



## Thermodynamics:

- Thermodynamics is the branch of physics that focuses on macroscopic systems consisting of a large number of microscopic constituents such as atoms and molecules.
- Most important is the study of a system's energy, how energy transforms, and how it is exchanged with the system's surroundings.
- It is impossible to analyze these systems using Newton's laws.
- To gain some understanding about these systems, we need to analyze a small set of average quantities that can be directly measured in an experiment.
- Thermodynamics studies these average quantities using statistical mathematics.



A balloon contains a large number of air molecules.

## Temperature & Thermal Equilibrium:

- The notion of “hot” and “cold” is a relative concept (it depends on who you ask).



- This is a simple idea, but it is related to an important idea in thermodynamics:

*Heat flows from a hotter object to a colder object.*

- The temperature of an object is a quantitative measure of this “hotness”.

- We will see later that the idea of “hotness” can be replaced by thermal energy

- When two objects with different temperatures are placed in **thermal contact**, then they are allowed to exchange energy, and heat will flow from the object with the higher temperature to the one with lower temperature.



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- Eventually both objects come to the same temperature and the two objects are said to be in **thermal equilibrium**.

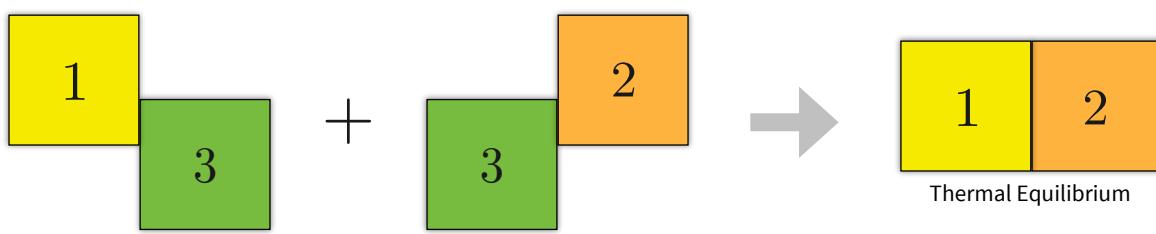
- If the objects do not exchange energy with their surroundings then the temperature will remain constant.



- Although two different people may disagree on whether an object is “hot” or “cold”, they will always agree on the temperature of an object.

Liquid in a thermos is nearly in thermal equilibrium.

- This is a statement of the **Zeroth Law of Thermodynamics**: If two objects are separately in thermal equilibrium with a third object, then they are in thermal equilibrium with each other.



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- We have talked about temperature, but we have not talked about measuring temperature.
- In order to measure temperature, we need a unit for temperature, and also a location to set as the zero for our temperature.
- Together, these two quantities define a **temperature scale**:

|                              | Freezing Water | Boiling Water |
|------------------------------|----------------|---------------|
| <u>Centigrade scale</u> (C): | 0C             | 100C          |
| Fahrenheit scale (F):        | 32F            | 212F          |

- These two temperatures scales are related as follows:  $T_F = \frac{9}{5}T_C + 32$  F

- Is there a maximum and minimum temperature?

- Maximum: We don't know, but it seems like no.
- Minimum: Yes! This minimum temperature is called **Absolute Zero**.

- Absolute zero is the zero value for the Kelvin temperature scale:

$$T_C = T_K - 273.15 \text{ C} \quad (\text{Room temperature} = 298\text{K})$$



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- If two objects in contact will reach thermal equilibrium, then why is it that the human body has a higher temperature than the air it is in contact with?
- The answer to this question has to do with the two fundamentally different types of thermodynamic systems: open and closed.

| Temperature                      | Celsius (°C) | Kelvin (K) | Fahrenheit (°F)   |
|----------------------------------|--------------|------------|-------------------|
| Helium liquefies                 | -269         | 4.2        | -452              |
| Nitrogen liquefies               | -196         | 77         | -321              |
| Dry ice ( $\text{CO}_2$ freezes) | -78          | 195        | -108              |
| Freezing point of water          | 0            | 273        | 32                |
| Human body (core)                | 37           | 310        | 98.6              |
| Boiling point of water           | 100          | 373        | 212               |
| Gas flame (stovetop)             | 1630         | 1900       | 2970              |
| Surface of sun                   | 5730         | 6000       | 10,350            |
| Center of Earth                  | 15,700       | 16,000     | 28,300            |
| Center of sun                    | $10^7$       | $10^7$     | $1.8 \times 10^7$ |

Various temperatures on the three important scales.

- **Closed** thermodynamical systems can exchange energy with their environment, but can not exchange mass.
- **Open** thermodynamical systems can exchange both energy and mass with their surroundings.
- Our previous discussion only dealt with closed systems. Humans and other animals exchange mass with their environment as are therefore open thermal systems.
- Closed systems can reach thermal equilibrium, open systems can reach **steady state**.
- In steady state there is a balance between the total input and output energies.



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## Thermal Expansion:

- Almost all materials expand when heated and shrink when cooled. (there is one extremely important exception!)
- This thermal expansion and contraction is related to the motion of the molecules in the object.
- When objects are heated, the molecules move faster, hit each other harder, and therefore push the material apart.
- Suppose we have a solid rod of length  $L$ . When the temperature is changed, the length of the rod increases proportionally to the change in temperature:

$$\Delta L = \alpha L \Delta T$$

- Here,  $\alpha$  is called the **coefficient of linear expansion** and for most materials is very small.

Ex. What is the change in length for a steel bridge with a length of 1000m when the temperature drops by 39°C?

$$\Delta L = (12 \times 10^{-6})(1000)(-38.9) = -0.47 \text{ m}$$

| Material      | Coefficient of Linear Expansion ( $10^{-6}/^\circ\text{C}$ ) | Coefficient of Volume Expansion ( $10^{-3}/^\circ\text{C}$ ) |
|---------------|--|--|
| Solids        | $\alpha$   | $\beta = 3\alpha$  |
| Quartz        | 0.4  |  |
| Glass         | 9  |  |
| Steel         | 12   |  |
| Aluminum      | 24   |  |
| Lead          | 29   |  |
| Ice           | 51   |  |
| Liquids       |  |  |
| Mercury       |  | 0.18   |
| Ethyl alcohol |  | 1.1  |
| Water         |  | 2.1  |

\* Room temperature values listed except for ice which is at 0°C.

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- This linear expansion/contraction is a problem when designing roads, bridges, and tall buildings.



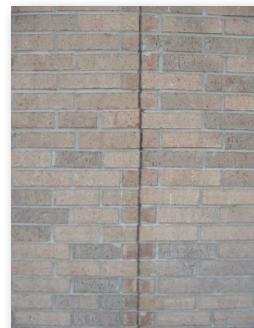
Cracks in road



Gap in road to prevent cracks



Bent train tracks



Cracks in a building wall

- Most objects expand or contract in all three-dimensions at the same time when heated or cooled.
- Imagine we have a cube of length  $L$  on each side. We can calculate the increase in volume to be

$$V + \Delta V = (L + \Delta L)^3 = L^3 \left(1 + \frac{\Delta L}{L}\right)^3 = L^3(1 + \alpha \Delta T)^3$$

- Since  $L^3 = V$  and  $\alpha$  is small so that we can Taylor expand the equation we have:

$$\Delta V = \beta V \Delta T$$

$\beta = 3\alpha$  "Coefficient of Volume Expansion"



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- Suppose we have an object with a hole in it, like a hoop.



- If the object is heated, does the hole get bigger or smaller?

- The hole will expand in the same way as the solid does. Every dimension expands by the same amount, even holes.



Ex. A steel bolt with diameter 0.635cm is to be inserted into a hole in an aluminum plate that is 0.633cm in diameter. Find the minimum temperature change needed for the bolt to fit in the hole?

Solution:

- We need only the linear expansion since we are comparing diameters (lengths)

- For the bolt to fit we require  $\Delta L_{\text{hole}} = \Delta L_{\text{bolt}} + 0.002 \text{ cm}$

- Using the values for linear expansion, this gives

$$\Delta L_{\text{hole}} = \alpha_{\text{Al}}(0.633)\Delta T = \Delta L_{\text{bolt}} + 0.002 \text{ cm} = \alpha_{\text{steel}}(0.635)\Delta T + 0.002$$

→  $\Delta T = 170 \text{ C}$

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Water:

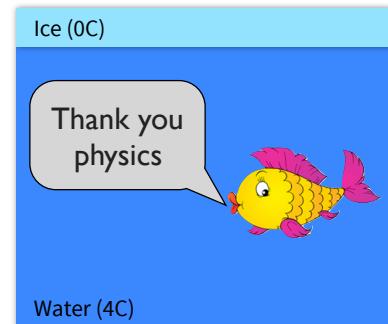
- We have seen that most materials expand when the temperature is increased and contract when the temperature is decreased.

- If the material expands then the density of the material goes down.
- If the material contracts then the density of the material goes up.
- Some materials do not follow this rule. **The most important example is water.**

- Above 4C, water behaves like a normal material. The density decreases with temperature.
- Between 0C and 4C, the density of water **increases** as the temperature increases.

→ The density of water is the greatest when the temperature is 4C

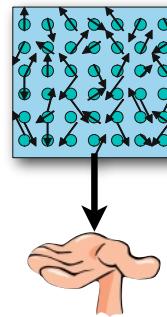
- This is why ice floats!
- When ice floats on the top of a river or lake, it forms an insulating layer keeping the water underneath at 4C.
- This keeps fish and other animals from freezing.



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## Internal Energy:

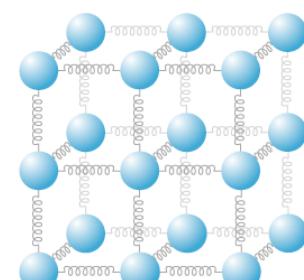
- When you drop a 1kg mass on your hand, all of the atoms in the mass collectively move downward by the same amount.
- This motion of the CM and around the CM is the motion we looked at using Newton's laws. The energy associated with this motion we call **external kinetic energy**.
- But the atoms also have random thermal motion inside of the mass. The kinetic energy associated with this motion is called **internal kinetic energy**.
- When the mass stops as it hits your hand, the external kinetic energy of the mass is transferred to your hand.
- The transfer of internal kinetic energy between two objects is associated with an objects temperature.
- If internal kinetic energy is transferred to your hand, then the object feels "hot"
- If internal kinetic energy is transferred from your hand, then the object feels "cold"



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- Of course, when we measure temperature we use a thermometer.
- If we measure temperature using the Kelvin scale then the temperature of an object is determined by the average internal kinetic of the atoms in the object.
- All objects are made up of molecules that interact via a variety of electrical interactions.
- Even though these interactions are very complex, we can write the energy for each molecule as a sum of internal kinetic and potential energy terms  $E=T+U$ .
- The molecules will move around their equilibrium positions, where we can again make a simplification: **The potential energy of an object near equilibrium looks like the potential for a spring.**

$$\rightarrow U_x = \frac{1}{2}k_s x^2 \quad (\text{x-direction only})$$



Atom+spring model of a solid.

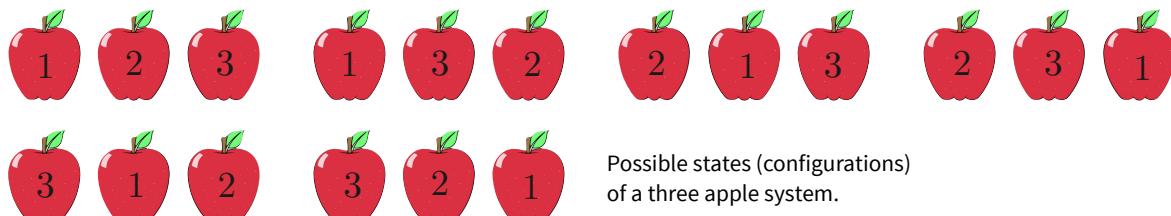
- The **internal energy** of an object, the sum of the internal kinetic energy and potential energy (like a spring) is the quantitative measure of an objects temperature.



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## Ideal Gas:

- When we study thermodynamics, we always divide the problem into two parts:
  - (I) The **System**: This is the thing we want to study
  - (II) The **Environment**: Everything else that is interacting with the system.
- We will only look at closed systems; there is only energy exchange with the environment.
- Because our system contains many many atoms, there are also many many possible configurations of our system, called **states**.



- States can have the same energy, or they can have different energies.
- These states can be described by a set of **state variables** that are measurable average properties of the system.
- For a gas, these state variables are the pressure, volume, and temperature of the gas.



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- Now we want to see how pressure and temperature are related for a specific amount of gas inside a fixed volume  $V$ .

- We will assume that our gas is formed by having  $N$  particles inside a cubical box with length  $L$ .

- We will also assume the molecules are very small so that we can ignore the amount of volume they take up.

- Finally, we will assume the gas is in thermal equilibrium

- Only energy is exchanged with the box (closed).

- Gas molecules only interact via elastic collisions.

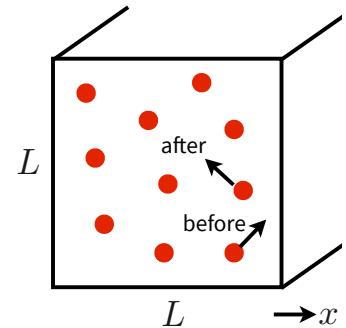
- Gas molecules interact with the box walls via elastic collisions creating a pressure.

- Lets look at a single molecule that moves with constant momentum before hitting the box wall and reversing the x-component of its momentum.

- The particle will bounce back and forth in the container, hitting the box wall on the right with a period of  $\Delta t = 2L/v_x$

- The average force, in the x-direction, from this single particle is therefore:

$$F_x = \frac{\Delta P_x}{\Delta t} = \frac{mv_x - (-mv_x)}{2L/v_x} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}$$



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- Now, to get the total force we must multiply our result by the total number of atoms
  - But we also need to use the average of the square of the molecule velocity since the velocities need not be the same.
- $$F_{x,\text{total}} = \frac{Nm\overline{v_x^2}}{L}$$
- The value  $\overline{v^2}$  is called the **mean-square velocity**. Note that  $\overline{v^2} \neq \overline{v}^2$ !
  - The square root of the mean-square velocity is called the **root-mean-square (rms) velocity**.
  - The pressure on the wall is found by dividing by the area  $A = L^2$

$$P = \frac{Nm\overline{v_x^2}}{L^3} = \frac{Nm\overline{v_x^2}}{V}$$

- Because there is no preferred direction for the molecules to travel we have:

$$\overline{v^2} = (\overline{v_x^2}, \overline{v_y^2}, \overline{v_z^2}) = 3\overline{v_x^2}$$

- The pressure can now be written in terms of the molecules net rms velocity:

$$P = \frac{Nm\overline{v^2}}{3V}$$



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- Because the term  $mv^2$  is twice the average kinetic energy  $\overline{KE}$  of a molecule we see that:

$$PV = \frac{2N\overline{KE}}{3} = \frac{2KE_{\text{total}}}{3}$$

- Experimentally it is found that the pressure is given by the **ideal gas law**:

$$PV = Nk_B T$$

$k_B = 1.38 \times 10^{-23} \text{ J/K}$ 
(Boltzmann Constant)

- Comparing these two equations we find that the average kinetic energy of a single gas molecule is related to the absolute temperature (in K)

$$\overline{KE} = \frac{3}{2}k_B T$$

**Key Idea:** The microscopic motion of individual molecules is directly related to the temperature of the gas.

- When you measure the temperature of a gas, you are measuring the rms velocity of the gas molecules.



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- The total kinetic energy of all of the atoms is therefore:

$$KE_{\text{total}} = \frac{3}{2} N k_B T$$

-This is called the **thermal energy** of the gas.

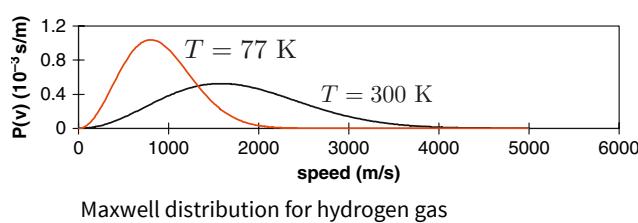
- It is this energy that changes when heat flows in or out of the system.

- The relation between average kinetic energy and temperature also lets us calculate the rms velocity as a function of temperature

$$v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}}$$

- Not all molecules have this velocity! This only tells us that the rms average is related to the temperature

- The actual velocity of gas molecules can have many different values given by the **Boltzmann distribution**.



- There are gas molecules that are moving with a velocity much higher than the average (higher kinetic energy)!



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