Chapter 20 Kinetic Theory

Thermodynamics deals with the macroscopically observed quantities, such as pressure, volume, and temperature. This is the source both of its power and its limitation.

Kinetic theory attempts to provide insight into the underlying microscopic basis for the macroscopically observed behavior of gases.

The **equipartition of energy** specifies how the total energy of a molecules is divided between *translational*, *rotational*, and *vibrational* degrees of freedom.

Kinetic theory and the equipartition of energy can be used to predict the values of the **specific heats** of an ideal gas.

20.1 The Model of an Ideal Gas

The following assumptions are made about the molecules in a gas.

1. Very large number, random motion.

- No internal structure, mainly translational kinetic energy.
- No interaction except during brief elastic collision.
- Diluted gas: the average distance between the molecules is much greater than their diameters.

20.2 The Kinetic Interpretation of Pressure

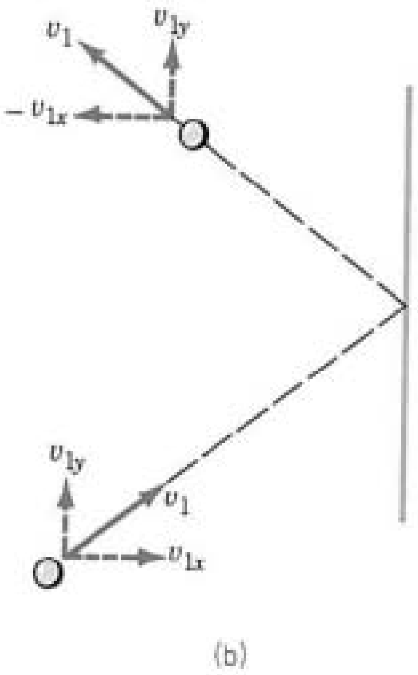
$$\text{Force}\quad F=\sum_{i=1..N}F_i=\sum_{i=1..N}\frac{\Delta P_i}{\Delta t}$$

$$=\sum_{i=1..N}\frac{2mv_{ix}}{2L/v_{ix}}=\sum_{i=1..N}\frac{mv_{ix}^2}{L}$$

$$=\frac{m}{L}\sum_{i=1..N}v_{ix}^2=\frac{m}{L}\frac{N}{3}\overline{v^2}$$

$$\text{Pressure}\quad P=F/A=\frac{mN}{3V}\overline{v^2}$$

$$=\frac{1}{3}\rho\, v_{rms}^2$$



20.3 Kinetic Interpretation of Temperature

$$P=\frac{mN}{3V}\overline{v^2}\quad\Rightarrow PV=\frac{2N}{3}\left(\frac{1}{2}m\overline{v^2}\right)$$

$$PV=NkT$$

$$\therefore\frac{1}{2}mv_{rms}^2=\frac{3}{2}kT$$

For an ideal gas, the *absolute temperature* is a measure of the average translational kinetic energy of the molecules.

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

20.3 Kinetic Interpretation of Temperature (II)

Why the temperature is risen when a gas is rapidly compressed, even though there is no influx of heat?

The kinetic theory help us understand this effect by elucidating the increase of the average speed. The increase average speed is manifested as a rise in temperature.

Examples:

Adiabatic quasistatic process: the receding piston causes the average speed of molecules to drop.

Adiabatic free expansion: the gas does no work, thus the average speed of molecules does not change.

20.4 Specific Heats of an Ideal Gas

$$U = N(\frac{1}{2}mv_{rms}^2) = \frac{3}{2}NkT = \frac{3}{2}nRT$$

We see that the internal energy of an ideal gas depends only on the temperature.

When the gas is heated at constant volume, the gas does no work, *W*=0. From the first law we have,

$$\Delta U = nC_v \Delta T$$

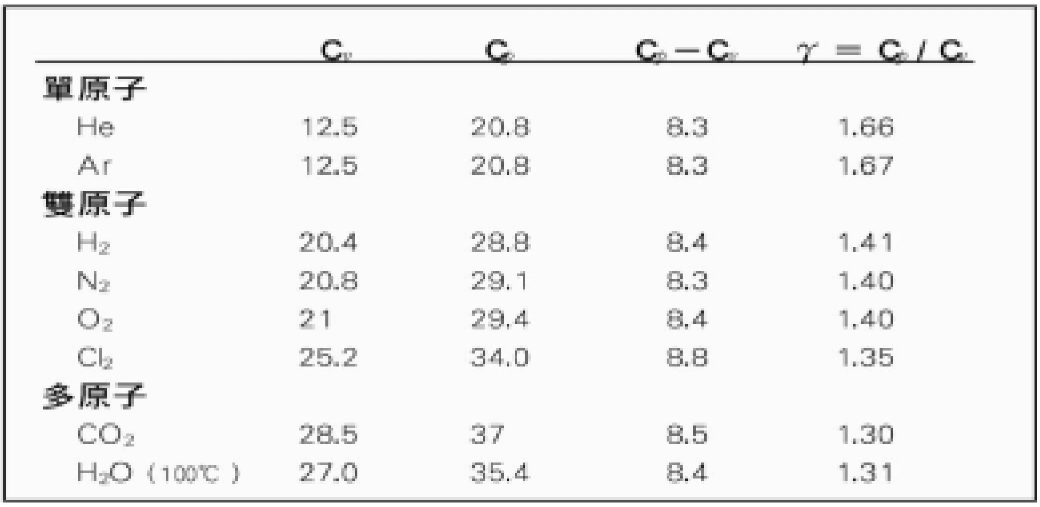
In general this equation is restricted to a constant-volume process. However, the internal energy of an ideal gas is a function only of temperature. Thus, Eq. 20.8 gives the change in internal energy of an ideal gas for ***any*** process, even if the volume is not constant.

20.4 Specific Heats of an Ideal Gas (II)

Monatomic ideal gas

$$\left.\begin{aligned} C_v &= \frac{3}{2}R \\ C_P &= \frac{5}{2}R \end{aligned}\right\} \qquad \gamma = \frac{C_P}{C_v} = \frac{5}{3}$$

表 20.1 300 K 與 1 atm 下的莫耳比熱（J/mol・K）



	C_v	C_p	$C_p - C_v$	$\gamma = C_p / C_v$
單原子				
He	12.5	20.8	8.3	1.66
Ar	12.5	20.8	8.3	1.67
雙原子				
H_2	20.4	28.8	8.4	1.41
N_2	20.8	29.1	8.3	1.40
O_2	21	29.4	8.4	1.40
Cl_2	25.2	34.0	8.8	1.35
多原子				
CO_2	28.5	37	8.5	1.30
H_2O（100℃）	27.0	35.4	8.4	1.31

20.5 Equipartition of Energy: Translation

We saw that the average translational kinetic energy of a molecular is given by

$$(\frac{1}{2}mv_{rms}^2) = \frac{3}{2}kT$$

$$\frac{1}{2}m\overline{v_x^2} = \frac{1}{2}m\overline{v_y^2} = \frac{1}{2}m\overline{v_z^2} = \frac{1}{2}kT$$

Since the molecule can move along three independent directions, we say that it has three translation degrees of freedom.

A degree of freedom of a molecule is a way in which it can possess kinetic or potential energy.

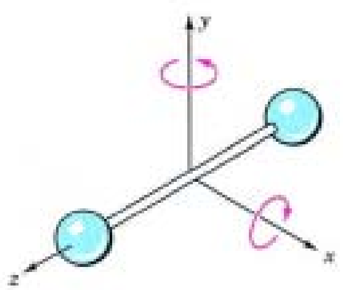
Each degree of freedom has an average energy 1/2kT.

20.5 Equipartition of Energy: Rotation

If the interatomic separation is fixed, the molecule can still rotate about three mutually perpendicular axes.

$$I_x = I_y >> I_z$$

$$K_{rot} = \frac{1}{2} I\omega_x^2 = \frac{1}{2} I\omega_y^2 = \frac{1}{2} kT$$



Two extra rational degrees of freedom is added in. Thus a total of five degrees of freedom, so its average energy is

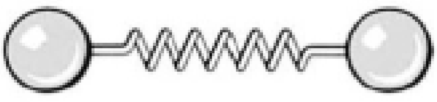
$$U = \frac{5}{2} NkT = \frac{5}{2} nRT$$

$$C_v = \frac{5}{2}, \quad C_P = \frac{7}{2}, \quad \gamma = \frac{7}{5} = 1.4$$

20.5 Equipartition of Energy: Vibration

If one relaxes the condition of rigidity, then the atoms in a diatomic molecule can vibrate along the line joining them.

$$E_{vib} = \frac{1}{2} mv^2 + \frac{1}{2} kx^2 = \frac{2}{2} kT$$



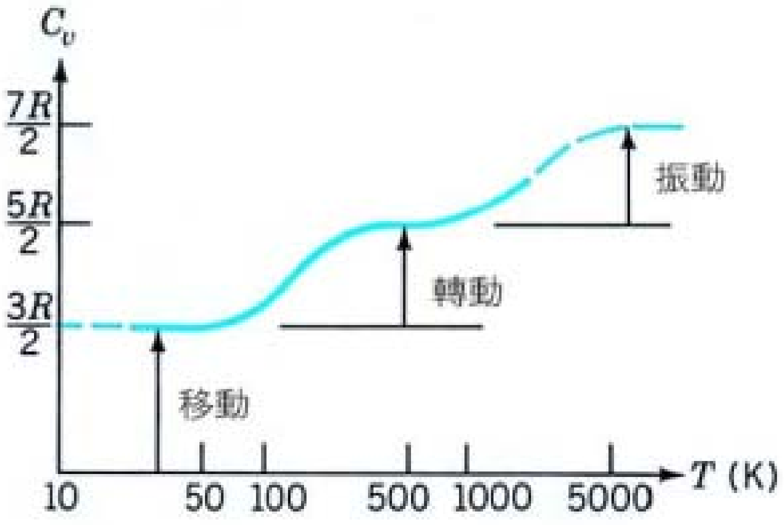
Two extra vibrational degrees of freedom is added in. Thus a total of seven degrees of freedom, so its average energy is

$$U = \frac{7}{2} NkT = \frac{7}{2} nRT$$

$$C_v = \frac{7}{2}, \quad C_P = \frac{9}{2}, \quad \gamma = \frac{9}{7} = 1.29$$

20.5 Equipartition of Energy: Temperature Relation

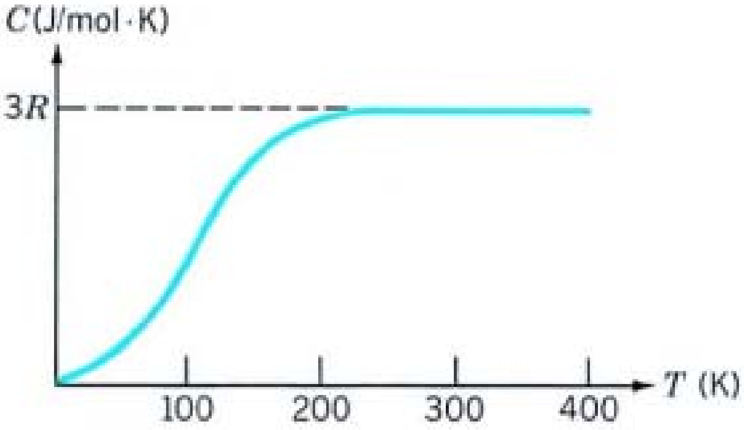
The specific heat of hydrogen as a function of temperature.



At what condition the equipartition theory can apply?

20.5 Equipartition of Energy: Problems when applying to Solids

In crystalline solids, the atoms are arranged in a three-dimensional array, called *lattice*. Each atom can *vibrate* three manually perpendicular directions, each of which has two degrees of freedom. Thus, each atom has a total of *six degrees of freedom*. $U=3nRT$, $C=3R$.



20.6 Maxwell-Boltzmann Distribution of Speeds

The Maxwell-Boltzmann distribution function:

$$f(v) = Av^2 e^{-mv^2/2kT}$$

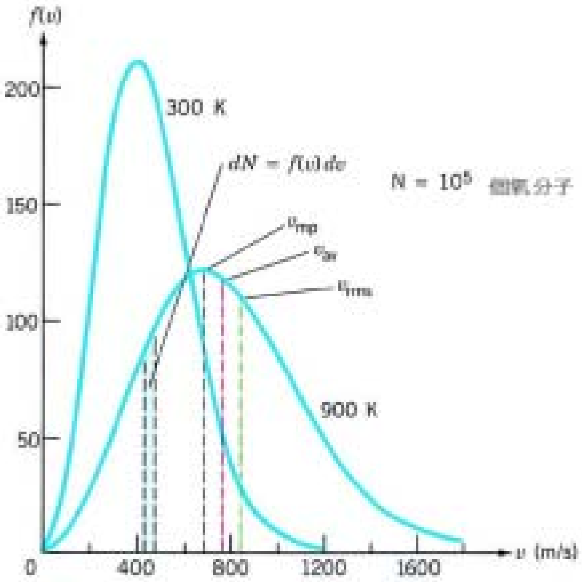
where $A = 4\pi N(m/2\pi kT)^{3/2}$

$$v_{mp} = \sqrt{\frac{2kT}{m}} \quad \text{when} \; \frac{df(v)}{dv} = 0$$

Since $dN = f(v)dv$

$$v_{av} = \int v dN = \int f(v) v dv = \sqrt{\frac{8kT}{\pi m}}$$

$$v_{rms} = \int v^2 dN = \int f(v) v^2 dv = \sqrt{\frac{3kT}{m}}$$



Exercises and Problems

Ch.20:

Ex. 21, 23

Prob. 4, 8