# Molecular Interpretation of Temperature

- 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

$$P = \frac{2}{3}\left(\frac{N}{V}\right)\left(\frac{1}{2}m\overline{v^2}\right) = Nk_{\mathrm{B}}T$$

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

# Temperature and 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,

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

with similar expressions for $v_y$ and $v_z$

- Each **translational degree of freedom** contributes an equal amount to the energy of the gas

# Total Kinetic Energy

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

$$K_{\text{tot trans}} = N\left(\frac{1}{2}m\overline{v^2}\right) = \frac{3}{2}Nk_{\mathrm{B}}T = \frac{3}{2}nRT$$

- 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

# Root Mean Square Speed

- 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**

$$v_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \ldots + v_N^2}{N}}$$

$$v_{\mathrm{rms}} = \sqrt{\frac{3k_{\mathrm{B}}T}{m}} = \sqrt{\frac{3RT}{M}}$$

- $M$ is the **molar mass** and $M = mN_A$ *in* ***kg/mol***

- *m is the* ***molecular mass in kg***

  - ***m = atomic mass(periodic table)×amu***

- *Atomic mass unit (amu)= 1.66 ´ $10^{-27}$ kg*

# Some Examples $v_{rms}$ Values

At a given temperature, lighter molecules move faster, **on the average**, than heavier molecules

**Table 21.1**

**Some rms Speeds**

| Gas | Molar mass (g/mol) | $v_{rms}$ at 20°C(m/s) |
|---|---|---|
| $H_2$ | 2.02 | 1 902 |
| He | 4.00 | 1 352 |
| $H_2O$ | 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 |

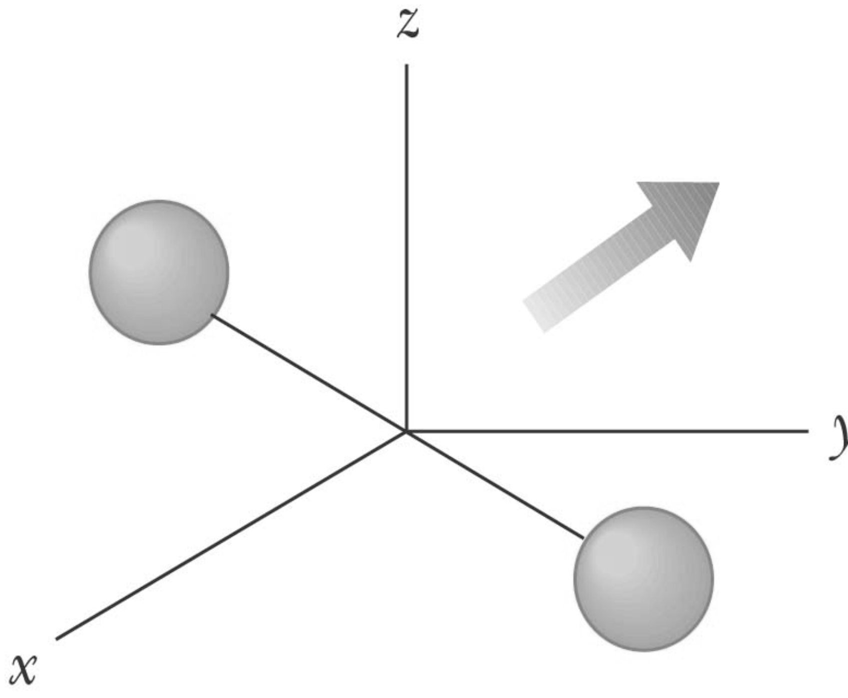
# Degrees of freedom

- 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**

# Degrees of freedom

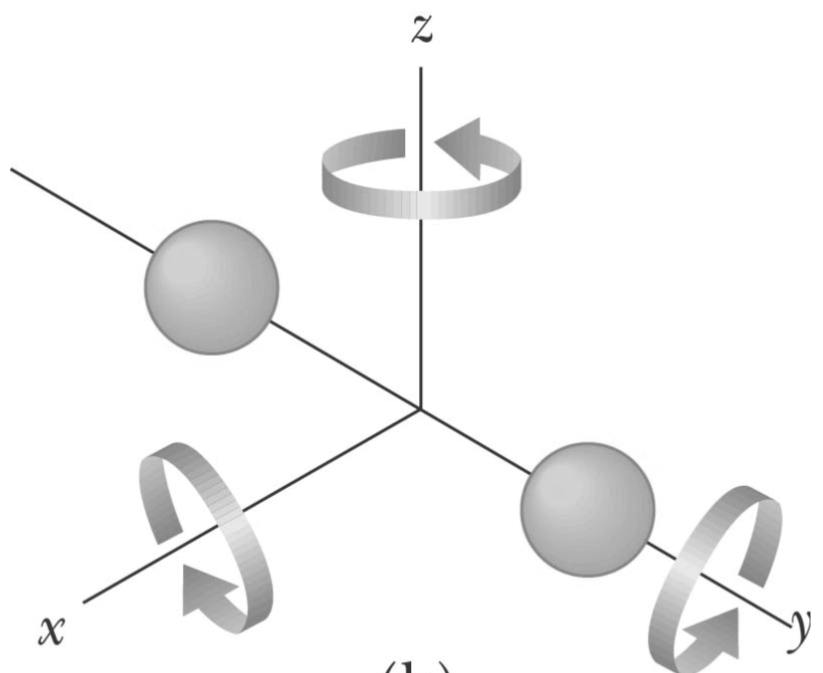
- With complex molecules, other contributions to internal energy must be taken into account
- One possible energy is the **translational** motion of the center of mass



(a)

# Degrees of freedom

- **Rotational motion** about the various axes also contributes
  - We can neglect the rotation around the *y* axis since it is negligible compared to the *x* and *z* axes

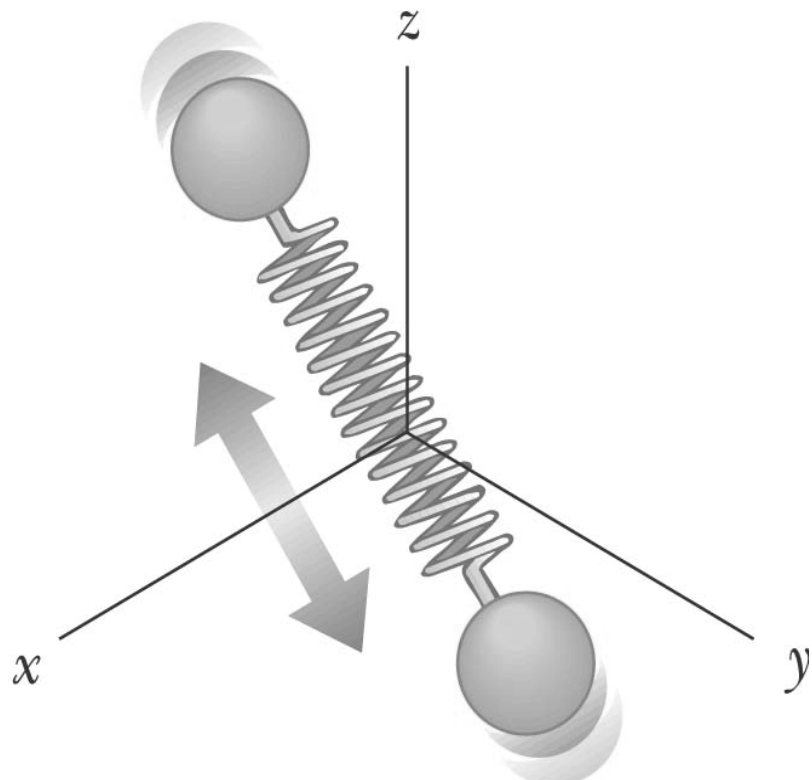


(b)

# Degrees of freedom

- The molecule can also **vibrate**

- There is **kinetic** energy and **potential** energy associated with the vibrations



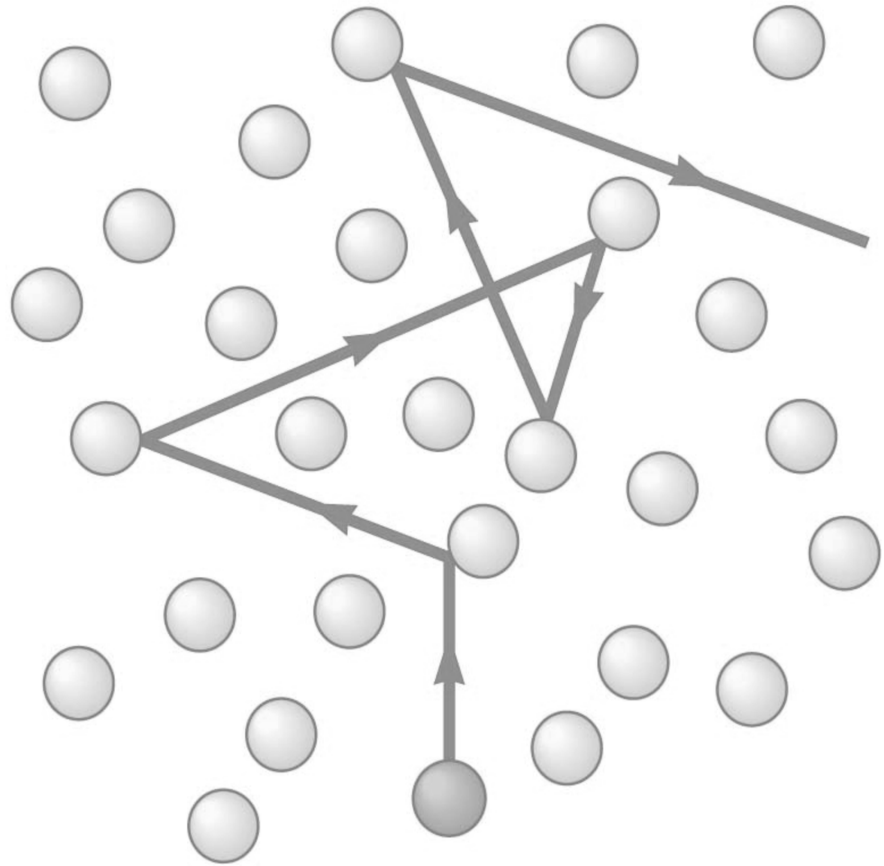

(c)

# Theorem of Equipartition of Energy

- **Each degree of freedom contributes $\frac{1}{2}k_BT$ 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

# Mean Free Path

- A molecule moving through a gas collides with other molecules in a random fashion
- This behavior is sometimes referred to as a *random-walk process*
- The **mean free path** increases as the number of molecules per unit volume decreases



# Mean Free Path

- The molecules move with constant speed along straight lines between collisions
- The **average distance between collisions** is called the **mean free path**
- The path of an individual molecule is random
  - The motion is not confined to the plane of the paper

# Mean Free Path

- The mean free path is related to the diameter of the molecules and the density of the gas
- We assume that the molecules are **spheres of diameter *d***
- No two molecules will collide unless their paths are less than a distance *d* apart as the molecules approach each other

# Mean Free Path

- The mean free path, $\ell$ **,** equals the average distance ***v***D***t*** traveled in a time interval D***t*** divided by the number of collisions that occur in that time interval:

$$\ell = \frac{\overline{v}\Delta t}{\left(\pi d^2 \overline{v}\Delta t\right) n_V} = \frac{1}{\pi d^2 n_V}$$

# Collision Frequency

- The number of collisions per unit time is the **collision frequency**:

$$f = \pi d^2 \overline{v} n_V$$

- The inverse of the collision frequency is the collision **mean free time**