



## 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**.

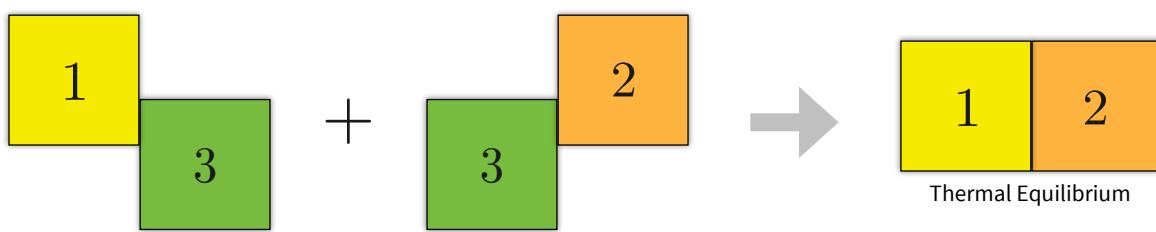
- If the objects do not exchange energy with their surroundings then the temperature will remain constant.



- 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 (C):</u>	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 39C?

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

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

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

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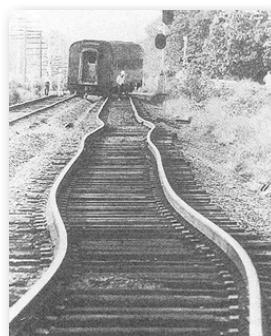
- This linear expansion/contraction is a problem when designing roads, bridges, and tall buildings.



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"



- 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.

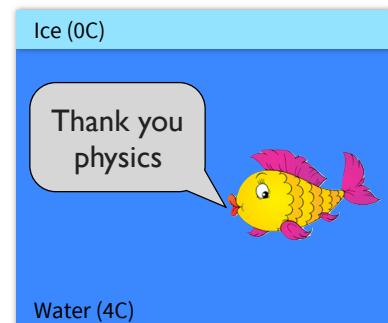
- Between 0C and 4C, the density of water **increases** as the temperature increases.

→ 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.

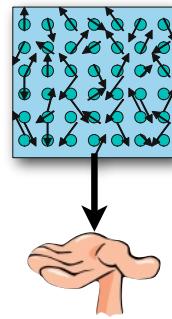
- This keeps fish and other animals from freezing.



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## Internal Energy:

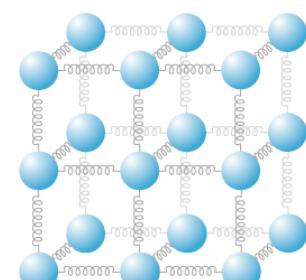
- When you drop a 1kg mass on your hand, all of the atoms in the mass collectively move downward by the same amount.
- This motion of the CM and around the CM is the motion we looked at using Newton's laws. The energy associated with this motion we call **external kinetic energy**.
- But the atoms also 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.

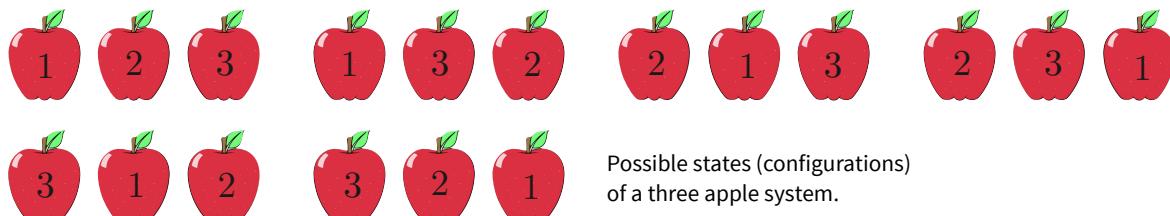
- The **internal energy** of an object, the sum of the internal kinetic energy and potential energy (like a spring) is the quantitative measure of an objects temperature.



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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.

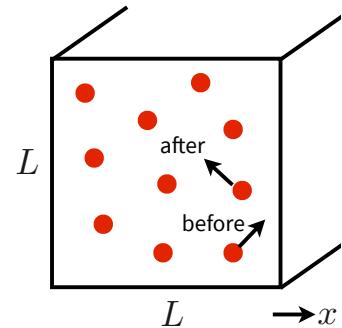
- Gas molecules interact with the box walls via elastic collisions creating a pressure.

- 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 **root-mean-square (rms) velocity**. Note that  $\overline{v^2} \neq \overline{v}^2$ !

- 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  $\overline{T}$  of a molecule we see that:

$$PV = \frac{2N\overline{T}}{3} = \frac{2T_{\text{total}}}{3}$$

- 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)

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

**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:

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

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

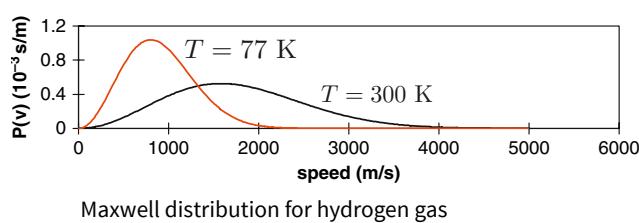
- It is this energy that changes when heat flows in or out of the system.

- 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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