Lecture 1: Temperature and Thermodynamics

**Thermodynamics**: is a branch of physics concerned with heat and temperature and their relationship to energy and work.

: How can we use fire to do work?

**Statistical Mechanics**: branch of physics/chemistry that studies (using probability) the average behavior of mechanical systems whose state is unknown. Connects thermodynamic quantities to microscopic behavior.

**Brainstorm**: gaps 23 mins.: what is heat? What is temperature?

Zeroth Law of Thermodynamics

\[ A - B \quad B - C \]

If A is in thermal equilibrium with B and B is in thermal equilibrium with C then A is in equilibrium with C and the quantities they have in common is temperature.

First Law of Thermodynamics (conservation of energy)

\[ \Delta E = \Delta Q - \Delta W \]

\( \Delta E \) = work it does

\( \Delta Q \) = heat we add

\( \Delta W \) = internal energy

Energy can be transformed from one form to another but cannot be created or destroyed.

(sorry, no perpetual motion machines)
Second law of thermodynamics

\[ S = \text{entropy} = \text{state function} \]

\[ ds \geq \frac{dq}{T} \]

equality for a reversible process

\[ ds \geq 0 \rightarrow \text{heat spontaneously flows from hot to cold} \]

let's examine this

\[ dq_2 : \text{heat going to} \ 2 \]

\[ dq_1 : \text{heat going to} \ 1 \]

\[ dq_1 = -dq_2 \]  \( \text{(no work is done)} \)

\[ ds_{tot} = ds_1 + ds_2 \]

\[ ds_{tot} = \frac{\partial S_2}{\partial Q_2} dq_2 + \frac{\partial S_1}{\partial Q_1} dq_1 \]

\[ ds_{tot} = \left( \frac{\partial S_2}{\partial Q_2} - \frac{\partial S_1}{\partial Q_1} \right) dq_2 \]

at equilibrium: nothing changes

\[ ds_{tot} = 0 \]

\[ \frac{\partial S_2}{\partial Q_2} = \frac{\partial S_1}{\partial Q_1} \]  \( \frac{ds \cdot dq}{T} \)

\[ \frac{1}{T_2} = \frac{1}{T_1} \]
away from equilibrium

$$dS = \left( \frac{1}{T_2} - \frac{1}{T_1} \right) dQ_2$$

heat flows from hot to cold.

$$dQ_2 \text{ positive if } T_1 > T_2$$

the goal of the next few weeks is to motivate the second law with mathematical arguments

but let's reflect on thermodynamics a bit more:

What is pressure?

molecule collides with wall

$$\Delta p = 2mV_x$$

time between collisions

$$\Delta t = \frac{2l}{V_x}$$

average force

$$F = \frac{\Delta p}{\Delta t} = \frac{2mV_x}{2l} V_x = \frac{mV_x^2}{l}$$

Pressure = \frac{\text{Force}}{\text{Area}}

$$P = \frac{1}{(2l \cdot \lambda)^2 \text{Volume}} \cdot \frac{mV_x^2}{V} \text{ (one molecule)}$$

N molecules:

$$PV = N \cdot m \cdot \langle V_x^2 \rangle$$

$$V^2 = V_x^2 + V_y^2 + V_z^2$$

$$\langle V^2 \rangle = \langle V_x^2 \rangle + \langle V_y^2 \rangle + \langle V_z^2 \rangle = 3 \langle V_x^2 \rangle$$

$$PV = N \cdot m \cdot \frac{1}{3} \langle V^2 \rangle$$
but kinetic energy is $\frac{1}{2}mv^2$ so $PV = \frac{2}{3} N \langle KE \rangle$

Temperature is a measure of the average kinetic energy of the molecules, related via the Boltzmann constant.

$$\langle KE \rangle = \frac{3}{2} kT \quad k = 1.38 \times 10^{-23} \text{ J/K}$$

Put these together:

$$PV = N kT \quad \text{(ideal gas law)}$$

$N$ = Standard # of molecules $\quad N_A = 6.022 \times 10^{23}$

$1$ mole = $N_A$ molecules $\quad n$ moles = $nN_A$

Define $R = N_A k = 8.31$ J/K (ideal gas constant)

Then $PV = nRT$

(this establishes a relationship between pressure and volume and temperature ... relationship to work)

Work done by an expanding gas

$$dW = F \, dx = P \, Adx = -P \, dV$$

$$dW = P \, dV \rightarrow W = \int P \, dV$$
example: isobaric expansion of an ideal gas (constant pressure)

\[ W = P \int dV = P(V_f - V_i) \]

example: ideal gas expanding at constant temperature.

\[ W = \int p dV \quad pV = NkT \]

\[ W = \int \frac{NkT}{V} dV = NkT \ln \left( \frac{V_f}{V_i} \right) \]

kinetic energy is not the only kind of energy a molecule can have:

\underline{Internal energy} : \[ E = \text{total internal energy of all molecules in a sample} \]

\underline{Equipartition principle} : total internal energy will be equally distributed into all forms of internal energy at temperature \( T \) each degree of freedom gets on average \( \frac{1}{2} kT \) of energy.

counting degrees of freedom can be tricky.

\underline{Translational} : \[ 3 \quad (x, y, z) \]

\underline{Rotational} : diatomic \[ 2 \]

polyatomic \[ 3 \]

\underline{Vibrational} : diatomic \[ 2 \]

total internal energy \[ E = N \bar{e} \frac{1}{2} kT \]
Lecture 12

Review:
1st law: \( dE = dQ - dw \)
2nd law: \( ds \geq \frac{dQ}{T} \) (entropy)

Equation: Total internal energy is distributed into all forms of internal energy, thermal energy.

At temp T, each degree of freedom gets \( \frac{1}{2} kT \) of energy.

Total internal energy: \( E = N \bar{d} \frac{1}{2} kT \)

Heat: Energy transferred from hot object to cold.

Heat is energy in transit.

Heat capacity: How much heat does it take to raise temperature by \( dT \).

\[ dQ = C dT \]
\( C = \text{heat capacity} \)

For solids/liquids:
\( C = \frac{MC}{\text{mass}} \)

For gases:
\( C_v = \frac{nC_v}{nC_p} \)

\( C_v \) - Molar heat capacity at constant volume (\( C_v \))
\( C_p \) - Molar heat capacity at constant pressure (\( C_p \))

\# of moles

Constant volume:
\( dE = dQ + dw \) \( \rightarrow \) become \( dV = 0 \)

\( dQ_v = dE - nC_v dT \)

Because \( E = N \frac{1}{2} kT \)

Question 1: Which has a higher heat capacity at \( C_v \)?

Nitrogen gas: \( N_2 \), 20.4 \( \text{cal} \) \( \text{mol}^{-1} \text{K}^{-1} \)

or Helium: \( \text{He} \), 12.5 \( \text{cal} \) \( \text{mol}^{-1} \text{K}^{-1} \) \( \text{mol}^{-1} \text{K}^{-1} \)

\( d = 3 + 2 + 2 \)
constant pressure
\[ dQ_p = dE + PdV = nC_vdT + PdV \]
\[ PV = nRT \rightarrow PdV = nRdT \]
\[ = nC_vdT + nRdT \]

Thus \( C_p = C_v + R \) \( R \): ideal gas constant \( 8.315 \text{ J/kg} \cdot \text{K} \)

entropy example
\[ ds \geq \frac{dQ}{T} \] (equality for a reversible process)

Controlled expansion of a gas

\[ \text{reversible} \]

Uncontrolled expansion of a gas

\[ \text{vacuum} \rightarrow \text{gas} \rightarrow \text{position} \]

The essence of a reversible process is that it proceeds by a succession of equilibrium steps.

Compare the change in entropy in each case.

Isothermal expansion
\[ \Delta S = \int_{V_1}^{V_2} \frac{dQ}{T} = ? \]
Isothermal expansion ... need to do this reversibly.

\[ dS = \int_{V_1}^{V_f} \frac{dQ}{T} \]

Note that total internal energy is constant.

\[ dE = 0 \quad \Rightarrow \quad dQ = PdV \]

\[ dS = \int_{V_1}^{V_f} \frac{PdT}{T} = \int_{V_1}^{V_f} \frac{\partial P}{\partial V} dV = n \frac{R \ln \left( \frac{V_f}{V_i} \right)}{V_i} \]

Adiabatic expansion: no heat in or out.

\[ dQ = 0 \]

\[ dS = \int_{V_1}^{V_f} \frac{dQ}{T} = 0 \]

No change in entropy.

\[ dE = dQ - dW \quad \Rightarrow \quad dE = -dW \]

temperature goes down.

Example: stretching rubber band

\[ A \rightarrow \text{stretched rubber band} \rightarrow \text{heat up} \]

\[ \rightarrow \text{cool down.} \]

In A to B you do work, no heat is exchanged with environment, so internal energy must increase.

Entropy plays a role here.

\[ \text{more configurations} \quad \text{fewer configurations} \]

Heat comes from internal thermal energy.
So far, we're thinking of energy and temperature as macroscopic quantities... the goal here is to see how these are a manifestation of the properties of large numbers.

Statistical Mechanics: theory of systems with lots of particles

(roughly \( N \approx \))

Because there are so many particles, it's impossible to keep track of each one—so we're not interested in the positions or velocities of each one (the microstate), but rather some gross feature of the whole system.

<table>
<thead>
<tr>
<th>Number of particles</th>
<th>( N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>( V )</td>
</tr>
<tr>
<td>Pressure</td>
<td>( P )</td>
</tr>
<tr>
<td>Temperature</td>
<td>( T )</td>
</tr>
<tr>
<td>Total energy</td>
<td>( E )</td>
</tr>
<tr>
<td>Entropy</td>
<td>( S )</td>
</tr>
</tbody>
</table>

These gross properties describe the macrostate.

Clearly, there are many different microstates corresponding to a given macrostate.

The number of microstates corresponding to a particular macrostate is called the multiplicity:

\[ \Omega \]

Multiplicity \( \Omega \) \# of ways

\[ S = k \ln \Omega \]

\( S = 0 \)
\[ Z_f = \binom{N}{N/2} \]

N choose N/2

\[ = \frac{N!}{\left(\frac{N}{2}\right)! \left(\frac{N}{2}\right)!} \]

Example: \( N = 4 \)

\[
\begin{align*}
\text{ab} & \quad \text{cd} \\
\text{ac} & \quad \text{bd} \\
\text{ad} & \quad \text{cb} \\
\text{bc} & \quad \text{ad} \\
\text{bd} & \quad \text{ac} \\
\text{cd} & \quad \text{ab}
\end{align*}
\]

\[ Z = 6 = \frac{4!}{2! \cdot 2!} = \frac{24}{4} = 6 \]

Stirling's approximation

\[ N! = \sqrt{2\pi N} \left( \frac{N^N}{e^N} \right) \]

\[ S_f = k \ln \left( \sqrt{\frac{2}{\pi N}} 2^N \right) = N k \ln 2 + \ln \sqrt{\frac{2}{\pi N}} \]

\[ S_f = k \ln (1) = 0 \]

\[ S_f = k \ln (\sqrt{\frac{2}{\pi N}} 2^N) \approx N k \ln 2 + \ln \sqrt{\frac{2}{\pi N}} \]

\[
\text{dominates. same small #}
\]
Recall that $N = nN_A$

$S = nN_A \text{ km}^2 = nR \pi \text{ m}^2$
\( Z(3,1) = 3, 0, 2 \quad \text{and} \quad Z(3,2) = 3, 3, 2 \quad \text{and} \quad Z(3,3) = 3 \quad \text{(with 1 and 3 distinguished)} \)

\[ \text{Example n = 3} \]

There can be many microstates for a given macrostate. We care about the macrostate, not the microstate. We will do a Gaussian version later.

What is the probability that all the air is southern on one side of the room?
\[ P(\text{H}) = \frac{1}{2} \left( \frac{1}{2} \right)^{10 \times 28} \]

\[ P(\text{N}) = \frac{1}{2^{10 \times 28}} \]

\[ \log_{10} (P) = 10 \times 28 \log_{10} \left( \frac{1}{2} \right) \approx P = 10^{-3 \times 28} \]

**Example:** In partition (a, b, c, \ldots, n)

- **Microstates**: \( n! \)
- **Multiplicity**: \( \Omega(a, b, c, \ldots, n) = \binom{n}{i} \)

Crucial idea: all the microstates are equally probable.

\[ P(a, b, c, \ldots, n) = \frac{n!}{N! (n-N)!} \]


- **N mole of molecules**
  - 6\times10^{25} moles in 20 L
  - 3\times10^{28} molecules
  - 6 \times 10^{25} mole\cdot L^{-1}

- **H mole of molecules**
  - 4 \times 10^{25} molecule
  - 6 \times 10^{25} mole\cdot L^{-1}
\[
\frac{N}{2}\left(1 + \frac{\hat{\pi}}{\sqrt{2\pi}}\right) = \frac{\pi}{\sqrt{\pi}}(\hat{\pi})^{(N)}(1) - \frac{\pi}{\sqrt{\pi}}(\hat{\pi})^{(N)}(N+\frac{1}{2}) - \frac{\pi}{\sqrt{\pi}}(\hat{\pi})^{(N)}(N-\frac{1}{2}) \frac{N+\frac{1}{2}}{N^{\frac{1}{2}}} \frac{N}{\sqrt{N}} \enspace \hat{\pi} = \lambda \enspace (N,\epsilon) = \lambda \enspace (N,\epsilon) =
\]

To simplify, take \( \epsilon = 0 \).

\[
\frac{N}{2} = \sqrt{N} \enspace \lambda(N,\epsilon) \]

From here, the \( Z(\epsilon) \) is:

\[
\frac{\pi}{\sqrt{\pi}}(\hat{\pi})^{(N)}(N-\frac{1}{2}) \frac{N+\frac{1}{2}}{N^{\frac{1}{2}}} \frac{N}{\sqrt{N}} \enspace \hat{\pi} \]

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\[
\frac{\pi}{\sqrt{\pi}}(\hat{\pi})^{(N)}(N-\frac{1}{2}) \frac{N+\frac{1}{2}}{N^{\frac{1}{2}}} \frac{N}{\sqrt{N}} \enspace \hat{\pi} \]
Call this equilibrium, for large $N$ it most probably state, i.e. is macroscopic, as i

\[ N \rightarrow \infty \]

which is $10^{-12}$ (part the trillion!), which is a very sharp Gaussian, i.e. which is $\frac{1}{\sqrt{2\pi N}}$.

This is $p(x) = p(s)$.

\[ \frac{N}{2}\frac{e^{-\frac{N}{2}}}{\sqrt{\frac{2\pi}{N}}} = \frac{\sqrt{\frac{N}{2\pi}}}{e^\frac{N}{2}} \]

where in terms of $s$,

\[ p(s) = \frac{N^2}{e^\frac{N}{2}} \]

\[ \frac{N}{2}\frac{e^{-\frac{N}{2}}}{\sqrt{\frac{2\pi}{N}}} = \frac{\sqrt{\frac{N}{2\pi}}}{e^\frac{N}{2}} \]

\[ s + \frac{N}{2} \eta (s - \frac{N}{2}) - \frac{N}{2} \eta - s - \frac{N}{2} \eta (s + \frac{N}{2}) - (\eta \frac{N}{2}) \varphi \]

\[ = \frac{N}{2} - s + \frac{N}{2} \eta (s - \frac{N}{2}) - \frac{N}{2} \eta - s - \frac{N}{2} \eta (s + \frac{N}{2}) - (\eta \frac{N}{2}) \varphi \]