Introductory material

(I am completing a lecturing commitment in France. I will be back for Friday’s lecture)
Our syllabus: Organizational material

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Web Site for course http://physics.arizona.edu/~lunine
Class time Monday, Wednesday and Friday 1:00 PM-1:50 PM in PAS 224.

Office hours: By appointment (or try to drop-in); my office is Space Science 522. Appointments made by calling me (621-2789), or Donita Vanture, 621-6939.

I will post these slides on the course website
Our syllabus: Course structure

Course description: An introduction to thermodynamics and statistical mechanics, for upper level undergraduates. We will cover the basic laws of thermal equilibrium, heat engines, ideal and non-ideal gases, phase transitions, irreversible processes, kinetic theory, and statistical thermodynamics. We will apply the fundamentals to problems of interest in physics and related fields. Prerequisites are MATH 223 + PHYS 242 or 252.

Attendance policy: Attendance required for lectures and exams.

Grading policy: Four homeworks totaling 40%, two midterm exams (February 7 and April 4) totalling 30%, a final exam equal to 30% of the grade. Homework is due the day specified; late homeworks will have a penalty applied to them (-20 points if handed in the same day after due, -40 points two class days after, null beyond....)

Textbook: Kittel and Kroemer, Thermal Physics (Freeman). It is concise and clear!
# Our syllabus: List of lectures

<table>
<thead>
<tr>
<th>Week of</th>
<th>Topic</th>
<th>Book chp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan. 10.</td>
<td>Introduction to Statistical Mechanics and thermodynamics</td>
<td>Chp. 1</td>
</tr>
<tr>
<td>Jan. 17.</td>
<td>Thermodynamic laws and the concept of entropy</td>
<td>Chp. 2</td>
</tr>
<tr>
<td>Jan. 22.</td>
<td>Partition function and thermodynamic free energy</td>
<td>Chp. 3</td>
</tr>
<tr>
<td>Jan. 29.</td>
<td>Statistical mechanics of photons</td>
<td>Chp. 4</td>
</tr>
<tr>
<td>Feb. 5.</td>
<td>Gibbs free energy (Exam Chps 1-4 on February 7)</td>
<td>Chp. 5</td>
</tr>
<tr>
<td>Feb. 12.</td>
<td>Fermi-Dirac and Bose-Einstein distributions</td>
<td>Chp. 6</td>
</tr>
<tr>
<td>Feb. 19.</td>
<td>Ultra-dense and ultra-cold matter</td>
<td>Chp. 7</td>
</tr>
<tr>
<td>Feb. 26.</td>
<td>Macroscopy: Heat, work and the Carnot cycle</td>
<td>Chp. 8</td>
</tr>
<tr>
<td>March 5.</td>
<td>Free energy treatment of chemical reactions</td>
<td>Chp. 9</td>
</tr>
<tr>
<td>March 12</td>
<td>Spring break (whew!)</td>
<td></td>
</tr>
<tr>
<td>March 19</td>
<td>Phase transformations</td>
<td>Chp. 10</td>
</tr>
<tr>
<td>March 26</td>
<td>Mixtures and phase equilibria</td>
<td>Chp. 11</td>
</tr>
<tr>
<td>April 2 .</td>
<td>Absolute zero (Exam Chps 5-10)</td>
<td>Chp. 12</td>
</tr>
<tr>
<td>April 9 .</td>
<td>Semiconductors</td>
<td>Chp. 13</td>
</tr>
<tr>
<td>April 16</td>
<td>Kinetic theory</td>
<td>Chp. 14</td>
</tr>
<tr>
<td>April 23</td>
<td>Heat conduction, phonons</td>
<td>Chp. 15</td>
</tr>
<tr>
<td>April 30</td>
<td>Special topics and review for the final exam.</td>
<td></td>
</tr>
</tbody>
</table>

---Final exam is Monday, May 7, from 11AM-1 PM in PAS 224--
Philosophy of Approach

• I follow Kittel and Kroemer because of its strong logical structure
• I will assume you have an elementary knowledge of the microscopic constitution of matter and of quantum mechanics
• I will introduce the three important laws governing thermal physics: (1) conservation of energy; (2) growth of entropy (will be defined); (3) entropy as temperature goes to zero)
• I will then show how the behavior of macroscopic systems connects to these concepts
Introductory Lecture

Based on Kittel and Kroemer pp. 1-4
The first law of thermodynamics

- Conservation of energy always applies!
- In an isolated system $\Delta E = 0$; $E$ the energy
- In thermal physics we will distinguish different forms of energy:
  - Internal to the system ($U$)
  - Energy available to do work (potential, kinetic)
  - Energy as heat (random kinetic energy)
  - Thermodynamics is really the study of energy transfer on a macroscopic scale (many particles)
  - Conservation of energy is the *first law of thermodynamics*
The second law of thermodynamics....

• sets limits on the ability of a system to do work. To introduce it requires introducing the concept of entropy.

• Entropy measures the number of “quantum states” (or microstates) of a system. An isolated “closed” systems can be in any quantum state that is accessible and consistent with the total system energy, volume, number of particles, etc. The system is equally likely to be in any of the accessible quantum states.

• The entropy is $S=k \log g(U, N, V,...)$, $k$ a constant.

• The number of quantum states of a macroscopic system can be large ($\sim 10^{23}$).
The second law derives from what happens to a system when it is allowed to change spontaneously

- Bring two initially isolated systems (1 and 2) into contact with each other so that a change can occur...such as flow of energy.

  Now the total possible number of accessible state is not $g_1 + g_2$, but $g_1 g_2$. (for each state in 1 there can be $g_2$ states)

  As energy flows from one system to the other, this will change the product $g_1 g_2$.

  Because each system can be in any of its $g_i$ accessible states with equal probability (fundamental assumption), the outcome of the energy transfer is strongly biased toward an outcome that maximized the number of accessible states: i.e., that increases the entropy.

- So the fundamental assumption implies that in a spontaneous change of a system, $\Delta S \geq 0$. This is the second law of thermodynamics.
But what happens to our two systems? (The zero-th law of thermodynamics)

• We will show (later) that the maximum of $g_1g_2$ occurs when

$$
\left( \frac{\partial S_1}{\partial U_1} \right)_{N_1,V_1,...} = \left( \frac{\partial S_2}{\partial U_2} \right)_{N_2,V_2,...}
$$

where $U_i$ is the internal energy for system $i$, likewise for the number of particles $N$ in each system, and other parameters (...). The state at which the maximum occurs is equilibrium, and no further change (except for fluctuations) should happen.

If the constant in the entropy is Boltzmann’s constant, then each of the two derivatives above is $1/T$, where $T$ is temperature. We will prove this.

Therefore, the statement above is that two systems brought into thermal contact with different initial temperatures will change so as to make $T_1 = T_2$. This is a partial statement of the zero-th law of thermodynamics, not complete because of the arbitrary way we introduced temperature.
But can we know the absolute value of the entropy?

- At zero temperature, all atoms are in their ground state of energy. That is, we know the state of all the atoms in the system at zero temperature--each atom can be in only one state. So \( g = 1 \) for any system at \( T=0 \), which implies that \( S=(k \log g) = 0 \) at \( T = 0 \).

- Well, this isn’t quite true, because we must approach absolute zero from a finite temperature, and frozen-in disorder makes the possible final state of the atoms not the ground state. But we can say that the entropy at absolute zero is a very small number. So
  \[ S \rightarrow 0 \text{ as } T \rightarrow 0 \]

- This is the *third law* of thermodynamics.
Summary of the laws of thermodynamics

• Zero-th law: If two systems are in equilibrium with a third system, they are in equilibrium with each other.

• First law: Energy is conserved, and heat is a form of energy.

• Second law: If a closed system is not in its equilibrium configuration, the most probable result is that its entropy will increase monotonically.

• Third law: The entropy tends toward a constant, small, value as the temperature goes to zero.
Derivation of the Boltzmann distribution I.

Let a small system (the cube, below) be connected to a very large system (the cylinder, which we will call a “reservoir”). The total energy of the coupled system is $U_o$. The cube can be in one of two energy states: when it is 0 the reservoir has energy $U_o$, and when the cube has energy $\varepsilon$ the reservoir has energy $U_o - \varepsilon$.

The small system has only two possible states. We desire to know the likelihood that the system would be in the state with energy $\varepsilon$ vs. the state with energy 0. It remains to enumerate the number of states of the large system.

Let $g(U_o)$ = number of states accessible to reservoir when small system has energy 0.
Let $g(U_o - \varepsilon)$ = number of states accessible to reservoir when small system has energy $\varepsilon$.

Then the ratio of probabilities of finding the small system in one of the two energy states is (with $\sigma = S/k$)

$$\frac{P(\varepsilon)}{P(0)} = \frac{g(U_o - \varepsilon)}{g(U_o)} = \frac{\exp[\sigma(U_o - \varepsilon)]}{\exp[\sigma(U_o)]}$$
Derivation of the Boltzmann distribution II.

Because the energy of the small system is presumed very much less than the total energy we can expand the previous equation in a Taylor series of just two terms, and then cancel out the first term \( \sigma(U_o) \) in numerator and denominator

\[
\sigma(U_o - \varepsilon) \approx \sigma(U_o) - \varepsilon \left( \frac{\partial \sigma}{\partial U_o} \right) = \sigma(U_o) - \varepsilon / kT
\]

so

\[
P(\varepsilon)/P(0) = \exp(-\varepsilon/kT)
\]

where we used \( \partial(U_o/\partial S)_{N,V} = T \)

Then the thermal average of the small system energy in contact with the reservoir is

\[
<\varepsilon> = \sum_i \varepsilon_i P(\varepsilon_i) = 0 \cdot P(0) + \varepsilon \cdot P(\varepsilon) = \frac{\varepsilon \cdot \exp(-\varepsilon/kT)}{1 + \varepsilon \cdot \exp(-\varepsilon/kT)}
\]

for \( P(0) + P(\varepsilon) = 1 \) (system is in one of the two states)
Derivation of the Boltzmann distribution III.

We can extend our result to a small system that also exchanges particles with a reservoir. It is only necessary to define the chemical potential $\mu$ such that

$$\partial(S/\partial N)_{U,V} = -\mu/kT$$

Now let the small system have either 0 or 1 particle in it; the reservoir then has $N_o$ or $N_o-1$ particles, respectively. When the small system has 0 particles its energy is 0; when it has 1 particle its energy is $\varepsilon$. Performing the equivalent Taylor expansion for $\sigma(U_o - \varepsilon; N_o-1)$ we find

$$P(1,\varepsilon)/P(0,0) = \exp [(\mu - \varepsilon)/kT]$$

or

$$P(1,\varepsilon) = 1 / [\exp(\varepsilon - \mu)/kT + 1]$$

The Fermi-Dirac distribution function

Finally, for an ideal gas $P(1,\varepsilon) << 1$ so that $P(1,\varepsilon) \simeq \exp(\mu - \varepsilon)/kT$
Read

• pp. 1-4: Introduction, immediately
• pp. 7-26 by Friday

........see you Friday!