Lecture 1 - Go over syllabus/course design/Qualify: last week of Summer Break

Topics: Intro to Thermodynamics
State Quantities
0th law and temperature
Kinetic Theory of the ideal gas
Maxwell-Boltzmann distribution
Heat & Heat Capacity

Some math

Examples of many-particle system: center of neutron star/supernova explosions/
big-bang → quarks/gluons/plasma/etc.

The properties of such many-particle system in thermal equilibrium

Thermodynamics → define state quantities which characterize macroscopic properties of matter (macrostate)

Relationship between macrostates is the equations of state & laws of thermodynamics

Empirically we define axiomatic laws of thermodynamics; independent of a special physical system

Empirically relations between state quantities: equation of state; valid for a particular physical system

Then once you know few state variable all the others state variables have a uniquely defined value.
Thermodynamic System: amount of matter confined by walls from the surroundings.

We distinguish

1. Isolated Systems: systems that do not interact with the surroundings. No exchange of energy/matter. Total energy $E$, $N$, $V$ conserved.

   $\rightarrow$ If the system is in equilibrium with its surroundings, the energy will have an average value. $\Rightarrow$ Temperature $T$, $N$, $V$, Temperature.

3. Open Systems: exchange energy and matter. Energy and particles numbers are NOT a conserved quantity.
   $\rightarrow$ If the system is in equilibrium $\langle E \rangle$, $\langle N \rangle$.

Other categories:

- Homogeneous SYSTEMS
- Heterogeneous

We call “phases” and separating surfaces “phase boundaries.” Homogeneous parts of a heterogeneous system.
Example:

\[ \begin{align*} 
\text{air} & \quad \text{gaseous phase} \\
\text{steam} & \quad \text{phase boundary} \\
\text{water} & \quad \text{liquid phase} 
\end{align*} \]

State Quantities: are the macroscopic quantities that describe a system:

- \( E \), \( V \), \( N \), \( S \), \( T \), \( p \), \( \mu \), \( \rho \), \( \eta \), \( \gamma \), \( \kappa \), \( \sigma \), \( \alpha \), etc.

Microscopic quantities, e.g., positions \( x \) and momenta \( p \), are not state quantities.

Gibbs' phase rule: number of state quantities that are necessary to uniquely define a thermodynamic state \( \Rightarrow \) # of phases of a system.

State Variables + Equations of State \( \Rightarrow \) all other state variables determined empirically.

Importance to notice that such empirical equations of state are valid only in a limited range of values of state variables.

Two classes of State Quantities:

a. Extensive State Quantities \( \Rightarrow \) quantities \( \propto N \) (# particles) \( \alpha \) mass
Examples: volume, energy, entropy

The extensive state quantities can be added. (so volume of a pot of water, steam, air can be added...)

b. Intensive State Quantity

Quantities not additive & not independent of the amount of matter.
Examples: refractive index, density, pressure, temperature
In general they can be defined locally.

Usually we go from extensive \( \rightarrow \) intensive variables

Example: energy \( \rightarrow \) energy density

Equilibrium & Temperature

Equilibrium state \( \rightarrow \) macroscopic state of a closed system which is obtained after a long time so the macroscopic state quantities don't change.

If the change of state variables is very slow we can talk on thermal equilibrium.

Example: Sun \( \Rightarrow \) Sun loses energy through radiation

but we can talk on \( T \); \( n \); \( g \) since the variation is slow.
Zeroth law of Thermodynamics

Situations have shown that all systems, which are in thermal equilibrium
with a given system, are also in thermal equilibrium with each other.

Systems which are in thermal equilibrium have the same T
no information about the time to reach thermal equilibrium.

How to measure?

Two systems are brought in
thermal equilibrium.

we can also talk about local thermal equilibrium instead of global thermal
equilibrium (example: slabs where different zones will have different
temperatures)

Procedure of measuring temperature is related with an equation of state.
We use a volume fixed gas to calibrate. 

\[
\frac{T}{T_0} = \frac{V}{V_0}
\]

\( \text{dilute gas} \)

\( \text{gas thermometer} \)

Unit: \( T = 273.15 \text{ K as the melting point of ice.} \)

\[
y \text{ (°C) = } (\frac{5}{9}) (x \text{ (°F) } - 32)
\]
idealized system when \( V = 0 \text{m}^3 \) @ \( T = 0 \text{K} \) (absolute temperature)

- from a statistical point of view \( T \propto \text{Kinetic energy of particles} \)
- therefore no negative kinetic energies, so no negative absolute temperatures

Example: Ideal Gas

- Ideal gas: non-interacting, point-like particles
  \[ pV = p_0V_0 \quad T \propto c_h^2 \]
  \[ V = \frac{T \cdot V_0}{T_0} \quad p_0 = c_h^2 \]

If we move from \((p_0, T_0, V_0) \rightarrow (p, T, V)\)

Step A) \( pV_0 = p_0V_0 \) i.e. \( T_0 \) vs. \( c_h^2 \) change the pressure

Step B) Changing the temperature at a constant pressure
  \[ V = \frac{T \cdot V_0}{T_0} \quad p \propto c_h \]
  \[ V = \frac{T \cdot p_0V_0}{T_0 \cdot p} \rightarrow \frac{pV}{T} = \frac{p_0V_0}{T} = kN \]

Boltzmann constant:
  \[ k = 1.38 \times 10^{-23} \text{J/K} \]
or \[ pV = NkT \] ideal gas law example of eq. of state

**Kinetic Theory of Ideal Gas**

Each particle has \( \vec{v} \)
In equilibrium state, on average, we will have same number of particles in an interval \( d^3v \)

\[ f(\vec{v}) \] velocity distribution probability

Number of particles: \( dN(\vec{v}) \) in the velocity interval around \( \vec{v} \)

\[
dN = N f(\vec{v}) d^3v, \quad f(\vec{v}) = \frac{N}{N} d\frac{N}{d^3v}
\]

\[
\int_{-\infty}^\infty f(\vec{v}) d^3v = 1
\]

Let say we have an area \( A \)
What's the pressure at \( A \) ?

One particle of velocity \( \vec{v} \) transfers momentum \( p = 2m \vec{v} \)

Particles with velocity \( \vec{v} \) will travel \( dv^3 = \vec{v} dt \)

Number of particles with velocity \( \vec{v} \)

\[
dN = N f(\vec{v}) d^3v, \quad dV = A\vec{v} dt
\]
Impulse per area A

\[ \frac{dF_A}{db} = \frac{2m v_e^2}{2} dN = \frac{2N m v_e^2}{V} f(A) d_3 v \frac{A d b}{V} \]

Total pressure = contribution of all possible \( v > 0 \)

\[ p = \frac{1}{A} \int dF_A = \frac{N}{V} \int_{-\infty}^{\infty} dV_x \int_{-\infty}^{\infty} dV_y \int_{-\infty}^{\infty} dV_z f(\vec{v}) 2m v_e^2 \]

\( f(\vec{v}) \) has to be \( f(1/v) \) so

\[ \int_{-\infty}^{\infty} dV_z f(\vec{v}) 2m v_e^2 = \frac{1}{2} \int_{-\infty}^{\infty} dV_z f(\vec{v}) 2m v_z^2 \]

\[ p V = m N \int_{-\infty}^{\infty} d^3 \vec{v} f(\vec{v}) v_z^2 \]

\[ = \langle V_z^2 \rangle = \langle V_y^2 \rangle = \langle V_x^2 \rangle \]

or since \( \vec{v}^2 = v_x^2 + v_y^2 + v_z^2 \)

\[ \langle V_z^2 \rangle = \frac{1}{3} \langle \vec{v}^2 \rangle = \frac{1}{3} \left( \langle V_x^2 \rangle + \langle V_y^2 \rangle + \langle V_z^2 \rangle \right) \]

so \( p V = m N \frac{1}{3} \langle \vec{v}^2 \rangle = \frac{2N}{3} \left( 6 \text{kin} \right) \)

\[ \Rightarrow N k T \]

\[ \therefore \langle \text{kin} \rangle = \frac{3}{2} k T \]
Second Example: Maxwell velocity distribution

Because of the isotropy of the gas, $f(v)$ can be a function of $v$ or $v^2$.

Let's assume that the velocity distribution are independent of each other, i.e.,

$$f(v_x^2 + v_y^2 + v_z^2) = f(v_x^2) f(v_y^2) f(v_z^2)$$

The function that fulfills this relation is $f(v^2) = C \exp \left( \frac{a v^2}{\sqrt{11}} \right)$

Let's normalize it:

$$\int_0^\infty dv_x f(v_x) = \int_0^\infty dv_y f(v_y) = \int_0^\infty dv_z f(v_z) = 1$$

so

$$C = \frac{1}{\sqrt{11} a}$$

For ideal gas, $kT = m \langle V_x^2 \rangle = m \int d^3 v f(v^2) V_x^2$

$$= m \int d v_x f(v_x^2) \int dv_y f(v_y^2) \int dv_z V_x^2 f(v_z^2)$$

$$= m \int dv_x V_x^2 f(V_x)$$

$$= m \int \frac{a}{\sqrt{11}} dV_x V_x^2 \exp \left( -a V_x^2 \right) = 2 m \sqrt{\frac{a}{\sqrt{11}}} \int_0^\infty dV_x \exp \left( -a V_x^2 \right) V_x^2$$

$$x = aV_x^2 ; \quad dV_x = \frac{1}{2\sqrt{a}} \frac{dx}{\sqrt{x}}$$

$$kT = 2m \sqrt{\frac{a}{\sqrt{11}}} \frac{1}{2\sqrt{a}} \int_0^\infty dx e^{-x} \sqrt{x}$$
\[ \Gamma(z) = \int_0^\infty dx \, e^{-x} x^{z-1} \]

\[ \Gamma(1/2) = \sqrt{\pi} \]
\[ \Gamma(1) = 1 \]
\[ \Gamma(z+1) = z \Gamma(z) \]
\[ \Gamma(3/2) = \frac{1}{2} \Gamma(1/2) = \frac{\sqrt{\pi}}{2} \]

\[ kT = 2m \frac{1}{\sqrt{\pi}} \frac{1}{2a \sqrt{a}} \int_0^\infty dx \, e^{-x} \sqrt{x} \]

\[ kT = m \frac{1}{a \sqrt{\pi}} \Gamma(3/2) = \frac{1}{2} \frac{m}{a} \sqrt{\frac{a}{2kT}} \]

\[ a = \frac{m}{2kT} \]

Therefore, for an ideal gas,

\[ f(w) = \frac{a^2}{\sqrt{\pi}} \exp\left(-aV_i^2\right) = \sqrt{\frac{m}{2\pi kT}} \exp\left(-\frac{mV_i^2}{2kT}\right) \]

\[ f(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mV_i^2}{2kT}\right) \]

Pressure

Avogadro's number \( N_A = 6.0221367 \times 10^{23} \)
Atomic mass \( u = \frac{1}{12} m^{12}C \) mass of 1 atom of carbon isotop 12C

\( N_A = \# \) of particles with mass 1 u that makes 1 g = 6.022 \( \times 10^{23} \) mol definitions:

Molar fraction \( X_i \) for a kind of particle "i":

\[
X_i = \frac{N_i}{N_1 + N_2 + \ldots + N_A}
\]

Pressure \( p = \frac{F}{A} \)

For ideal gas \( p = \frac{2}{3} p \langle E_{kin} \rangle = \frac{2}{3} E \) where \( E \) is energy density

Energy → in thermodynamics we only treat the total energy of a system.

Heat & Heat Capacity

\[
\Delta Q = C \Delta T
\]

\( \Delta Q \) small amount of heat which causes increase dT

C: total heat capacity unit J/K.

Qualitative difference between work and heat →

heat in energy which is statistically distributed over all particles

If you have particles with ordered momenta \( \rightarrow \) it's easier to convert kinetic energy \( \Rightarrow \) other forms of energy \( \Rightarrow \)

If particles \( \Rightarrow \) it's hard to convert \( \Rightarrow \) (some particles will be accelerated)

Heat Capacity \( C = mc \)

\( \Rightarrow \) specific heat
We have $C_1, C_2$ specific heat at constant volume & constant pressure.

Now a break... & some math...

**Exact and Inexact Differentials, Line Integrals**

$$z = f(x, y)$$

Differential: $dz = \frac{\partial f}{\partial x} \, dx + \frac{\partial f}{\partial y} \, dy$

or $df(x^2) = \nabla f(x^2) \cdot \, dx^2$

Line integral:

$$f(x^2) - f_0(x_0^2) = \int_c \nabla f(x^2) \cdot \, dx^2$$

C goes from $x_0, y_0$ to $x, y$

or

$$f(x^2) - f_0(x_0^2) = \int_0^1 \frac{d\mathbf{r}(t)}{dt} \cdot \nabla f(x^2(t)) \, dt$$

If this is a function:

$$\mathbf{F}(x) = \nabla f(x) \quad \text{and} \quad \nabla \times \mathbf{F} = 0$$

the integral will be independent of integration contour.

So $\nabla \times \mathbf{F} = 0$ or $\frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y} = 0$

$\frac{\partial F_x}{\partial x} - \frac{\partial F_y}{\partial y} = 0$

$\frac{\partial F_y}{\partial y} - \frac{\partial F_x}{\partial x} = 0$
Example #1

\[ P \cdot dx^2 = y \cdot dx + x^2 \cdot dy \]

is it exact?

\[
\frac{\partial F_x}{\partial y} - \frac{\partial F_y}{\partial x} = \frac{\partial (xy)}{\partial y} - \frac{\partial x^2}{\partial x} = x - 2x = -x \neq 0
\]

so it's not exact.

Now, \[ P \cdot dx = y \cdot dx + x \cdot dy \]

\[
\frac{\partial F_x}{\partial y} - \frac{\partial F_y}{\partial x} = \frac{\partial y}{\partial y} - \frac{\partial x}{\partial x} = 0
\]

so we can find the function \( F \) : \( P = \nabla F \)

or

\[
f(x(t)) - f(x_0) = \int_0^1 \frac{dt}{\partial} \cdot dx^3
\]

we integrate along the curve \( C_t = \left( x(t), y(t) \right) = \left( x_0 + t(x-x_0), y_0 + t(y-y_0) \right) \)

and

\[
\int_0^1 \int_0^1 \left[ (y_0 + t(y-y_0))(x-x_0) + \right.
\]

\[ + (x_0 + t(x-x_0))(y-y_0) \] \]

\[ = y_0(x-x_0) + \frac{1}{2}(y-y_0)(x-x_0) + x_0(y-y_0) + \frac{1}{2}(x-x_0)(y-y_0)
\]

\[ = xy - x_0y_0 \]
And \( \frac{\partial f}{\partial x} = y \) \( \frac{\partial f}{\partial y} = x \)

Now, if you integrate by another curve \( C_2 \) the result should be the same:

\[
C_2 \text{ is } 1 + 2 \quad = \quad \left\{ \begin{array}{c}
\int (y) + 1 \\
\int (x) + 2
\end{array} \right.
\]

\[
f(x, y) - f_0(x_0, y_0) = \int_{x_0}^{x} dt (y_0 \cdot 1 + t \cdot 0) + \int_{y_0}^{y} dt (t \cdot 0 + x \cdot 1)
\]

\[
= y_0 (x - x_0) + x (y - y_0)
\]

\[
= xy - x_0 y_0
\]

Example 2: "The integrating factor"

Suppose that we have \( F \cdot dx = y x \cdot dx + x^2 dy \)

that we saw it's not exact — let's now try to find a function \( g \) such that

\( g \cdot F \cdot dx \) will be exact or

\[
\frac{\partial}{\partial x} (g(x, y) x^2) = \frac{\partial}{\partial y} (g(x, y) xy)
\]

Let's use an "ansatz" \( g(x, y) = g(x) g(y) \)

\[
2xg_1(x)g_2(y) + x^2g_2(y) \frac{dg_1(x)}{dx}
\]
\[
= x g_1(x) g_2(y) + xy g_1(x) \frac{dq_2(y)}{dy}
\]

\[
\frac{dq_1(x)}{dx} = \frac{1}{g_1(x)} \left( \frac{y dq_2(y)}{dy} \right) \quad \text{complete separation of variables } x, y
\]

\[
1 + \frac{x}{g_1(x)} \frac{dq_1(x)}{dx} = C
\]

\[
y \frac{dq_2(y)}{dy} = C
\]

...solving...

\[
\ln g_1(x) = (c-1) \ln x + K_1
\]

\[
\ln g_2(y) = C \ln y + K_2
\]

or

\[
g(x, y) = g_1(x) g_2(y) = x^{c-1} y^c K, \quad K = e^{K_1 + K_2}
\]

\[
C, K_1, K_2 \text{ are arbitrary.}
\]

We only want one special function so we choose

\[
C = 0, \quad K_1 = -K_2
\]

\[
i.e.; \quad g(x, y) = x^{-1}
\]

\[
\Rightarrow g^2 \, dx^2 = \frac{1}{x} (xy \, dx + x^2 \, dy) = y \, dx + x \, dy
\]
Exercise #1
Consider the differential
\[ F \cdot dx = (x^2 - y)dx + xdy \]
Is it exact?
Calculate \[ \int_{C_1} F \cdot dx \] and \[ \int_{C_2} F \cdot dx \]
If it is not exact, what is the integrating factor?
Determine \( f(x, y) \).

Solution pages 29-32 of Greiner

--- end of 1st class ---

2nd Class
--- for the class: tell me what we saw last class

Today's topics: The equation of state for a real gas
Specific heat
Reversible & Irreversible processes
First law of thermodynamics
Entropy
Second law of Thermodynamics
Microscopic interpretation of entropy
Global & local equilibrium