Quiz 2 next Tues, Feb 8

Cover all material since Quiz 1, including today's lecture and HW3.

Will post list of topics to focus on this Sat.

Will provide formulas on future quizzes and exams. You show me you know how to use the formulas.

Homework: email if you're not.

HW3 answers Sat

Mon

Chapter 1: discussed energy, work, heat
1st law of thermodynamics, conservation of energy
relation of temperature to molecular motion

Two big questions:

1. how to think of temperature for non-gases?
   - liquids, solids, magnets
   - polymers, black hole, metals

2. how to understand spontaneous behavior?
   - why does heat transfer from hot to cold system?
   - gas automatically, spontaneously spread to entire container even though no change in energy
   - open up hole in partition (no work done, no heat exchanged)

Also: 40
Any Chapter 1 questions before beginning Chapter 2?

Heat capacity:
\[ C = \frac{\partial Q}{\partial T} \text{ at constant volume} \]
\[ C_v = \left( \frac{\partial Q}{\partial T} \right)_v \]

Specific heat:
\[ C = \frac{C_v}{\rho} \text{ per mass} \]
\[ C = \frac{C_v}{\text{mol}} \text{ per mol} \]

Adiabatic exponent \( \gamma \):
\[ 1 < \gamma = \frac{P + 2}{Q} \leq 5 \]
\[ \frac{C_p}{C_v} = \gamma \text{ for ideal gas} \]

\( C_p = C_v + N k \) ideal gas

Latent heat:
\[ L = \frac{\partial Q}{\partial m} \text{ constant pressure} \]

energy needed to melt amount of mass \( m \)

\( \begin{cases} \text{sublimation} & s \rightarrow g \\ \text{melting} & s \rightarrow l \\ \text{vaporization} & l \rightarrow g \end{cases} \)
Entropy $S(U,V,N)$ of

Macroscopic Isolated System

We will introduce a new concept related to macroscopic systems called the entropy that can explain our key question about temperature and about spontaneous behavior, and nearly all other questions about equilibrium macroscopic behavior.

Consider isolated macroscopic system like gas, liquid, solid, magnet, etc.

"Isolated" is code word for "conserved quantities"

- Total energy $U$ conserved
- Total number of particles $N$ conserved
- Total volume of system fixed, $V$

This does not imply $U$, $V$, $N$ conserved for macroscopic subsystems.

Energy and particles can move back and forth between subsystems.
When there is a non-negative number $S = S(U_{tot}, N_{tot}, V)$ called the entropy of the macroscopic system such that $S$ has a maximum value when system is in thermodynamic equilibrium monatomic ideal gas: $S = N \left[ \frac{5}{2} + \ln \left( \frac{V}{\sqrt{2\pi R N}} \right) \right]$

$s$ not meaningful for small systems or single particles like electron, atomic magnetic spin, photon etc.

\[ S \]

\[ \text{system in equilibrium when } S \text{ hits maximum value} \]

\[ \text{time } t \]

$S$ increases its value by system distributing energy and particles between subsystems until temperature, pressure, chemical potential equal everywhere in system.

\[ \frac{dS}{dt} > 0 \]

\[ \frac{dS}{dt} > 0 \quad \text{nonequilibrium} \]

\[ \frac{dS}{dt} = 0 \quad \text{equilibrium} \]
Outline of Key Argument

Why Entropy is Important

Following is one of the most arguments of course, will take time to appreciate it but let me put it before you so you can quickly see kinds of assumptions and conclusions used.

Make sure you understand assumptions and can reproduce logic of this argument.

Consider macroscopic system that is isolated so total energy, total number of particles is conserved.

Consider partition that divide system into two macroscopic subsystems such that only energy can move back and forth.

Partition (say made of impermeable metal)

\[
\begin{align*}
E_1 + E_2 &= E = \text{constant} \\
N_1 + N_2 &= N = \text{constant} \\
V_1 + V_2 &= V = \text{constant}
\end{align*}
\]

Partition only allows \( E_1, E_2 \) to change.
Entropy Argument Cont'd

Turns out that entropy $S$ is an additive quantity just like energy, entropy of two subsystems is sum of their individual entropies.

So for our isolated macroscopic system with two subsystems of energy $E_1, E_2$ we have

$$S(E, N, V) = S_1(E_1, N_1, V_1) + S_2(E_2, N_2, V_2)$$

$$= S_1(E_1) + S_2(E_2)$$

if partition doesn't allow $N_1, N_2, V_1, V_2$ to change.

Let us assume that entropy will have a maximum value when entire system is in equilibrium, will justify this insight later. Since system is isolated and energy conserved

$$E = E_1 + E_2$$

so total entropy is really function of $E_1$:

$$S = S_1(E_1) + S_2(E_2) = S_1(E_1) + S_2(E - E_1)$$
Condition for entropy to have maximum value with respect to change of energy $E_i$: 

$0 = \frac{dS}{dE_i} = \frac{d}{dE_i} \left( S_1(E_i) + S_2(E_i) \right) \Rightarrow \frac{dE_2}{dE_1} = -1$

$= \frac{dS_1}{dE_1} + \frac{dS_2}{dE_2} \cdot \frac{dE_2}{dE_1}$

so we conclude that equilibrium requires that the quantity

$\frac{dS_1}{dE_1}$

be same for all subsystems. We will define a temperature $T$ by:

$\frac{1}{T} = \frac{dS_1}{dE_1}$

more carefully $\frac{1}{T} = \left( \frac{2S}{S+1} \right)_{V,N}$

since $V,N$ constant

Then $T_1 = T_2$ for equilibrium;

will show later this reduces to our favorite concept of $T$ for an ideal gas so this definition turns out to be reasonable.
Temperature Defined by \( \frac{1}{\gamma} (\frac{dS}{dE})_{N,v} \)

Indicates Flow of Heat From Hot to Cold

For nonequilibrium system such that \( T_1 \neq T_2 \),
entropy will increase over time: \( \frac{dS}{dt} > 0 \)

But \( S = S_1(E_1) + S_2(E_2) \) implies

\[
\frac{dS}{dt} = \frac{dS_1}{dE_1} \frac{dE_1}{dt} + \frac{dS_2}{dE_2} \frac{dE_2}{dt}
\]

\[
= \frac{dE_1}{dt} \left( \frac{dS_1}{dE_1} - \frac{dS_2}{dE_2} \right)
\]

\[
\frac{dS}{dt} = \frac{dE_1}{dt} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) > 0
\]

since entropy increase over time

assume \( T_1 > T_2 > 0 \) \( \Rightarrow \) \( \frac{1}{T_2} > \frac{1}{T_1} \) so \( \frac{1}{T_1} - \frac{1}{T_2} < 0 \)

Hence \( \frac{dE_1}{dt} < 0 \) so product \( \frac{dE_1}{dt} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) > 0 \)

this implies \( E_1 \) decreases with time, \( E_2 \) increases with time so heat "flows" from high \( T_1 \) to low \( T_2 \)
Fact that $T_1 > T_2$ implies $\frac{dT}{dt} < 0$

is key reason to define

$$\frac{1}{T} = \frac{\partial S}{\partial E} \mu \nu$$

rather than by $T = \frac{\partial S}{\partial E} \mu \nu$

Note key assumptions:

$$\frac{dS}{dt} > 0 \text{ nonequilibrium}$$

$S$ maximum equilibrium

$S$ additive $S = S_1 + S_2$

conserved quantity $E = E_1 + E_2$
Outline of Chapter 2

We are going to define entropy $S$ in terms of another quantity called the multiplicity $\Omega$ (upper case Greek omega) of the macroscopic system.

$\Omega(E,V,N)$ is an integer, it counts number of ways that energy, particles, volume can be spread over various subsystems.

Introduce idea of "macromstate," subsystem characterized by macroscopic values of $E, V, N$.

Introduce idea of microstate, but all state of each microscopic component of system for macroscopic values $E, V, N$.

Then $\Omega(E,V,N)$ is number of microstates consistent with given macroscopic values of $E, V, N$.

$\Omega$ tends to be a very big $\Omega \sim 10^{10^{23}}$.

Define $S = k \ln \Omega$.

Boltzmann's great discovery:

$S = 0(NA)$

Boltzmann constant $k = \frac{1}{10^{-23} \text{J}}$.
Examples of Microstates and

Microstates

Consider three coins, these are microscopic pieces
state of coin is heads H or tails T
microstate of 3 coins is specific list of state of each coin

TTT TTH THT HTT THH ... 2 microstates

there are 2 x 2 x 2 = 2^3 = 8 microstates for 3 coins
define macrostate by number of heads, for 3 coins
there are four macrostates: 0, 1, 2, or 3 heads

Define multiplicity \( S_c(N_h, N) \) to be the total number
of microstates that have \( N_h \) heads, given \( N \) coins

<table>
<thead>
<tr>
<th>macrostate (# heads)</th>
<th>microstate</th>
<th>( S_c(N_h, 3) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>TTT</td>
<td>4</td>
</tr>
<tr>
<td>1</td>
<td>TTH, THT, HTT</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>THH, HTH, HHT</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>HHH</td>
<td>1</td>
</tr>
</tbody>
</table>
Can generalize to "macroscopic" system containing \( N \) coins

\[ \text{# of microstates is } 2^N \text{ since } 2 \times 2 \times \cdots \times 2 \]

\[ \text{# of macrostates is much smaller, } N+1 \]

- no heads, 1 head, \( \ldots \), \( N \) heads

What is multiplicity \( \mathcal{S}(N, N) \), number of microstates consistent with total \# of heads \( N_H \)?

This is classic combinatoric problem: given \( N \) slots, in how many ways can I place \( N_H \) objects in those slots?

Answer is binomial coefficient \( \binom{N}{N_H} \) pronounced \( N \) choose \( N_H \)

Here are \( N \) ways to choose 1st slot

- \( N-1 \) ways 2nd slot

\[ \binom{N}{N_H+1} \quad \cdots \quad \binom{N}{N_H} \]

But if coins are identical, can't distinguish cases where locations of heads are switched. So

\[ \mathcal{S}(N, N) = \frac{N!}{N_H! (N-N_H)!} \]

\[ \text{where } N! = 1 \cdot 2 \cdot 3 \cdots N \]
Properties of Binomial Coefficients

0! = 1 1! = 1 2! = 2 3! = 6 4! = 24

\[ \binom{n}{k} = \binom{n}{n-k} \quad \text{kind of symmetry} \]

\[ \binom{n}{0} = 1 \quad \binom{n}{1} = n \]

\[ (a + b)^n = \binom{n}{0}a^n + \binom{n}{1}a^{n-1}b + \binom{n}{2}a^{n-2}b^2 + \cdots + \binom{n}{n-1}ab^{n-1} + \binom{n}{n}b^n \]

Setting \( a = b = 1 \), we conclude

\[ 2^n = \binom{n}{0} + \binom{n}{1} + \cdots + \binom{n}{n} \]

Mathematica \( f^n \) is \( \text{Binomial}[n, k] = \binom{n}{k} \)

Watch out! For most cases, use decimal point not integer to avoid expensive exact integer arithmetic type \( \text{Binomial}[10, 5] \) not \( \text{Binomial}[10.5] \)

\( \text{Factorial}[n] \) is \( n! \), defined through Gamma \( \Gamma \)
Probability of Macростate

For \( N \) coins, probability of observing macrstate with \( N_h \) heads is

\[
P(N_h, N) = \frac{\binom{N}{N_h}}{2^N}
\]

provided all microstates are equally likely.

If we flip 100 coins many times, we will see macrstates that have \( \sim 50\% \) heads. Some macrstates much more probable than other microstates.

Exactly the same situation for macrscopic thermodynamic systems; only most likely macrstates are observed, these are the ones with the most microstates, i.e. \( \mathcal{S} \) is a max.

Problem 2.32 of Schweek

\[
\text{prob} = \text{Table}\left[\text{Binomial}[50, n] / 2^{50}, \{n, 0, 50\}\right]
\]

\text{ListLinePlot}[\text{prob}]