



Thermodynamics
Molecular Model of a Gas
Molar Heat Capacities
(Monatomic Gases)

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Last time

- heat transfer mechanisms: radiation
- modeling an ideal gas at the microscopic level
- pressure from the microscopic model

Overview

- pressure, temperature, and internal energy from the microscopic model
- rms speed of molecules
- equipartition of energy

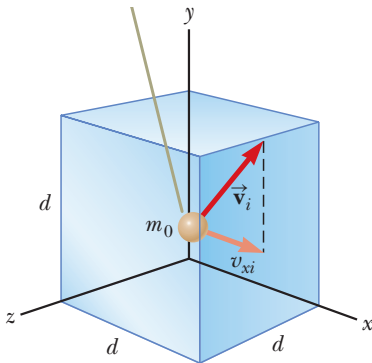
Kinetic Theory of Gases

Previously, we studied what happens in thermodynamic systems to bulk properties in various transformations.

Now we want to understand how these macroscopic quantities arise from the microscopic behavior of particles, *on average*.

We cannot model every the motion of every single particle in a substance, but we can say a lot about the **ensemble** of particles statistically.

Reminder: Molecular Model of an Ideal Gas



We modeled the particles of gas as small, identical, and obeying Newton's laws, with no long range interactions.

We assumed all collisions are elastic.

¹Figure from Serway & Jewett.

Reminder: Molecular Model of an Ideal Gas

Yesterday, we arrived at this expression for the force on a wall from particle collisions:

$$F = \frac{m_0}{d} N \overline{v_x^2}$$

We can already relate this force to a pressure, $P = F/A$, since $V = Ad = d^3$:

$$P = \frac{m_0}{V} N \overline{v_x^2}$$

and next, we will relate it to the average translational kinetic energy of a particle.

Molecular Model of an Ideal Gas

For a particle in 3-dimensions:

$$v_i^2 = v_{xi}^2 + v_{yi}^2 + v_{zi}^2$$

If this is true for each individual particle, it is true for averages over many particles automatically:

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$$

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No! We assume **isotropy**: the gas behaves the same way in each direction.

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$$

and

$$\overline{v^2} = 3\overline{v_x^2}$$

Molecular Model of an Ideal Gas

$$P = \frac{m_0}{V} N \overline{v_x^2}$$

becomes:

$$\begin{aligned} P &= \frac{1}{3} \frac{m_0}{V} N \overline{v^2} \\ &= \frac{2}{3} \frac{N}{V} \bar{K}_{\text{trans}} \end{aligned}$$

where $\bar{K}_{\text{trans}} = \frac{1}{2} m_0 \overline{v^2}$ is the average translational kinetic energy of a particle.

Pressure from the Molecular Model

$$P = \frac{2}{3} \frac{N}{V} \bar{K}_{\text{trans}}$$

This relates the pressure in the gas to the average translational kinetic energy of a particle in the gas.

More K.E., or less volume \Rightarrow higher pressure.

Relation to Macroscopic view of an Ideal Gas

Ideal gas equation:

$$PV = nRT$$

or equivalently:

$$PV = Nk_B T$$

If we put our new expression for pressure into this equation:

$$\frac{2}{3} N \bar{K}_{\text{trans}} = Nk_B T$$

We can cancel N from both sides and re-arrange:

$$\bar{K}_{\text{trans}} = \frac{1}{2} m_0 \overline{v^2} = \frac{3}{2} k_B T$$

Temperature from the Molecular Model

We can also relate temperature to molecular motion!

$$T = \frac{2}{3k_b} \bar{K}_{\text{trans}}$$

Temperature is directly proportional to the average translational kinetic energy of a particle in the gas.

RMS Speed and Temperature

$$\bar{K} = \frac{1}{2} m_0 \overline{v^2} = \frac{3}{2} k_B T$$

It would also be useful to express the average molecular speed in terms of the temperature.

Since the motion of the gas molecules are isotropic, the average velocity is zero.

RMS Speed and Temperature

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Since the motion of the gas molecules are isotropic, the average velocity is zero.

However, we can instead consider the **root-mean-square (rms) speed**.

That is convenient here because, at the top of the slide, we have the average of the squares of the speed, not the average speed itself.

RMS Speed and Temperature

root-mean-square (rms) speed:

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m_0}}$$

Alternatively, it can be expressed

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

where M is the molar mass. ($nR = Nk_B$ and $m = nM = Nm_0$)

rms speed is higher for less massive molecules for a given temperature.

RMS Speed Question

An ideal gas is maintained at constant pressure. If the temperature of the gas is increased from 200 K to 600 K, what happens to the rms speed of the molecules?

- (A) It increases by a factor of 3.
- (B) It remains the same.
- (C) It is one-third the original speed.
- (D) It is $\sqrt{3}$ times the original speed.

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Kinetic Energy and Internal Energy

We have shown:

$$\bar{K}_{\text{trans}} = \frac{1}{2} m_0 \overline{v^2} = \frac{3}{2} k_B T$$

So the total translational kinetic energy of an ideal gas of N particles is:

$$K_{\text{tot,trans}} = \frac{3}{2} N k_B T = \frac{3}{2} n R T$$

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This is also the total kinetic energy of an ideal **monatomic** gas because in a **monatomic** gas the three translational motions are the only *degrees of freedom*.

Equipartition of Energy

In physics, the number of **degrees of freedom** a system has is the number of real number variables we need to specify to describe a system.

For our purposes here, we can say that each degree of freedom counts another way that a particle can possess energy.

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For our purposes here, we can say that each degree of freedom counts another way that a particle can possess energy.

It can move in the x -direction, having kinetic energy, but also in the y and z directions. That's 3 ways. 3 degrees of freedom.

Degrees of freedom count rotational and vibrational motion as well as translational K.E.

Equipartition of energy theorem

Each degree of freedom for a molecule contributes an additional $\frac{1}{2}k_B T$ of energy to the system.

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It can be proven starting from the Boltzmann distribution of energies (to come).

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This assumes a continuum of possible energies, so we expect problems when we are in settings where the thermal energy $k_B T$ is much less than the energy spacing between energy levels predicted by quantum mechanics.

Kinetic Energy and Internal Energy

The total kinetic energy of an ideal **monatomic** gas of N particles is the total translational K.E.

$$K_{\text{tot,trans}} = \frac{3}{2} N k_B T = \frac{3}{2} n R T$$

In a **monatomic** gas these are the three translational motions are the only *degrees of freedom*. We can choose

$$E_{\text{int}} = K_{\text{tot,trans}} = N \left(\frac{3}{2} k_B T \right) = \frac{3}{2} n R T$$

(This is the thermal energy, so we choose to define the bond energy as zero – if we liquify the gas the bond energy becomes negative.)

Question

Quick Quiz 21.1¹ Two containers hold an ideal gas at the same temperature and pressure. Both containers hold the same type of gas, but container B has twice the volume of container A.

(i) What is the average translational kinetic energy per molecule in container B?

- (A) twice that of container A
- (B) the same as that of container A
- (C) half that of container A
- (D) impossible to determine

¹Serway & Jewett, page 631.

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(ii) From the same choices, describe the internal energy of the gas in container B.

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Summary

- molecular models
- rms speed of molecules
- equipartition of energy

Test on Ch 19&20, tomorrow.

Homework Serway & Jewett:

- Ch 21, CQs: 7; Probs: 47