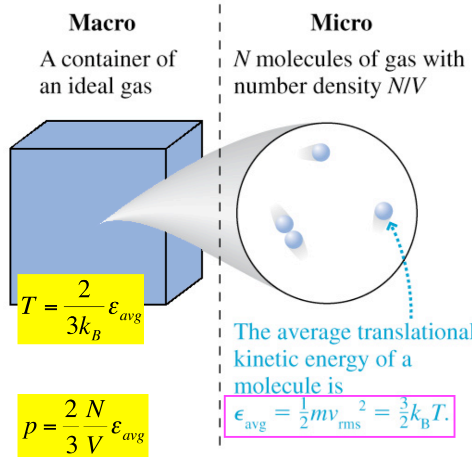
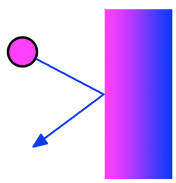
## The micro-macro connection

Kinetic theory connects the micro- and macroscopic aspects of systems.
It relates the macroscopic properties of a system to the motion and collisions of its atoms and molecules. *Average* p and T.




What we call temperature T is a direct measure of the average translational kinetic energy

$$T = \frac{2}{3k_B}\varepsilon_{avg}$$



What we call pressure p is a direct measure of the number density of molecules, and how fast they are moving ($v_{rms}$)

$$p = \frac{2}{3}\frac{N}{V}\varepsilon_{avg}$$

$$v_{rms} = \sqrt{\left(v^2\right)_{avg}} = \sqrt{\frac{3k_BT}{m}}$$

## Kinetic energy of a gas

The average kinetic energy of the molecules of an ideal gas at 10°C has the value $K_{10}$. At what temperature $T_1$ (in degrees Celsius) will the average kinetic energy of the same gas be twice this value, $2K_{10}$?

$T_1$ = 20°C
$T_1$ = 293°C
$T_1$ = 100°C

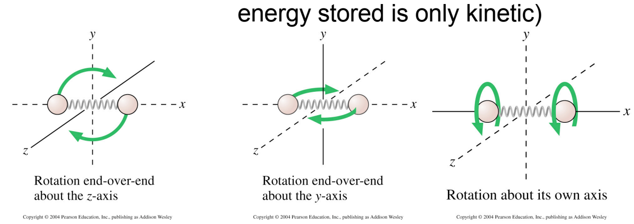
The molecules in an ideal gas at 10°C have a root-mean-square (rms) speed $v_{rms}$. At what temperature $T_2$ (in degrees Celsius) will the molecules have twice the rms speed, $2v_{rms}$?

$T_2$ = 859°C
$T_2$ = 20°C
$T_2$ = 786°C

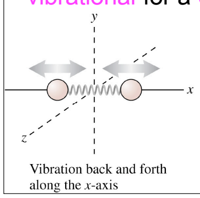
## degrees of freedom or "modes"

Degrees of freedom, or modes of energy storage into the system, can be:

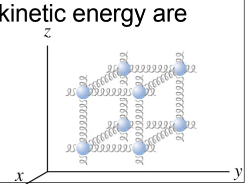
- translational for a monoatomic gas (translation along x, y, z axes, energy stored is only kinetic)
- rotational for a diatomic gas (rotation about x, y, z axes, energy stored is only kinetic)




- vibrational for a diatomic gas (two atoms joined by a spring-like molecular bond vibrate back and forth, both potential and kinetic energy are stored in this vibration)




- in a solid, each atom has microscopic translational kinetic energy *and* microscopic potential energy along all three axes.




## degrees of freedom or "modes"

A monoatomic gas has 3 degrees of freedom (kin. en. only)

A diatomic gas has 8 degrees of freedom
3 translational, 3 rotational, 2 vibrational (kin.& pot. en.)

A solid has 6 degrees of freedom
3 translational (kin. en.), 3 vibrational (pot. en.)

## the equipartition theorem

The equipartition theorem tells us how collisions distribute the energy in the system. The energy is *stored equally* in each degree of freedom of the system.

The thermal energy of each degree of freedom is:

$$E_{th} = \frac{1}{2} N k_B T = \frac{1}{2} nRT$$

A monoatomic gas has 3 degrees of freedom $E_{th} = \frac{3}{2} N k_B T = \frac{3}{2} nRT$

A diatomic gas has 8 degrees of freedom $E_{th} = \frac{5}{2} N k_B T = \frac{5}{2} nRT$ Not 4 but 5/2 because of quantum effects!

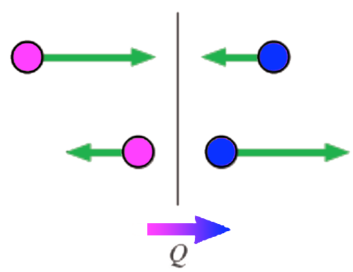
A solid has 6 degrees of freedom $E_{th} = 3 N k_B T = 3nRT$

Molar specific heats can be predicted from the thermal energy, because $\Delta E_{th} = nC\Delta T$

| Monoatomic gas | Diatomic gas | Elemental solid |
|---|---|---|
| $C_V = \frac{3}{2} R$ | $C_V = \frac{5}{2} R$ | $C = 3R$ |

## Thermal interaction: the systems exchange energy

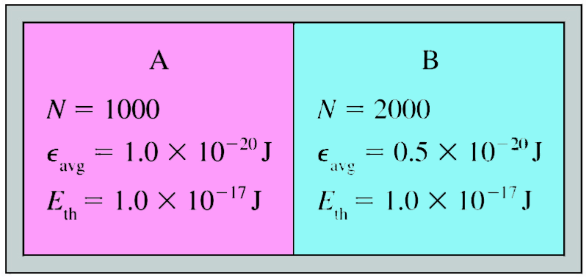
Heat is energy transferred via collisions from more-energetic molecules on one side to less energetic molecules on the other.




Equilibrium is reached when $(\varepsilon_1)_{avg} = (\varepsilon_2)_{avg}$

which implies $T_{1f} = T_{2f}$

## Thermal interaction: the systems exchange energy




Systems A and B are interacting thermally. At this instant of time,

$T_A > T_B$
$T_A = T_B$
$T_A < T_B$

Temperature measures the average translational kinetic energy per molecule, *not* the thermal energy of the entire system, nor the number of molecules colliding.

**Second law:** "The entropy of an isolated system never decreases. It can only increase, or, in equilibrium, remain constant."

Entropy measures the probability that a macroscopic state will occur or, equivalently, it measures the amount of disorder in a system

Increasing entropy 

The second law tells us how collisions move a system toward equilibrium.

$$(\varepsilon_1)_{avg} = (\varepsilon_2)_{avg}$$
$$T_{1f} = T_{2f}$$

Order turns into disorder and randomness

Information is lost rather than gained

Heat energy is transferred *spontaneously* from the hotter to the colder system, never from colder to hotter.

The laws of probability dictate that a system will evolve towards the most probable and most random macroscopic state

The time direction in which entropy increases is the future.

## entropy

Two identical boxes each contain 1,000,000 molecules.
In box A, 750,000 molecules happen to be in the left half of the box while 250,000 are in the right half. In box B, 499,900 molecules happen to be in the left half of the box while 500,100 are in the right half.

At this instant of time:

- The entropy of box A is larger than the entropy of box B.
- The entropy of box A is equal to the entropy of box B.
- The entropy of box A is smaller than the entropy of box B.

## increasing entropy

Quantity A of an ideal gas is at absolute temperature T, and a second quantity B of the same gas is at absolute temperature 2T. Heat is added to each gas, and both gases are allowed to expand isothermally.

If both gases undergo the same entropy change, is more heat added to gas A or gas B?

More heat is added to gas A.
More heat is added to gas B.
The same amount of heat is added to each gas.

Assume that gas A and gas B receive the same amount of heat determined above: Q to A and 2Q to B.
If both gases were initially at the same absolute temperature, would they still undergo the same entropy change?

No, gas A would undergo the greater entropy change.
No, gas B would undergo the greater entropy change.
Yes, both gases would have the same entropy.

## irreversible versus reversible processes

Which of the following conditions should be met to make a process perfectly reversible?

1. Any mechanical interactions taking place in the process should be frictionless.
2. Any thermal interactions taking place in the process should occur across ***infinitesimal*** temperature or pressure gradients.
3. The system should not be close to equilibrium.
4. The system should satisfy the first law of thermodynamics.

Based on the above answers, which of the following processes are not reversible?

1. Melting of ice in an insulated ice-water mixture at 0°C.
2. Lowering a frictionless piston in a cylinder by placing a bag of sand on top of the piston.
3. Lifting the piston described in the previous statement by removing one grain of sand at a time.
4. Freezing water originally at 5°C.