</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>(1,4) (2,3) (3,2) (4,1)</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>(1,5) (2,4) (3,3) (4,2) (5,1)</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>(1,6) (2,5) (3,4) (4,3) (5,2) (6,1)</td>
<td>6</td>
</tr>
<tr>
<td>8</td>
<td>(2,6) (3,5) (4,4) (5,3) (6,2)</td>
<td>5</td>
</tr>
<tr>
<td>9</td>
<td>(3,6) (4,5) (5,4) (6,3)</td>
<td>4</td>
</tr>
<tr>
<td>10</td>
<td>(4,6) (5,5) (6,4)</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>

There are 6 microscopic states that yield a 7 for our macroscopic value – 7 is the most popular macroscopic value, it corresponds to the most microscopic states, i.e., the most disorder, the greatest entropy.

*When the class rolled pairs of dice, 10 times per pair of students (30 times total), the number of occurrences of the macroscopic values tracked pretty well with the number of microstates that would yield them.*

- **Effect of N**
  - **1:** With just one dice making up a system, there were just 6 possible states, each is equally probable.
  - **2:** With two dice we have 6*6 or $6^2 = 36$ possible microstates, (1,1; 1,2; 1, 3;…6,5; 6,6). And we saw that there was a definite peak in the probabilities, tending toward a macrostate value of 7.
  - **3:** With three dice, we have $6^3$ possible microstates, and a much sharper peak.

- **Homework**: Work out the micro – macrostate table for 3 dice. Observe the location and strength of the peak.
You’ll find that the peak is much stronger.

- **Statistical Weight $\Omega$**
  - This is the number of microstates that yield the same macrostate (in the case of the dice, there were 6 ways to get a value of 7, $\Omega = 6$ for that macro state).
  - Consider a magnetic material. Each of N atoms has a magnetic dipole, and for simplicity, let’s say that it can either be pointed up or down. A macroscopic state variable would be the magnetization of the whole chunk, that depends directly on how many dipoles are pointed up and how many down. So we are interested in the macroscopic state defined by $n$, the number of dipoles pointed up.
    - $\Omega(n) = \binom{N}{n} = \frac{N!}{n!(N-n)!}$ reads “N choose n”.
  - We’re actually going to be interested in the natural log of this:
    \[
    \ln\left(\Omega(n)\right) = \ln\left(\frac{N!}{n!(N-n)!}\right) = \ln(N!) - (\ln(n!) + \ln((N-n)!)).
    \]
    - I’ve started breaking up the natural log so I can make use of Stirling’s Approximation for $\ln(N!)$, I’ll want to do this, partly because $N!$ is going to be awfully huge (say $N = 10^{23}$) and partly because this will be useful later.
    - Stirling’s Approximation:
      \[
      \ln(N!) = \ln(N) + \ln(N-1) + \ln(N-2) + \ldots + \ln(1) = \sum_{p=1}^{N} \ln(p) = \int_{1}^{N} \ln(p)dp = N \ln(N) - N + 1
      \]
      or, $\ln(N!) \approx N \ln(N) - N + 1$. Going about it more rigorously, the 1 is replaced by a series of terms, the highest order of which is $\frac{1}{2} \ln(N)$, which, for large N, is nothing compared to the $N \ln(N)$ term we’ve kept.
      \[
      \ln\left(\Omega(n)\right) = \ln(N!) - (\ln(n!) + \ln((N-n)!))
      \]
      - $\ln\left(\Omega(n)\right) \approx (N \ln(N) - N) - (n \ln(n) - n + (N-n) \ln(N-n) - (N-n))$
      - $\ln\left(\Omega(n)\right) \approx N \ln(N) - n \ln(n) + (N-n) \ln(N-n) - N + N + n - n$
      - $\ln\left(\Omega(n)\right) \approx N \ln(N) - n \ln(n) + (N-n) \ln(N-n)$

Now you’re ready for the homework!