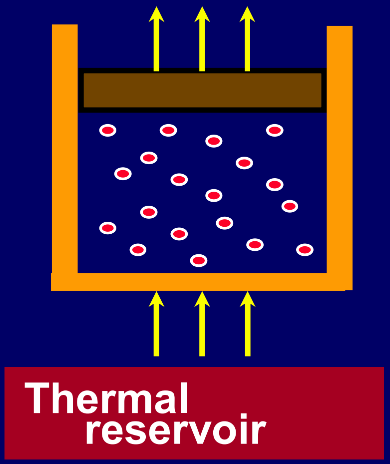
Lecture 2: Ideal Gases

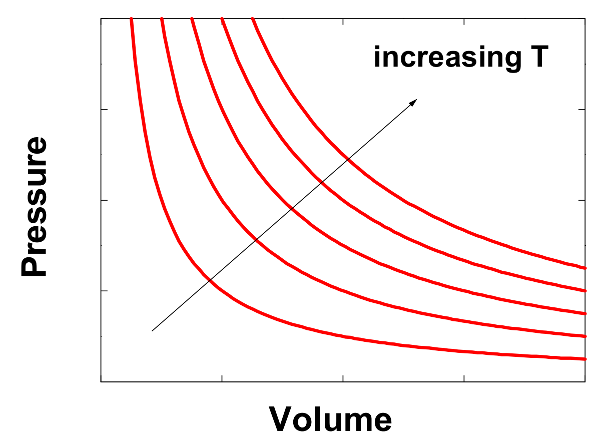
Today:

Equipartition

First Law of Thermodynamics

- Internal energy
- Heat





Reading: Elements Ch. 3

Equipartition & Absolute Temperature

One of the principal aims of this course is to gain a generally applicable definition of absolute temperature from statistical mechanics (counting).

For now: absolute temperature T is proportional to the average translational kinetic energy of a particle in a gas:

$$\langle KE_{trans} \rangle = \text{constant} \times T$$

In fact, each independent quadratic term in the energy of a particle in the gas (e.g., $\frac{1}{2} m v_x^2$, $\frac{1}{2}\kappa x^2$, $\frac{1}{2} I\omega^2$, but not mgh) is found to have the average energy:

$\langle Energy_{mode} \rangle = \frac{1}{2} kT$ Equipartition Theorem

k = Boltzmann constant = 1.38×10^{-23} J/K
is independent of the particle's properties (mass, charge, *etc.*)

We will show later why and when this theorem applies.

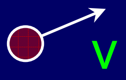
Equipartition of Energy: Examples

½kT per quadratic degree of freedom

- Free point particles: only translational kinetic energy *(x, y, z components)*

  $\langle \frac{1}{2} m v_x^2 \rangle + \langle \frac{1}{2} m v_y^2 \rangle + \langle \frac{1}{2} m v_z^2 \rangle = 3(\frac{1}{2}kT)$

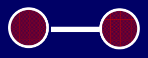
  Average energy is independent of mass!



- Diatomic molecules: translational and rotational kinetic energy

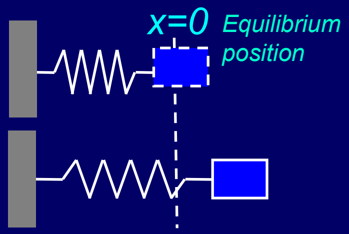
  $\langle \frac{1}{2} m v_x^2 \rangle + \langle \frac{1}{2} m v_y^2 \rangle + \langle \frac{1}{2} m v_z^2 \rangle + \langle \frac{1}{2} I \omega_1^2 \rangle + \langle \frac{1}{2} I \omega_2^2 \rangle = 5(\frac{1}{2}kT)$

  At normal temperatures, vibrations aren't active in molecules. We'll see why later.



- Mass on a spring: Kinetic and potential energy

  $\langle \frac{1}{2} k x^2 \rangle + \langle \frac{1}{2} m v_x^2 \rangle = kT$



- Vibrations in solids: Kinetic + potential energy in 3 dimensions

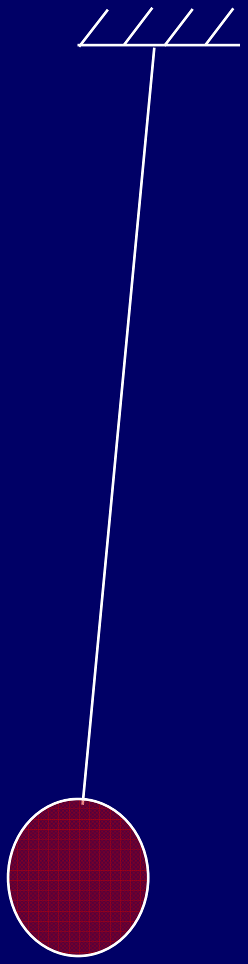
  $\langle \frac{1}{2} \kappa x^2 \rangle + \langle \frac{1}{2} m v_x^2 \rangle + \langle \frac{1}{2} \kappa y^2 \rangle + \langle \frac{1}{2} m v_y^2 \rangle + \langle \frac{1}{2} \kappa z^2 \rangle + \langle \frac{1}{2} m v_z^2 \rangle = 3kT$

  This is the average thermal energy per atom.

  If there are N atoms in the solid, the total thermal energy is 3NkT.

http://intro.chem.okstate.edu/1314F00/Laboratory/GLP.htm

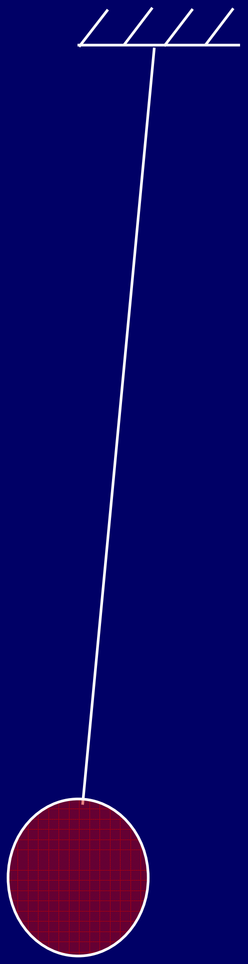
Bowling Ball Puzzle



Why does the Bowling ball slow down? Explain using the Equipartition Theorem. (Hint: Treat the ball as one big particle.)

What's the average speed of the bowling ball after it comes into equilibrium with the room? Assume that M = 10 kg and T = 300 K. Neglect the motion in the z direction.

Bowling Ball Solution



Why does the Bowling ball slow down? Explain using the Equipartition Theorem. (Hint: Treat the ball as one big particle.)

The center of mass velocity of this “large particle” is given by the Equipartition Theorem:

$$\mathrm{v}_{\mathrm{rms}} = \sqrt{\langle \mathrm{v}^2 \rangle} \propto \sqrt{\frac{1}{\mathrm{M}}}$$

What’s the average speed of the bowling ball after it comes into equilibrium with the room? Assume that M = 10 kg and T = 300 K. Neglect the motion in the z direction.

$$\frac{1}{2}m\langle v^2\rangle = \frac{1}{2}m(\langle v_x^2\rangle + \langle v_y^2\rangle) = \frac{1}{2}kT + \frac{1}{2}kT$$

$$\langle v^2\rangle = \frac{2kT}{m} = \frac{2(1.38\times10^{-23}\ \mathrm{J/K})(300\ \mathrm{K})}{10\ \mathrm{kg}} = 8.28\times10^{-22}\ \mathrm{m^2/s^2}$$

$$v_{rms} = 2.9\times10^{-11}\ \mathrm{m/s}$$

Example: Speed of Sound

The speed of sound in a gas is roughly equal to the average speed of the particles. Compare the speed of a typical helium atom (m_{He} = 4 amu) to that of a typical nitrogen molecule (m_{N2} = 2 x 14 amu) in a gas mixture in thermal equilibrium. What do you expect to be the ratio of sound speeds in pure helium and nitrogen?

Solution

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$\langle KE_{tran} \rangle_{He} = \langle KE_{tran} \rangle_{N2}$	Equipartition of translational kinetic energy. The rotational energy of nitrogen molecules is not important here.
$m_{He}/m_{N_2} = 4/28$	Helium doesn't form molecules.
$v_{He}/v_{N_2} = (28/4)^{1/2} = 2.65$	$KE = mv^2/2$ so the speed ratio is the inverse square root of the mass ratio.
The ratio of sound speeds should be approximately the same as this ratio.	The actual ratio of sound speeds is 2.76.

From Last Lecture:
The Ideal Gas Law

Recall that we derived this pressure-energy relation:

$$p = \frac{2}{3}\frac{N}{V}\langle KE_{TRANS}\rangle$$

Let's add equipartition:

$$\langle KE_{TRANS}\rangle = \tfrac{1}{2}m\left(\langle v_x^2\rangle + \langle v_y^2\rangle + \langle v_z^2\rangle\right) = \tfrac{3}{2}kT$$

This gives us the Ideal Gas Law:

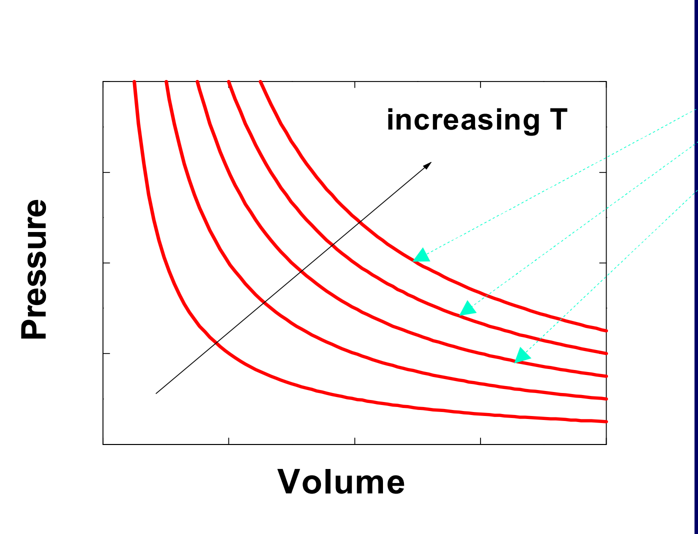
$$\boxed{pV = NkT}$$

This relation is independent of the internal modes of the molecules, but it does require that the molecules don't interact much with each other.

Ideal Gas p-V, p-T Diagrams

$$p = \frac{NkT}{V}$$

p *vs* V at various constant T's

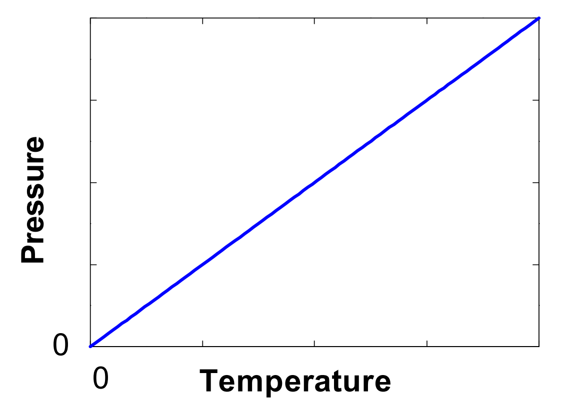


Isotherms

For an ideal gas at constant T,
p is inversely proportional
to the volume.

Constant Volume
Gas Thermometer

p *vs* T at constant V

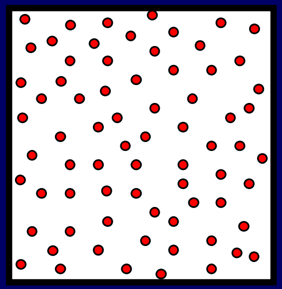


Pressure → zero as
T → absolute zero, because
the thermal kinetic energy of
the molecules vanishes.

Real gases may obey more complicated equations of state, but two of these variables always determine the third.

Ordinary gases are often quite close to ideal.

ACT 1: Ideal gas behavior

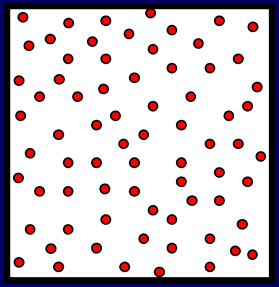


Consider a fixed volume of an ideal gas. Because $pV = NkT$, if you double either T or N, p goes up by a factor of 2.

If you double N, how many times as often will a particular molecule hit the container walls?

A) x1 B) x1.4 C) x2 D) x4

Solution



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$\boxed{\text{A) x1}}$ B) x1.4 C) x2 D) x4

In an ideal gas, the molecules are non-interacting except for occasional elastic collisions, so the motion of an individual molecule does not depend on the others.

The total collision rate is proportional to N, but the rate per molecule is independent of N.

Dalton's Law of Partial Pressures for Ideal Gases

In the derivation of pV=NkT, we never assumed that the molecules were all the same. All we used was equipartition and that they don't interact much.
So, N is the total number of molecules in the gas, independent of type.

Because p is proportional to N, if a gas has multiple components, the total pressure is the sum of the individual partial pressures:

$$p_{total} = p_1 + p_2 + p_3 + \ldots, \quad \text{where } p_i = N_i kT / V$$

Example:
Air is 78% N_2 (by number of molecules, not by mass), so the partial Pressure of the N_2 is 0.78 atmospheres.

NOTE: Dalton's law does not hold for internal energy, because the energy per molecule ***does*** depend on the type.
The energy per molecule is proportional to the number of energy modes.

The Avogadro Constant, N_A and the Gas Constant, R

Sometimes it is useful to specify the number of moles *n* instead of the number of atoms or molecules *N:*

$$n \equiv \frac{N}{N_A}$$

N_A = 6.022 x 10^{23} molecules/mole
≡ the Avogadro constant

The ideal gas law can be written in terms of *n* or *N*:

$$pV = NkT = n(N_A k)T = nRT$$

$R \equiv N_A k$ is the gas constant = 8.314 J/mol-K

Example:

Consider one mole of an ideal gas at atmospheric pressure and 0° C:

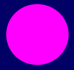
T = 0° C = 273 K, and p = 1 atm = 1.01×10^5 Pa

$$V = \frac{nRT}{p} = \frac{(1\text{ mole})(8.31\text{ J/mol}\cdot\text{K})(273\text{ K})}{1.01\times10^5\text{ Pa}} = 22.4\times10^{-3}\text{ m}^3 = 22.4\text{ liters}$$

Internal Energy of a Classical Ideal Gas

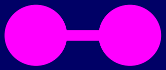
"Classical" means Equipartition applies: U = αNkT.
"Ideal" means that the molecules interact very weakly (no liquids or solids).
α is constant over limited ranges of temperatures (cf Elements, Ch. 3C).

At room temperature, for most gases:



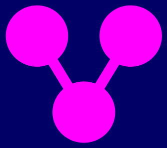
Monatomic gas (He, Ne, Ar, …)
3 translational modes (x, y, z)

$$\boxed{U = \tfrac{3}{2}NkT}$$



Diatomic rigid molecules (N$_2$, O$_2$, CO, …)
3 translational modes (x, y, z)
+ 2 rotational modes (ω_x, ω_y)

$$\boxed{U = \tfrac{5}{2}NkT}$$



Non-linear rigid molecules (H$_2$O, NH$_3$, …)
3 translational modes (x, y, z)
+ 3 rotational modes (ω_x, ω_y, ω_z)

$$\boxed{U = 3NkT}$$

Any classical ideal gas:
α depends on the type of molecule.

$$\boxed{U = \alpha NkT = \alpha pV}$$

These relations for ideal gases only apply in some ranges of T.

Internal Energy of a Gas

A pressurized gas bottle ($V = 0.05\ m^3$), contains helium gas at a pressure $p = 1\text{x}10^7$ Pa and temperature $T = 300$ K. What is the internal thermal energy of this gas?

Solution

A pressurized gas bottle ($V = 0.05\ m^3$), contains helium gas at a pressure $p = 1\times10^7$ Pa and temperature $T = 300$ K. What is the internal thermal energy of this gas?

Solution:

$$U = \alpha pV = \frac{3}{2}pV \quad = 1.5\times\left(10^7\,Pa\right)\times\left(0.05m^3\right) = \boxed{7.5\times10^5\ \mathrm{J}}$$

This is a LOT of energy!

Act 2: Internal Energy of a Gas

Container A contains helium gas (a monatomic gas) at a pressure p and volume V. Container B contains hydrogen (a diatomic gas) at the same p, V.

1. Compare the thermal energies in the two cases.

A: $U_{He} < U_H$ B: $U_{He} = U_H$ C: $U_{He} > U_H$

2. Compare the temperatures in the two cases.

A: $T_{He} < T_H$ B: $T_{He} = T_H$ C: $T_{He} > T_H$

Act 2: Solution

Container A contains helium gas (a monatomic gas) at a pressure p and volume V. Container B contains hydrogen (a diatomic gas) at the same p, V. Assume each container contains 1 mole of gas.

1. Compare the thermal energies in the two cases.

$\boxed{A: U_{He} < U_H}$ B: $U_{He} = U_H$ C: $U_{He} > U_H$

Each quadratic degree of freedom gets kT/2.
The monatomic gas has 3 degrees of freedom.
The diatomic gas has 3 + 2.

$$U = \alpha p V$$

$$\frac{U_H}{U_{He}} = \frac{\alpha_{diatomic}}{\alpha_{montomic}} = \frac{5/2}{3/2} = \frac{5}{3}$$

2. Compare the temperatures in the two cases.

A: $T_{He} < T_H$ B: $T_{He} = T_H$ C: $T_{He} > T_H$

Act 2: Solution

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A: $T_{He} < T_H$ $\boxed{\text{B: } T_{He} = T_H}$ C: $T_{He} > T_H$

$pV = NkT$

As we have defined it thus far, the temperature depends only on the *translational kinetic energy*.

Example: Kinetic Energy of a Gas

- A small room at room temperature (T = 300 K) and atmospheric pressure measures 3.0 m × 2.4 m × 5.2 m.
- 1) Estimate the number of molecules in the room.
- 2) Estimate the total translational KE associated with the molecules.
- 3) If we assume these molecules are primarily nitrogen (N_2) molecules, what is their average (rms) speed?

Solution

- A small room at room temperature (T = 300 K) and atmospheric pressure measures 3.0 m × 2.4 m × 5.2 m.
- 1) Estimate the number of molecules in the room.

$$N = \frac{pV}{kT} = \frac{\left(1.013\times10^5\ \text{Pa}\right)\times\left(3\times2.4\times5.2\ \text{m}^3\right)}{\left(1.38\times10^{-23}\ \text{J/K}\right)\times\left(300\ \text{K}\right)} = \boxed{9.2\times10^{26}\ \text{molecules}}$$

- 2) Estimate the total translational KE associated with the molecules.

$$U_{\text{trans}} = N\langle KE_{\text{trans}}\rangle = \tfrac{3}{2}pV = 1.5\times\left(1.013\times10^5\ \text{Pa}\right)\times\left(3\times2.4\times5.2\ \text{m}^3\right) = \boxed{5.7\times10^6\ \text{J}}$$

- 3) If we assume these molecules are primarily nitrogen (N_2) molecules, what is their average (rms) speed?

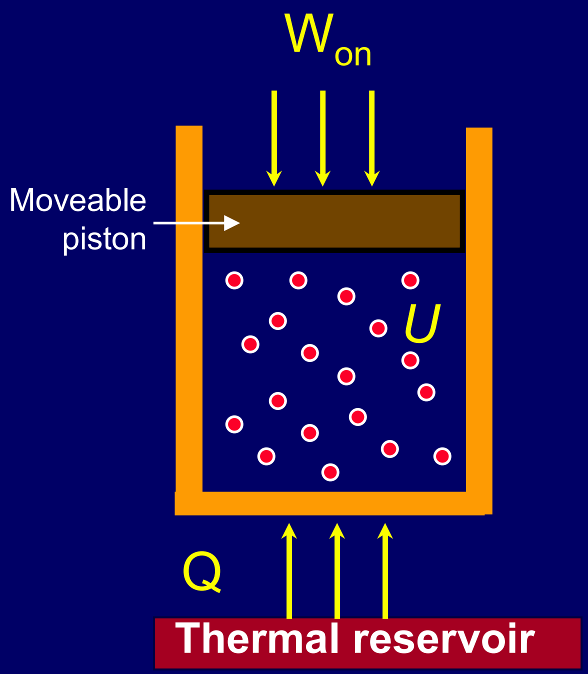
$$\langle KE_{\text{trans}}\rangle = \tfrac{1}{2}m_{N_2}\langle v^2\rangle = \tfrac{3}{2}kT$$

$$\langle v\rangle_{\text{rms}} = \sqrt{\frac{3kT}{m_{N_2}}} = \sqrt{\frac{3\times\left(1.38\times10^{-23}\ \text{J/K}\right)\times300\ \text{K}}{\left(2\times14\times1.67\times10^{-27}\ \text{kg}\right)}} = \boxed{515\ \text{m/s}}$$

Changing the Internal Energy

There are two simple ways to change the internal energy (U) of a system:

- Let the environment do Work (W) on the system.
- Let Heat (Q) flow into the system from the environment.



U is a "state" function. It depends only on the state of the system (that is, on N, *p*, *V*, *T* , etc.)
U does not depend on the history.

W and Q are "process" energies. They only tell you about the flow of energy, not how much there is.
W and Q depend on the history of the system, as it evolves from one state to another.

Nomenclature: One can also talk about work done by the system on the environment: $W_{by} = - W_{on}$. Be careful about ± signs.

W_{by} is positive if the system expands; W_{on} is positive if the system is compressed.

The First Law of Thermodynamics

Energy is conserved !!!

$$\boxed{\Delta U \;=\; Q \;+\; W_{on}}$$

change in
total internal energy

heat added
to system

work done
on the system

alternatively:

$$\Delta U \;=\; Q \;-\; W_{by}$$

Note: For the rest of the course, unless explicitly stated, we will ignore KE_{CM}, and only consider internal energy that does not contribute to the motion of the system as a whole.

What is Heat?

Up to mid-1800's heat was usually considered to be a distinct substance, caloric fluid, stored in an objects and transferred between objects. In the 1840s Joule, Rumford, and others discovered that heat is energy.

The term "heat" (Q) is now used to describe thermal energy flow - thermal energy transferred into or out of a system from some other object that has thermal energy.
(cf. cash transfers into and out of your bank account)

Do not confuse heat (Q) with the system's internal thermal energy (U). That's confusing the account balance with the deposits and withdrawals.

Sign convention:

$Q > 0$: Thermal energy is flowing in.
$Q < 0$: Thermal energy is flowing out.

Next Time

- Heat capacity
- Work!
- The four principal processes

  -isochoric

  -isobaric

  -isothermal

  -adiabatic