Chapter 4 — Elements of Kinetic Theory and Irreversible Phenomena

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1 Elements of the Kinetic Theory of Gases

The kinetic theory of gases aims to explain the macroscopic properties of a gas (pressure, temperature, thermal conductivity, viscosity, etc.) from the microscopic behavior of its molecules. It relies on a statistical model in which molecules are assumed to be in incessant motion and to undergo collisions among themselves and with the walls of the container.

1.1 Cross-Section, Time of Flight, and Mean Free Path

1.1.1 Collision Cross-Section (σ)

The cross-section is a quantity that characterizes the probability of a particle undergoing a collision with another. For molecules modeled as hard spheres of diameter d, the geometric cross-section is written:

$$\sigma = \pi d^2 \qquad (1.1) \tag{1}$$

It is expressed in m^2. If the molecules interact through a potential (for example, a Lennard-Jones potential), the cross-section depends on the collision energy and becomes a differential cross-section.

1.1.2 Time of Flight (τ)

The time of flight (or mean collision time) is the average duration separating two successive collisions of the same molecule. If $\bar{v}$ is the mean speed of the molecules and λ the mean free path, then:

$$\tau = \frac{\lambda}{\bar{v}} \qquad (1.2) \tag{2}$$

1.1.3 Mean Free Path (λ)

The mean free path is the average distance traveled by a molecule between two successive collisions. For a dilute gas of particle density n, it can be shown that:

$$\lambda = \frac{1}{\sqrt{2} n \sigma} = \frac{k_B T}{\sqrt{2} \sigma P} \qquad (1.3) \tag{3}$$

where:

- n: number of molecules per unit volume (m^{-3});
- $k_B = 1.380649 \times 10^{-23}$ J·K^{-1}: Boltzmann constant;
- P: pressure of the gas;
- T: temperature.

Order of magnitude

For air at room temperature ($T \approx 300$ K) and atmospheric pressure ($P \approx 10^5$ Pa), the mean free path is $\lambda \approx 70$ nm, approximately 200 times the molecular diameter.

1.2 Kinetic Temperature and Pressure

1.2.1 Kinetic Interpretation of Temperature

In the ideal gas model, temperature is directly related to the mean translational kinetic energy of the molecules. The equipartition theorem gives:

$$\langle E_c \rangle = \frac{3}{2} k_B T \qquad (1.4) \tag{4}$$

or, for a molecule of mass m:

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T \qquad (1.5) \tag{5}$$

The root-mean-square speed follows:

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_B T}{m}} \qquad (1.6) \tag{6}$$

The speed distribution follows the Maxwell-Boltzmann law:

$$f(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T} \right) \qquad (1.7) \tag{7}$$

The associated characteristic speeds are:

$$v_{avg} = \sqrt{\frac{8k_B T}{\pi m}} \qquad \text{(mean speed)} \tag{1.8}$$

$$v_{rms} = \sqrt{\frac{3k_B T}{m}} \qquad \text{(root-mean-square speed)} \tag{1.9}$$

$$v_p = \sqrt{\frac{2k_B T}{m}} \qquad \text{(most probable speed)} \tag{1.10}$$

1.2.2 Kinetic Interpretation of Pressure

The pressure of a gas results from the collisions of molecules with the walls of the container. By applying Newtonian mechanics to a molecule rebounding on a wall, it can be shown that:

$$P = \frac{1}{3} n m \langle v^2 \rangle \tag{1.11}$$

Combining with $P = nk_B T$, we recover the ideal gas law:

$$PV = Nk_B T = nRT \tag{1.12}$$

where N is the total number of molecules and R the ideal gas constant.

Part I
Irreversible Phenomena and Physical Laws

Irreversible phenomena are transport processes that appear when a system is subjected to a gradient (of temperature, concentration, or velocity). They generate entropy production and are governed by linear phenomenological laws (Fourier, Fick, Newton laws).

2 Examples of Irreversible Physical Laws

2.1 Fourier's Law (Thermal Conduction)

Thermal conduction is described by Fourier's law:

$$\vec{J_Q} = -\kappa \nabla T \qquad (2.1) \tag{8}$$

where J_Q is the heat flux ($\mathrm{W{\cdot}m^{-2}}$) and κ the thermal conductivity ($\mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$).

2.2 Fick's Law (Mass Diffusion)

Mass diffusion is described by Fick's law:

$$\vec{J_N} = -D \nabla n \qquad (2.2) \tag{9}$$

where J_N is the particle flux ($\mathrm{m^{-2}{\cdot}s^{-1}}$) and D the diffusion coefficient ($\mathrm{m^{2}{\cdot}s^{-1}}$).

2.3 Newton's Law (Viscosity)

The transport of momentum in a viscous fluid is described by Newton's law:

$$\tau_{xy} = -\eta \frac{\partial u_x}{\partial y} \qquad (2.3) \tag{10}$$

where τ_{xy} is the shear stress (Pa) and η the dynamic viscosity (Pa·s).

2.4 Ohm's Law (Electrical Conduction)

Charge transport is described by Ohm's law:

$$\vec{J_e} = -\sigma_e \nabla V \qquad (2.4) \tag{11}$$

where σ_e is the electrical conductivity and V the electric potential.

2.5 Soret Law (Thermodiffusion)

A temperature gradient can induce a mass flux (Soret effect), and conversely a concentration gradient can induce a heat flux (Dufour effect).

3 Mean Free Path Approximation

The mean free path approximation consists in assuming that molecules travel in a straight line over a distance λ, then transfer their energy, momentum, or mass to another molecule. This simple approach allows the transport coefficients to be expressed in terms of microscopic quantities.

3.1 General Principle

Consider a flux of particles crossing an imaginary surface in a gas subjected to a gradient. The particles coming from either side of the surface originate on average from a distance λ and carry with them the physical quantity X (energy, momentum, number of particles). The net flux is then written:

$$\bar{J_X} \approx -\frac{1}{3} n \bar{v} \lambda \nabla X \qquad (2.5) \tag{12}$$

This universal formula is the basis for the expressions of the transport coefficients.

4 Thermal Conductivity (κ)

In the mean free path approximation, the thermal conductivity of a monatomic ideal gas is written:

$$\kappa \approx \frac{1}{3} C_V \bar{v} \lambda \qquad (2.6) \tag{13}$$

where C_V is the molar heat capacity at constant volume. Using the expressions for $\bar{v}$ and λ:

$$\kappa \approx \frac{1}{3} n c_v \bar{v} \lambda = \frac{1}{3} n c_v \bar{v} \frac{1}{\sqrt{2} n \sigma} \qquad (2.7) \tag{14}$$

We deduce that:

- κ is independent of pressure (since n cancels out in the numerator and denominator).
- κ varies as $\sqrt{T}$ (since $\bar{v} \propto \sqrt{T}$).

Classical result
For a monatomic ideal gas, kinetic theory gives:

$$\kappa = \frac{1}{3} n c_v \bar{v} \lambda \approx \frac{1}{\sigma} \sqrt{\frac{k_B T}{m}}$$

5 Diffusion Coefficient (D)

The diffusion coefficient measures the ability of a gas to homogenize its concentration. In the mean free path approximation:

$$D \approx \frac{1}{3} \bar{v} \lambda \qquad (2.8) \tag{15}$$

Substituting $\bar{v}$ and λ by their expressions:

$$D \approx \frac{1}{3} \sqrt{\frac{8 k_B T}{\pi m}} \cdot \frac{1}{\sqrt{2} n \sigma} = \frac{1}{3\sqrt{2}} \cdot \frac{1}{n \sigma} \sqrt{\frac{8 k_B T}{\pi m}} \qquad (2.9) \tag{16}$$

Properties:

- D is inversely proportional to pressure ($D \propto 1/P$) since $\lambda \propto 1/P$.
- D varies as $T^{3/2}$ (since $\bar{v} \propto \sqrt{T}$ and λ is constant at a given pressure).

6 Viscosity (η)

The dynamic viscosity of a gas, in the same approximation, is written:

$$\eta \approx \frac{1}{3} n m \bar{v} \lambda \qquad (2.10) \tag{17}$$

As for thermal conductivity:

- η is independent of pressure (a counter-intuitive result verified experimentally).
- η varies as $\sqrt{T}$.

7 Relations Between Transport Coefficients

For a monatomic ideal gas, simple relations can be established between the coefficients:

$$\frac{\kappa}{\eta c_v} \approx 1 \quad \text{(Prandtl number } Pr \approx 2/3) \tag{2.11}$$

$$D = \frac{\eta}{\rho} \quad \text{(Einstein-Stokes relation)} \tag{2.12}$$

Table 1: Dependencies of transport coefficients on T and P

Coefficient	**Symbol**	**Dependence on T**	**Dependence on P**
Thermal conductivity	κ	$\sqrt{T}$	independent
Dynamic viscosity	η	$\sqrt{T}$	independent
Diffusion coefficient	D	$T^{3/2}$	$1/P$

Chapter Summary

Table 2: Summary of key concepts of Chapter 4

Concept	**Essential idea**
Cross-section (σ)	Collision probability, $\sigma = \pi d^2$.
Mean free path (λ)	Average distance between two collisions, $\lambda = 1/(\sqrt{2}n\sigma)$.
Time of flight (τ)	$\tau = \lambda/\bar{v}$.
Kinetic temperature	$\langle E_c \rangle = (3/2)k_B T$.
Kinetic pressure	$P = (1/3)nm\langle v^2 \rangle$.
Fourier's law	$J_Q = -\kappa \nabla T$.
Fick's law	$J_N = -D\nabla n$.
Newton's law	$\tau_{xy} = -\eta \partial u_x/\partial y$.
Mean free path approximation	$J_X \approx -(1/3)n\bar{v}\lambda\nabla X$.
Diffusion coefficient	$D \approx (1/3)\bar{v}\lambda$.
Thermal conductivity	$\kappa \approx (1/3)C_V \bar{v}\lambda$.