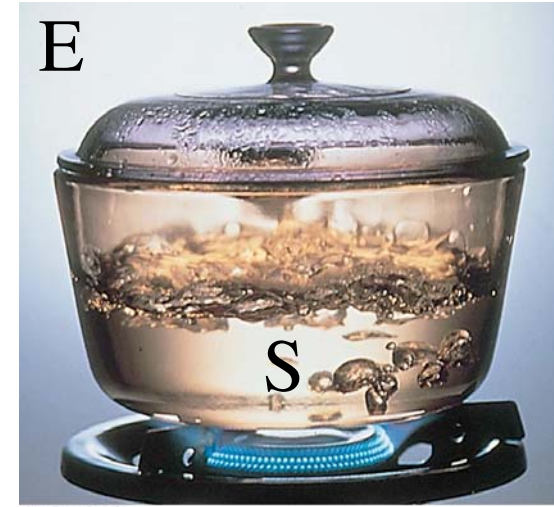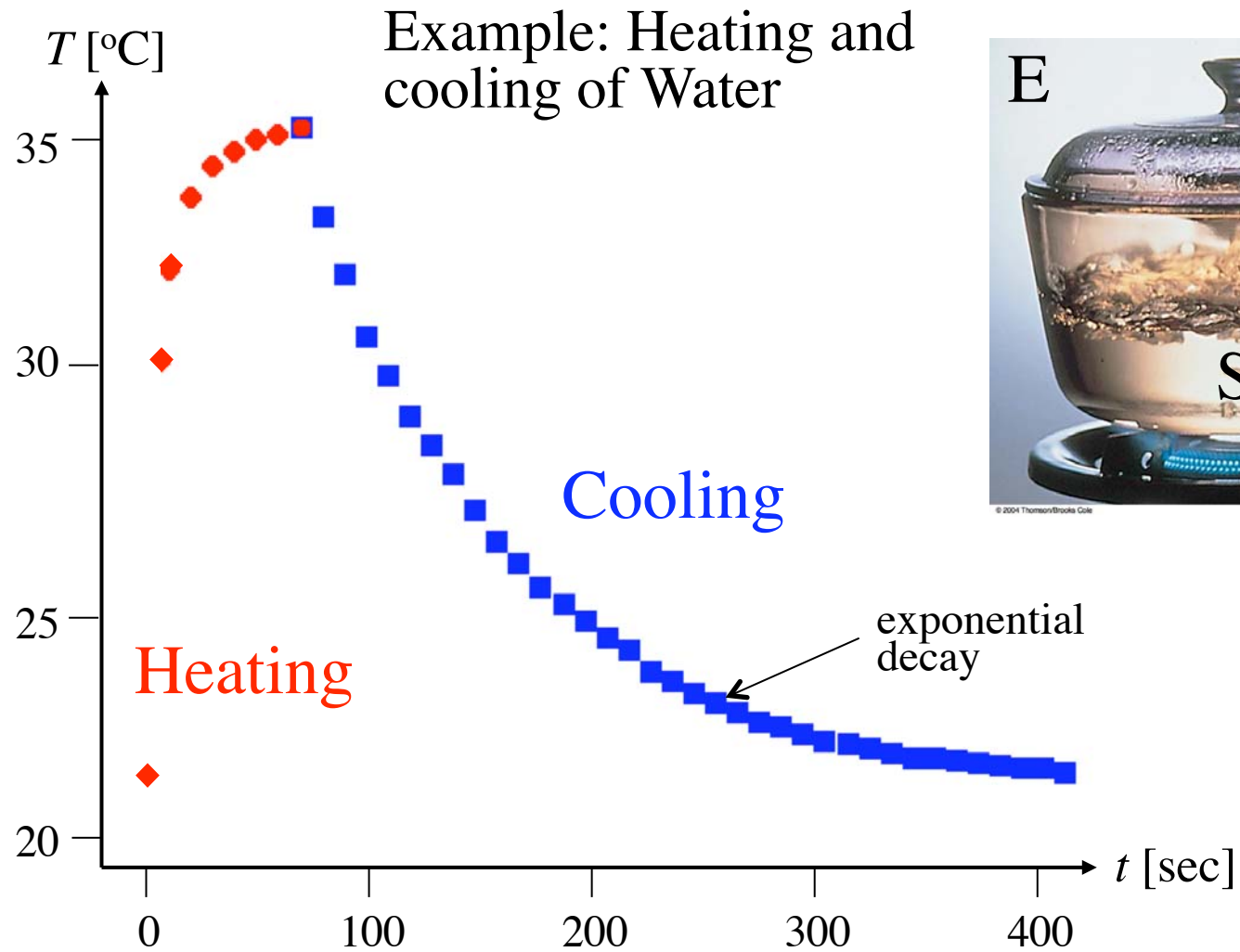# Rate of Heating and Cooling

Example: Heating and cooling of Water

Newton's Law of Cooling

■ $T_S > T_E$: System S cools until it is in thermal equilibrium with E. In an isolated system T_S decreases while T_E increases.

■ The cooling rate is following the exponential decay law also known as **Newton's Law of Cooling**:

$$\Delta T = \Delta T_0 e^{-at}$$

(ΔT falls to 0.37 ΔT_0 (37% of ΔT_0) at time $t = 1/a$)

■ ΔT_0 is the temperature difference at the starting point of the measurement ($t=0$), ΔT is the temperature difference at t

- Differentiating Newton's law of cooling

$$\frac{d\Delta T}{dt} = -a\Delta T \qquad \begin{pmatrix} Rate \ of \\ cooling \end{pmatrix} \propto \begin{pmatrix} temperature \\ difference \ \Delta T \end{pmatrix}$$

- Rate constant a determines how fast $\Delta T \rightarrow 0$
- a depends on:
  - convection, h
  - conduction, k
  - mass, m
  - specific heat, c
- Newton cooling law can be rewritten as $ln\left(\frac{\Delta T}{\Delta T_0}\right) = -at$

- By ploting $ln\left(\frac{\Delta T}{\Delta T_0}\right)$ against t the rate constant a can be determined.

- For time derivatives a "dot" is used:

$$\Delta \dot{T} \equiv \frac{d\Delta T}{dt} = -a\Delta T$$

- If we are interested in the rate of the heat released we use

$$Q(t) = -cm\left[\Delta T_0 - \Delta T\right]$$

If we assume that m and c approximately stays constant in the cooling process we get

$$\dot{Q} = \frac{dQ}{dt} = cm\frac{d\Delta T}{dt} = -acm\Delta T$$

■ <u>Example</u>: Cooling a cup of coffee with milk.

Question: At what time t should the milk be added to cool down
the coffee more efficiently?

Answer: T_C= 94 ºC   ideal brewing temperature for coffee

           T_E= 21 ºC   room temperature

           T_D= 40 ºC   ideal drinking temperature of coffee

           T_M=   4 ºC   temperature of milk out of the fridge

           V_C= 500 mL volume of coffee

           V_M= 50 mL volume of milk

           $c_M = c_C$ specific heat of milk and coffee are the
same

Experiment 1: Instant mixture ($t=0$) of water and milk

$$Q_{cold} = -Q_{hot} \Rightarrow c_M m_M \Delta T_M = -c_C m_C \Delta T_C \overset{c_C = c_M}{\Rightarrow} m_M (T_M - T) = -m_C (T_C - T)$$

$$T = \frac{m_M T_M + m_C T_C}{m_M + m_C}$$

$$T = \frac{0.5\text{kg} \; 94^\circ\text{C} + 0.05\text{kg} \; 4^\circ\text{C}}{0.5\text{kg} + 0.05\text{kg}} = 85.81^\circ\text{C}$$

Experiment 2: Milk is added at $t_1 > 0$ such that $T=T_D$ at t_1. Temperature of coffee at mixture time t_1:

$$T_C(t_1) = \frac{m_M (T_D - T_M) + m_C T_D}{m_C} = 43.6^\circ\text{C}$$

The question now is whether water cools faster from 85.81ºC to 40ºC or from 94ºC to 43.6ºC

Newton's Law

$$T(t) = T_E + (T_i - T_E)e^{-at} \Rightarrow t = -\frac{1}{a}\left[ln\left(T - T_E\right) - ln\left(T_i - T_E\right)\right]$$

We do not know the rate constant a, therefore we use ($T_E = 20$ºC)

Exp.1: $\quad t_1 = -\frac{1}{a}\left[ln\left(T_1 - T_E\right) - ln\left(T_{1,i} - T_E\right)\right]$ $\qquad$ $T_{1,i} = 85.8$ ºC
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad T_1 = 40.0$ ºC

Exp.2: $\quad t_2 = -\frac{1}{a}\left[ln\left(T_2 - T_E\right) - ln\left(T_{2,i} - T_E\right)\right]$ $\qquad$ $T_{2,i} = 90.0$ ºC
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad T_2 = 43.6$ ºC

where 1 and 2 stands for experiment 1 and 2. We divide both equations:

$$\frac{t_1}{t_2} = \frac{\left[ln\left(T_1 - T_E\right) - ln\left(T_{1,i} - T_E\right)\right]}{\left[ln\left(T_2 - T_E\right) - ln\left(T_{2,i} - T_E\right)\right]} = 1.046$$

Therefore $t_1 > t_2$ and experiment 2 is about 4.6% faster.

Kinetic Theory of the Gases

Higher temperature in a gas translates into higher kinetic energies of the gas atoms or molecules. Molecules in the gas phase undergo translational, rotational and vibrational motions, which are described by quantum theory.

Translational motion

E_{kin}
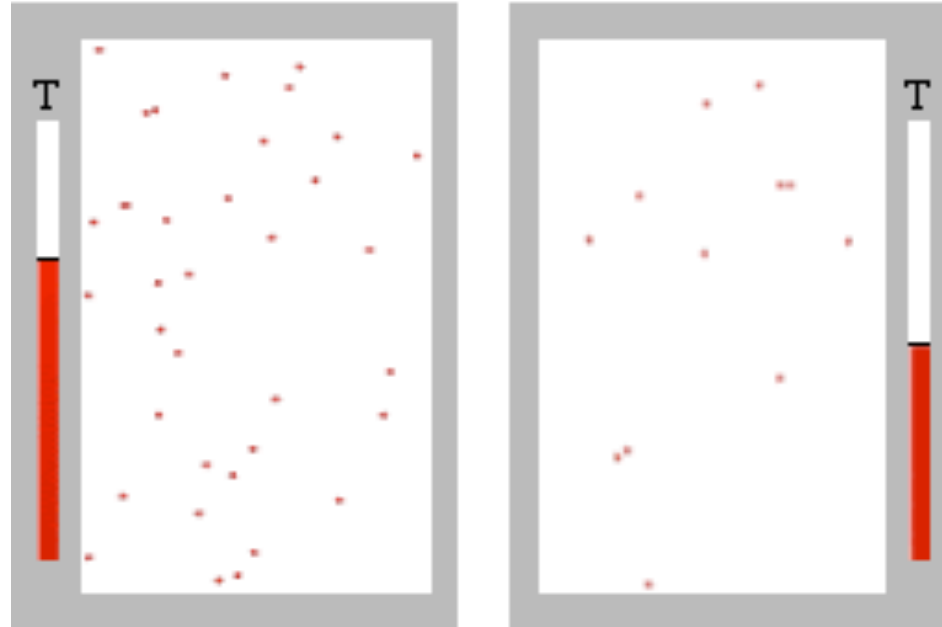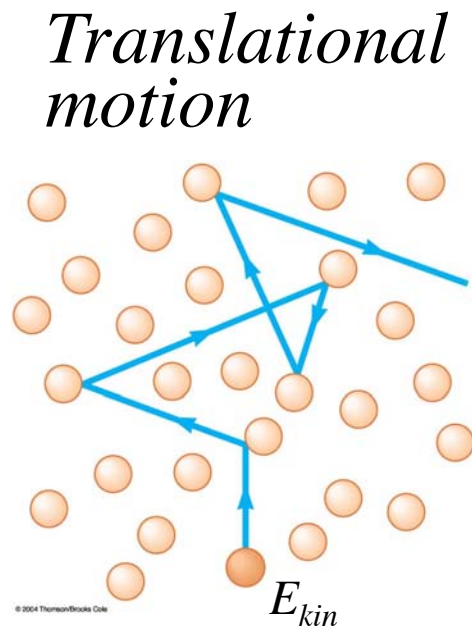
The Ideal Gas

- For gases, the interatomic forces within the gas are very weak.
  - □ We can imagine these forces to be nonexistent
- Note that there is no equilibrium separation for the atoms or molecules
  - □ Thus, no "standard" volume at a given temperature, a gas expands. For a gas, the volume is entirely determined by the container holding the gas.
- The equation that interrelates these quantities is called the **equation of state**

- The equation of state for an ideal gas

$$PV = nRT$$

- This is known as the **ideal gas law**
- R is a constant, called the **Universal Gas Constant**
  - $R = 8.314$ J/mol K $= 0.08214$ L atm/mol K
- 1 mole of any gas at 1 atm and 0° C is 22.4 L
- The ideal gas law is often expressed in terms of the total number of molecules, N, present in the sample
- $PV = nRT = (N/N_A)\,RT = Nk_BT$
  - $k_B = 1.38 \times 10^{-23}$ J/K is the **Boltzmann constant**
  - $N_A = 6.023 \times 10^{23}$ mol^{-1} is **Avogadro's constant**

- The molecules obey Newton's laws of motion, but as a whole they move randomly.
  - Any molecule can move in any direction with any speed
  - At any given moment, a certain percentage of molecules move at high speeds
  - Also, a certain percentage move at low speeds
- The molecules interact only by short-range forces during elastic collisions
- The molecules make elastic collisions with the walls
- The gas under consideration is a pure substance
  - All molecules are identical

- An ideal gas is often pictured as consisting of single atoms

- Molecular rotations and vibrations have no effect, on average, on the motions considered

- In a real gas all these assumptions are not valid anymore. However, the behavior of molecular gases approximate that of ideal gases quite well
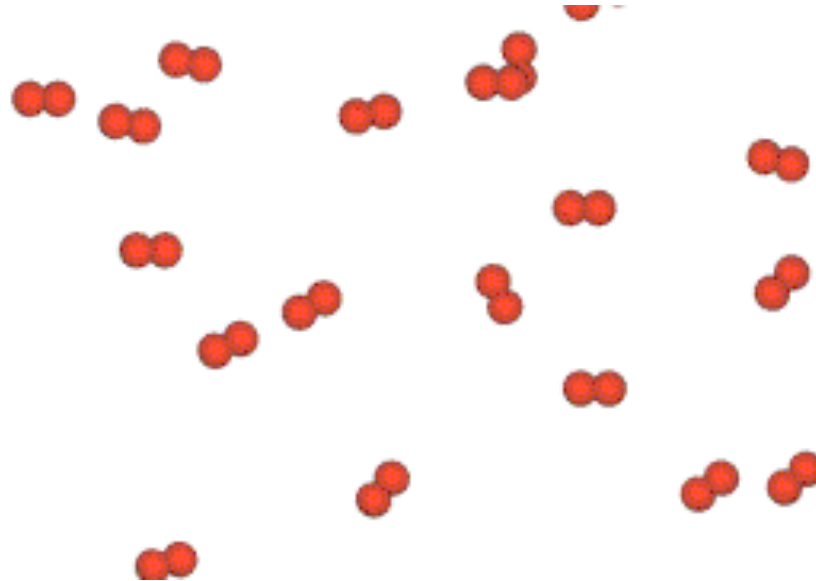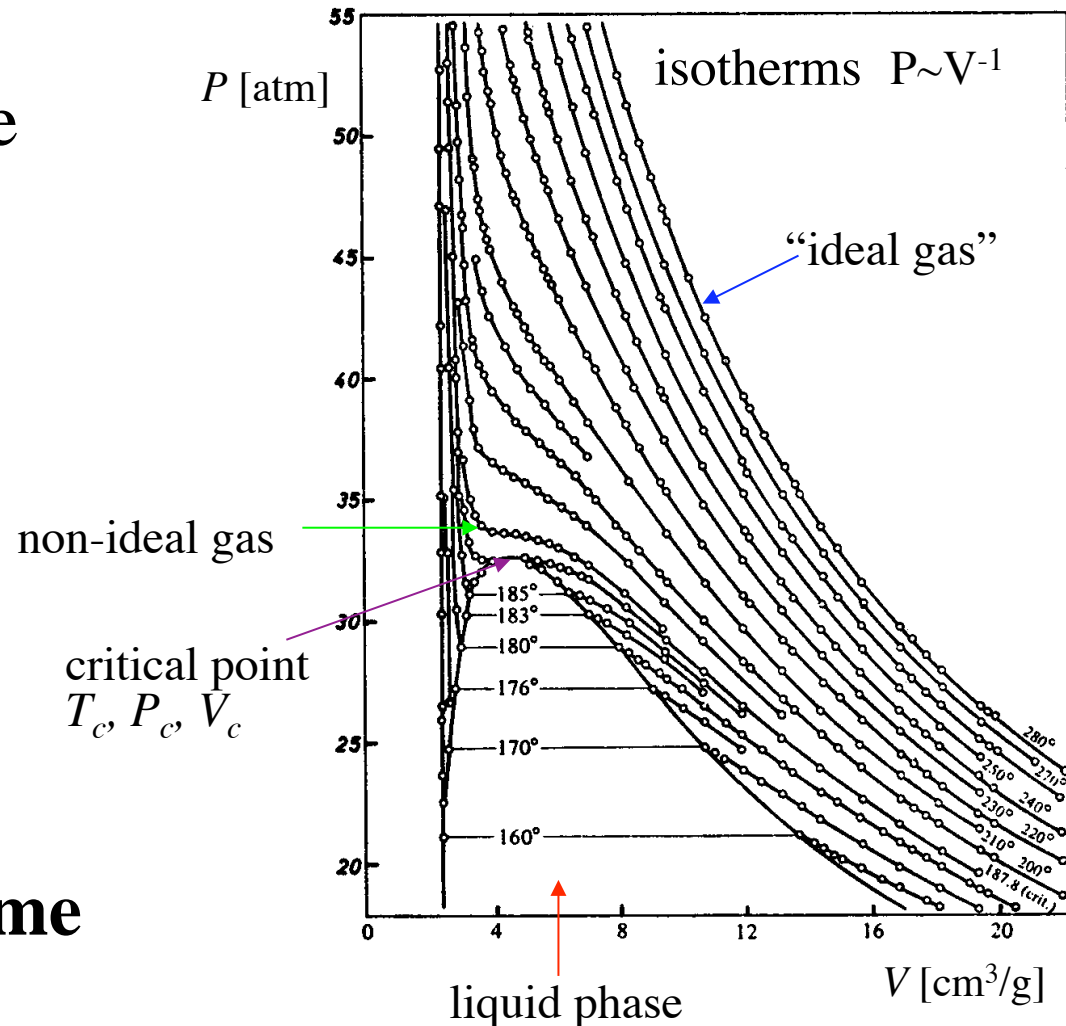
The Non-ideal Gas
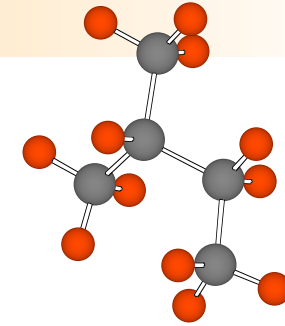
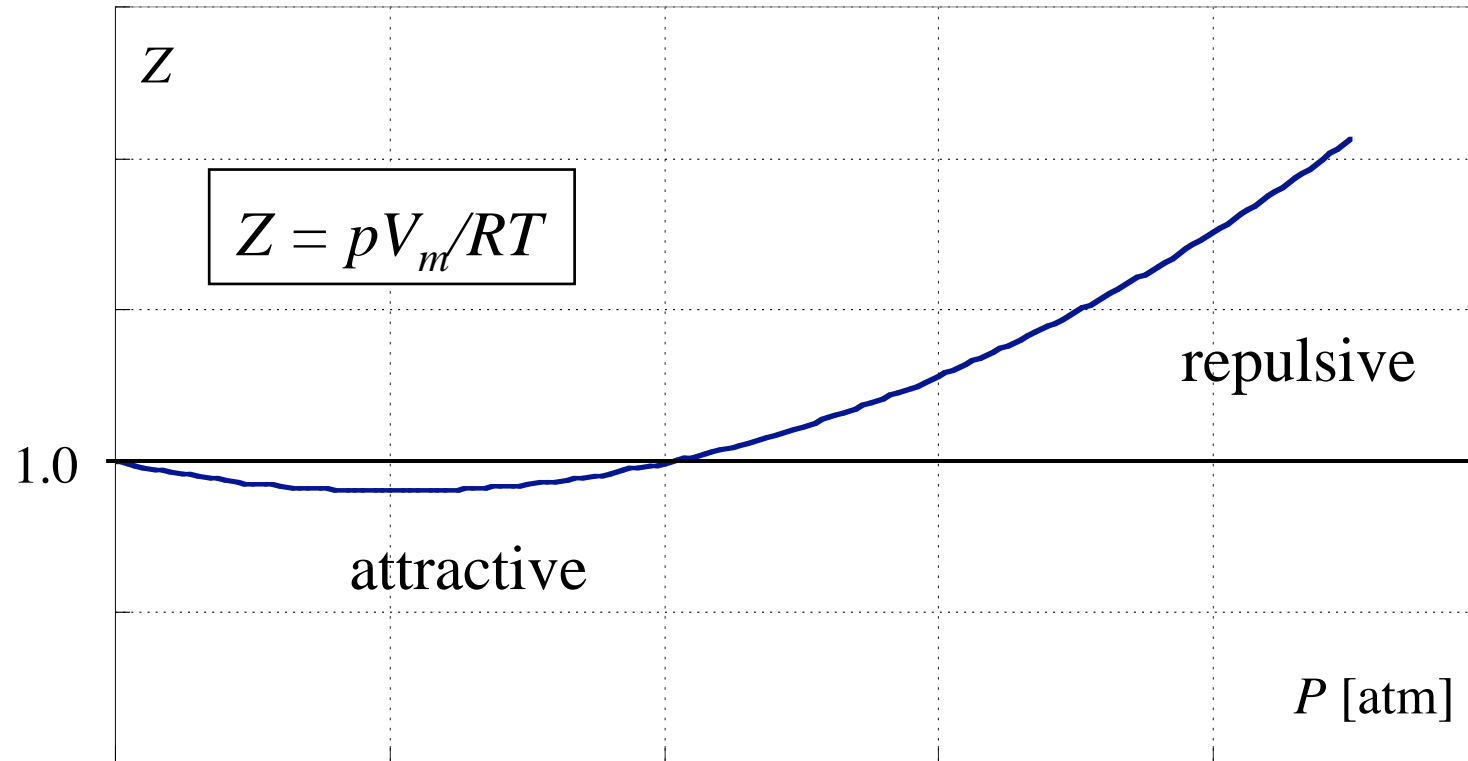- The isotherms of a real gas: Isopentane

- For an ideal gas the **compressibility** Z is exactly 1.0 at all pressures and temperatures:

$$Z = \frac{pV_m}{RT} = 1$$

$$\boxed{V_m = \frac{V}{n}}$$ **molar volume**

isotherms $P \sim V^{-1}$

"ideal gas"

non-ideal gas

critical point
T_c, P_c, V_c

P [atm]

V [cm^3/g]

liquid phase

185°
183°
180°
176°
170°
160°

280°
270°
250° 240°
230° 220°
210° 200°
187.8 (crit.)

The **compressibility** of Ar

Attractive and repulsive regions due to intermolecular forces
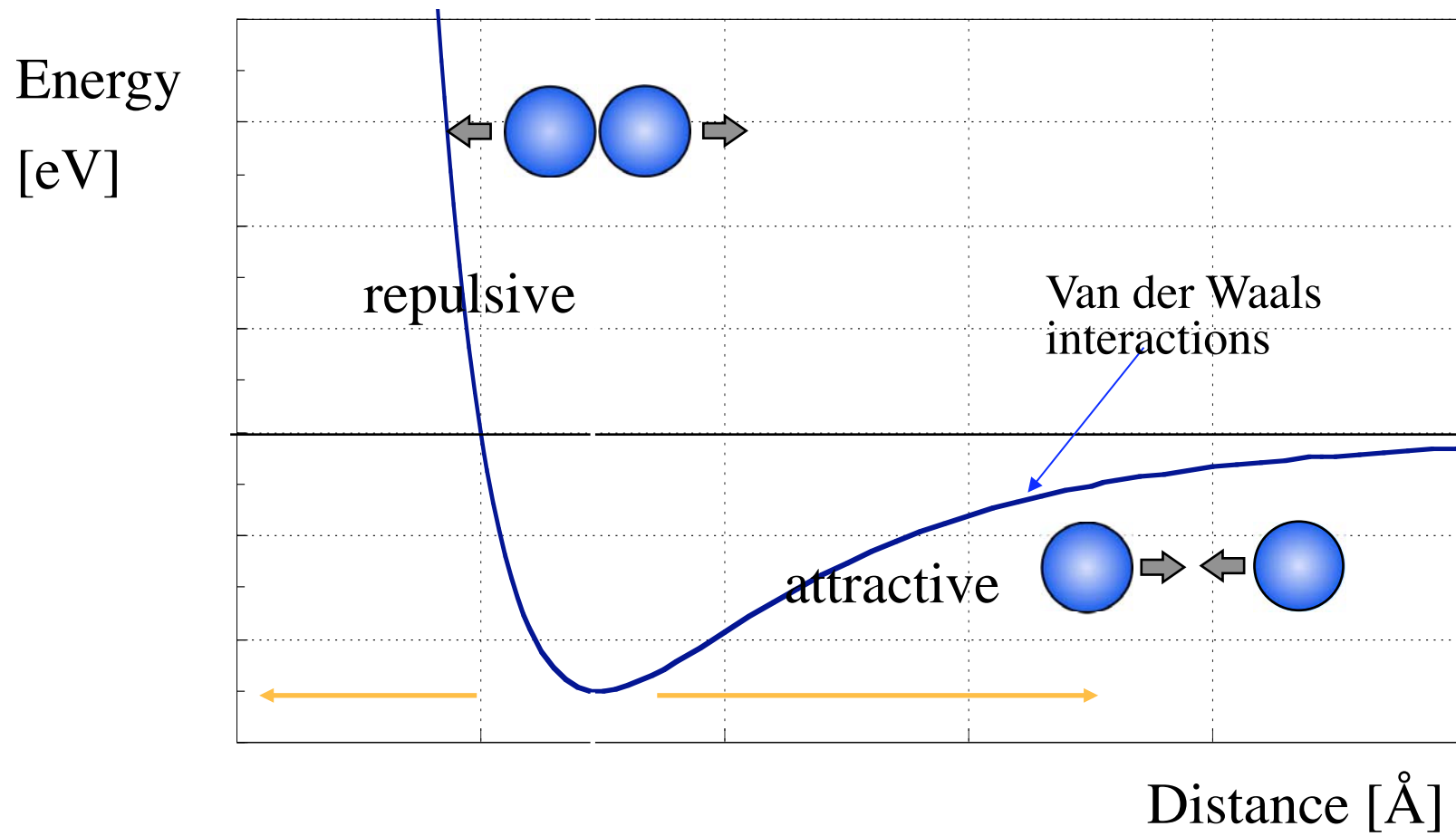
- The equation of state for an real gas

$$PV_m = RT\left(1 + B(T)/V_m + C(T)/V_m^2 + D(T)/V_m^3 + \ldots\right)$$

$$PV_m = RT\left(1 + B'(T)/P + C'(T)/P^2 + D'(T)/P^3 + \ldots\right)$$

- The equations are simple Taylor expansions in V_m or P
- The temperature dependent coefficients $B(T)$, $C(T)$ etc. are called **virial coefficients**
- $B(T)$ is the second virial coefficient, $C(T)$ the third virial coefficient etc. These coefficients are often used as constants, i.e. $B(T)=B$ and $C(T)=C$
- For both equations the virial coefficients are approximately related to each other

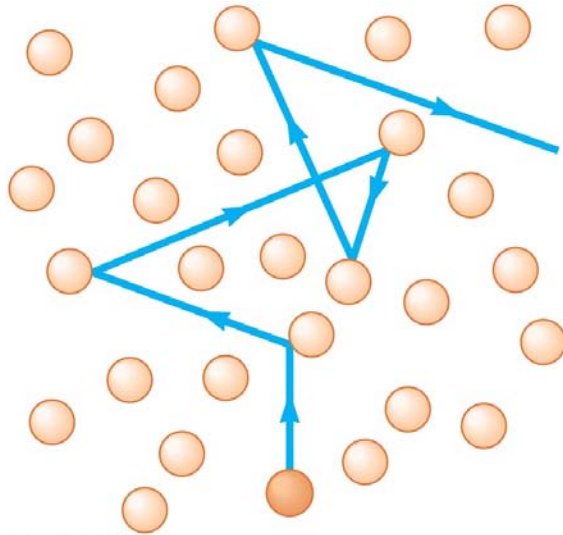$$B' = \frac{B}{RT} \qquad C' = \frac{C - B^2}{(RT)^2}$$

Second Virial Coefficients $B(T)$

	100 K	273 K	373 K	600 K
He	11.4	12.0	11.3	10.4
Ar	-187.0	-21.7	-4.2	11.9
N_2	-160.0	-10.5	6.2	21.7
O_2	-197.5	-22.0	-3.7	12.9
CO_2		-149.7	-72.2	-12.4

He is pretty much an ideal gas!

Kinetic gas theory

Microscopic World   Macroscopic World

$x_i, v_i, m_i, \dots$ P, V, T, n

- Assume a container is a cube of length d (e.g. unit length 1m)
- Look at the motion of the molecule in terms of its velocity components
- Look at its momentum and the average force
- Assume perfectly elastic collisions with the walls of the container
- The relationship between the pressure and the molecular kinetic energy comes from momentum and Newton's Laws
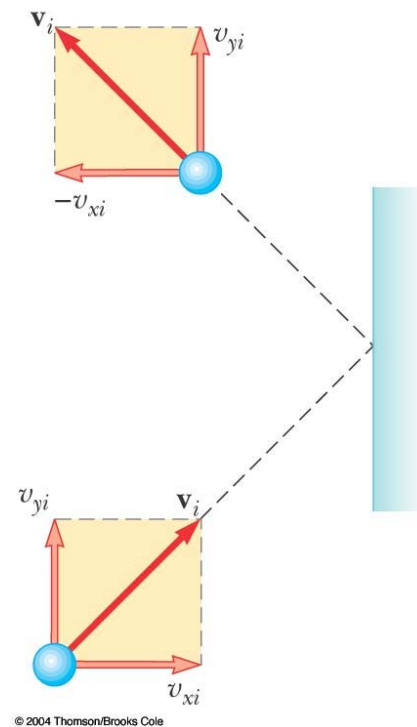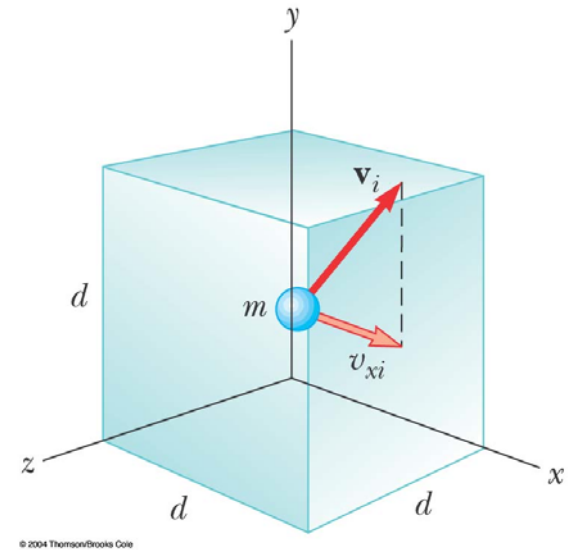
- The relationship between pressure and kinetic energy

$$P = \frac{2}{3}\frac{N}{V}\left(\frac{1}{2}\overline{mv^2}\right) = \frac{2}{3}\frac{N}{V}\overline{E_{kin}}$$

- This tells us that pressure is proportional to the number of atoms / molecules per (unit) volume (*N/V*) and to the average *translational kinetic energy* of the atoms / molecules

- The derivation of this formula is given in the textbook

- This equation also relates the **macroscopic quantity** of pressure with a **microscopic quantity** of the average value of the square of the molecular speed
- One way to increase the pressure is to increase the number of molecules per unit volume
- The pressure can also be increased by increasing the speed (kinetic energy) of the molecules
- We can take the pressure as it relates to the kinetic energy and compare it to the pressure from the equation of state for an ideal gas

$$P = \frac{2}{3}\frac{N}{V}\left(\frac{1}{2}m\overline{v^2}\right) = \frac{2}{3}\frac{N}{V}\overline{E_{kin}} = \frac{N}{V}k_BT$$

- Therefore, the **temperature is a direct measure of the average molecular kinetic energy** !

- Simplifying the equation relating temperature and kinetic energy gives

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T$$

- This can be applied to each direction, e.g. for a single atom or molecule

$$\frac{1}{2}mv_x^2 = \frac{1}{2}k_B T$$

with similar expressions for v_y and v_z and

$$\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 = \frac{1}{2}mv^2 = \frac{3}{2}k_B T$$

- Each translational degree of freedom contributes an equal amount to the energy of the gas
  - In general, a degree of freedom refers to an independent means by which a molecule can possess energy
- A generalization of this result is called the **theorem of equipartition of energy**
- Each degree of freedom contributes $\frac{1}{2} k_B T$ to the energy of a system, where possible degrees of freedom in addition to those associated with translation arise from rotation and vibration of molecules

- The total kinetic energy is just N times the kinetic energy of each molecule

$$E_{tot\ kin} = N\left(\frac{1}{2}m\overline{v^2}\right) = \frac{3}{2}Nk_BT = \frac{3}{2}nRT$$

- If we have a gas with only translational energy, this is the internal energy of the gas!

- This tells us that the internal energy of an ideal gas depends only on the temperature

- The root mean square (*rms*) speed is the square root of the average of the squares of the speeds
  - Square, average, take the square root

- Solving for v_{rms} we find

$$v_{rms} = \sqrt{\frac{\sum v_i^2}{N}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_BT}{m}} = \sqrt{\frac{3RT}{M}}$$

- M is the molar mass and $M = mN_A$

At a given temperature, lighter molecules move faster, on the average, than heavier molecules because of the mass m

Some *rms* speeds		
Gas	*Molar mass (g/mol)*	v_{rms} *at* 20ºC *(m/s)*
H_2	2.02	1902
He	4.00	1352
H_2O	18.0	637
Ne	20.2	602
N_2 or CO	28.0	511
NO	30.0	494
O_2	32.0	478
CO_2	44.0	408
SO_2	64.1	338

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