



Part I

Theory

1 Kinetic Theory

1.1 Introduction

The primary aim of kinetic theory is to relate molecular level behavior to macroscopic gas dynamics. This is achieved by consideration of the behavior of individual particles, and integrating their collective properties up to the macroscopic level. Consider the simple case of a gas at rest as illustrated in Fig. 1.1. At the macroscopic level, this is an uninteresting situation because all the gas properties, such as density (ρ), pressure (p), and temperature (T), are constants. However, at the molecular level, there is a great deal of activity with particles traveling individually at relatively high speed, and undergoing collisions with other particles. When one considers the behavior of particles at the molecular level, they really only undergo two processes: translational motion in space due to their velocity, and intermolecular collisions with other particles in the gas. While kinetic theory analysis has to consider these two physical phenomena, we will see that it is a complex process. For example, the motions of particles will be divided into consideration of bulk, directed motion, and random, thermal motion. Collisions of particles involve a nonlinear process that includes elastic events where only the particle velocities change, and inelastic processes involving energy exchange with internal modes and even chemical reactions.

1.2 Fundamental Concepts

In this section, we first provide an introduction to some basic concepts and definitions that will be needed to achieve our goal of relating molecular behavior to macroscopic gas dynamics. We then employ these concepts later in the chapter to analyze a number of different gas flow situations.

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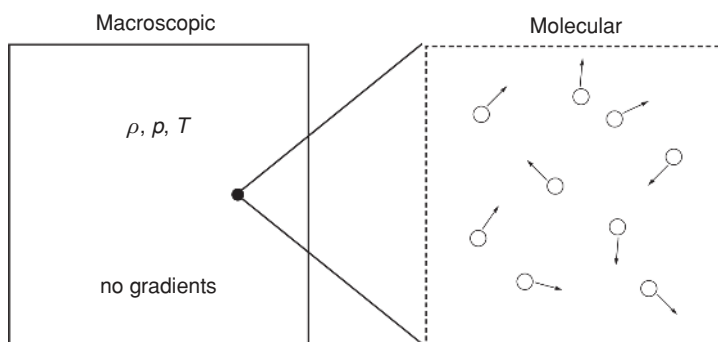


Figure 1.1

Macroscopic and molecular views of a gas at rest.

1.2.1 Particle Model

The *particle* is the fundamental unit in kinetic theory and we will use this term generically to refer to atoms and molecules. Each particle has the following properties:

- Mass (typically around 10^{-26} to 10^{-25} kg)
- Size (typically a few 10^{-10} m)
- Position, velocity, and internal energy

The mass of a particle is simply the sum of the masses of its constituent atoms. Position is the center of mass location of the constituent atoms and velocity is the center-of-mass velocity of those atoms. For molecules, atomic motion relative to the center of mass (i.e., rotation and vibration) contributes to the internal energy of the particle. The sources of internal energy that a particle of a particular chemical species can possess will be treated in detail using quantum mechanics in Chapter 2. In our introductory treatment of kinetic theory, we will ignore the internal energy for now. In addition, to fix ideas, let us focus on a *simple gas*, i.e., one in which all particles are of the same species.

Particle mass is a well-defined quantity, size is not so clear. An atom consists of a nucleus, composed of neutrons and protons, surrounded by orbiting electrons, so how large is it? This is an important question, as particle size determines the nature of intermolecular collisions. In real collisions, particles interact through the field that is formed as a result of the electrostatic Coulomb forces that act between the elementary charges, the protons and electrons, of the interacting bodies. Figure 1.2 shows an example of the potential energy acting between two argon atoms as a function of their distance of separation. The curve illustrates two main points: (1) At large distances of separation, there is a weak attractive force bringing particles closer together; and (2) at small distances of separation, there are strong repulsive forces pushing the particles apart.

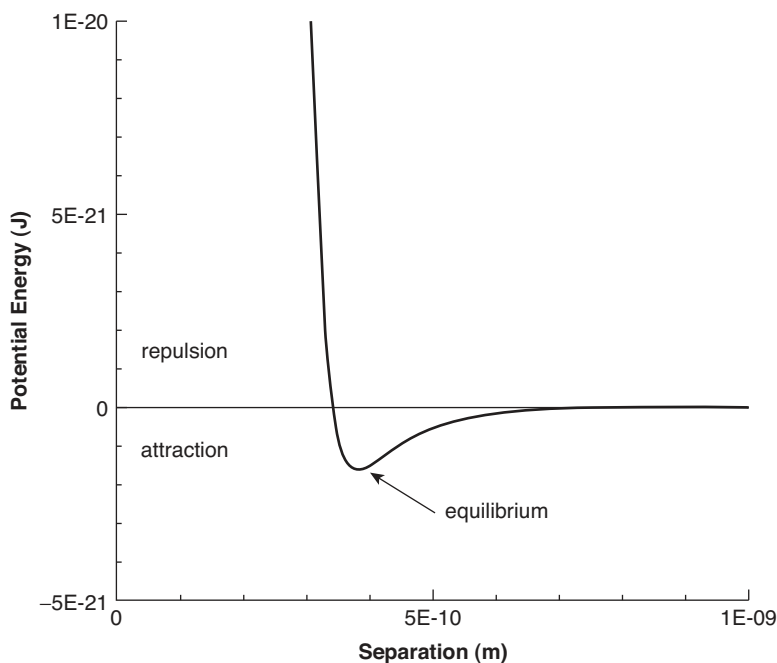


Figure 1.2

Interaction potential for two argon particles.

The weak forces causing *attraction* are important only at very low gas temperature (e.g., less than 100 K) for the relatively simple species that we will focus on, and so this effect can usually be ignored. We therefore concentrate our attention on the repulsive part of the potential field, and, to simplify mathematical analysis, we limit our consideration to two simple models.

(i) Hard sphere (rigid elastic sphere)

This model assumes that each particle has a hard shell, and that a collision occurs only when the surface of one particle is in contact with the surface of another, and so the dynamics resembles that of two billiard balls colliding. Mathematically, this says that the force field between two particles is zero everywhere except at a distance of separation equal to the diameter of one of the spheres. The diameter of the sphere is approximately located at a separation distance in Fig. 1.3, where the potential energy increases rapidly to infinity, at about 3.3×10^{-10} m.

(ii) Inverse power law

It is clear that in the real potential energy field, there is a finite slope as the energy rises, rather than going immediately to infinity, as assumed in the hard sphere model. The next best level of assumption is the inverse power law model that aims to better represent the repulsive part of the real potential using an inverse power law for force:

$$F = \frac{a}{r^n}$$

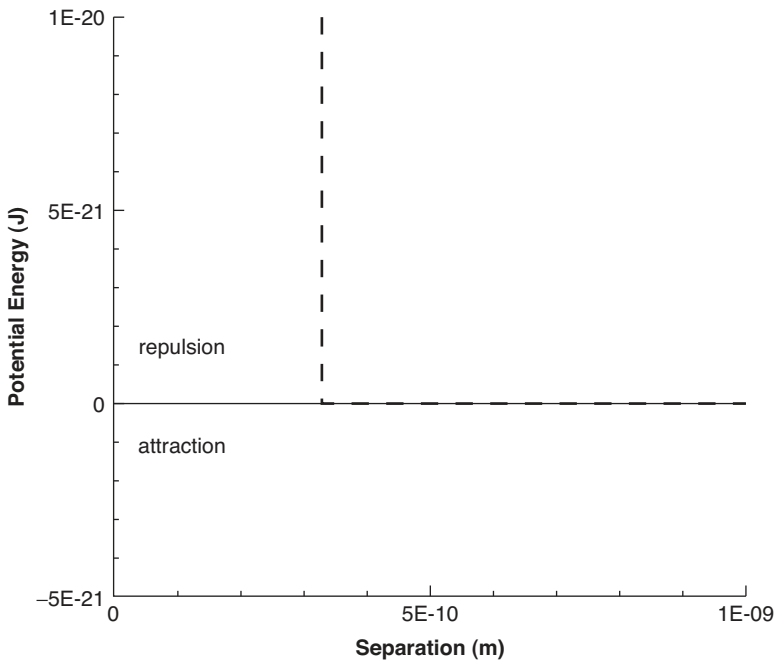


Figure 1.3 Hard-sphere interaction potential for two argon particles.

e.g., for argon, $\eta = 10$, and the associated potential is shown in Fig. 1.4. The parameters a and η can be determined through comparisons with viscosity measurements. In this model, there is no well-defined particle size, the model provides a softer interaction than the hard sphere, and in doing so better reproduces the viscosity temperature dependence of the gas at a macroscopic level. This is formulated rigorously in Chapter 5.

1.2.2 Macroscopic Quantities from Molecular Behavior

To begin to develop relationships between particle behavior and macroscopic gas flow quantities, we start with some simple results based on a collection of particles. As mentioned previously, we assume a small number of basic properties for each particle, i : a mass (m_i), a hard-sphere diameter (d_i), a position $\vec{r}_i = (r_1, r_2, r_3)_i$, and a velocity $\vec{C}_i = (C_1, C_2, C_3)_i$. In the following, we develop simple relations for some of the most fundamental gas flow properties of density, pressure, temperature, and velocity.

(i) Density

Consider a small volume containing a total of N particles. The number density is the number of particles per unit volume, and is given by

$$n = \frac{\sum_{i=1}^N 1}{\delta V} \quad (1.1)$$

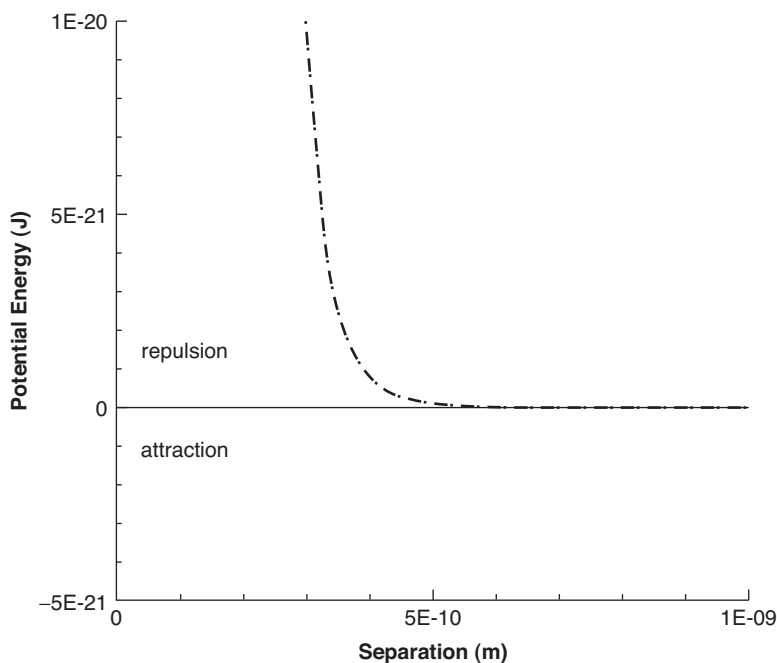


Figure 1.4

Inverse power law interaction potential for two argon particles.

The corresponding *mass density* is given by

$$\rho = \frac{\sum_{i=1}^N m_i}{\delta V} \quad (1.2)$$

Note that the results obtained with these expressions are independent of the spatial distribution of the particles within the small volume.

(ii) Pressure

Consider a gas in a state of rest, meaning there is no net velocity, inside a cube of volume $V = l^3$. Inside the cubic volume, each particle i will have a unique velocity, \vec{C}_i . To derive a result for pressure, we make a number of assumptions:

- The gas is in a state of *thermal equilibrium*: This means that there is no variation of the *number density* and the *velocity distribution function* (VDF) anywhere in the volume. We will discuss the VDF in more depth later; for now it can be considered the probability density function of finding a particle at a particular velocity.
- We will ignore collisions between particles: This is acceptable because we have already assumed equilibrium.
- The interaction of particles with walls is specular, i.e., the sign of the velocity component normal to the wall is reversed and its overall speed is unchanged. Figure 1.5 illustrates the dynamics of a specular wall collision. Also, we implicitly assume that for every wall collision $\vec{C}_i \rightarrow \vec{C}_R$ there is simultaneously somewhere in the system a

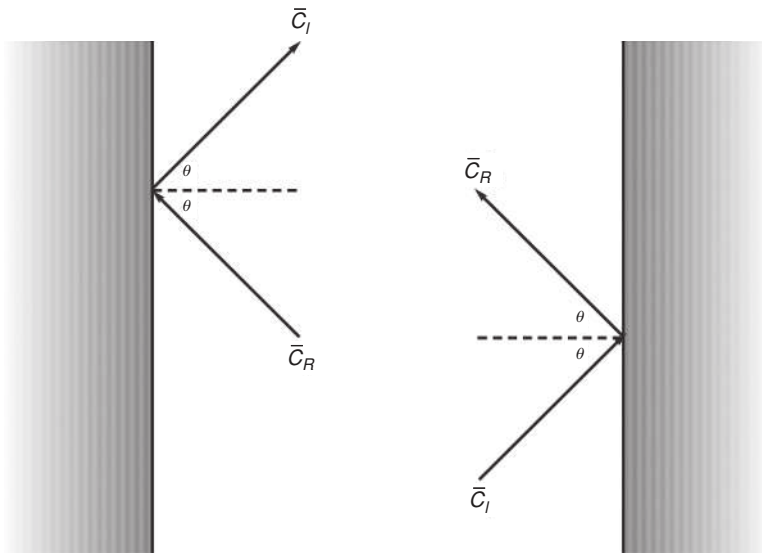


Figure 1.5

A particle undergoing specular reflection from a wall.

corresponding wall collision $\bar{C}_R \rightarrow \bar{C}_i$. This assumption is required to maintain the VDF everywhere as constant.

Since there are no intermolecular collisions, and wall collisions only lead to sign changes of velocity components, which means that each particle always has the magnitude of its three velocity components at constant values, then all that changes as a function of time is the sign of those components. Hence, the trajectory of each particle follows that illustrated in Fig. 1.6.

When particle i undergoes a collision with a wall in a r_2 - r_3 plane, let us say the plane located at $r_1 = l$, the change of momentum per collision is $2m|C_{1i}|$. Since the particle traverses a distance $2l$ between such collisions, the number of its wall collisions per unit time is $|C_{1i}|/2l$.

The total force exerted by this one particle on this wall

$$\begin{aligned}
 &= \text{Rate of change of momentum of the particle} \\
 &= (\text{Change of momentum per collision}) \\
 &\quad \times (\text{Rate of collisions per unit time}) \\
 &= 2m|C_{1i}| \times \frac{|C_{1i}|}{2l} = \frac{m}{l} C_{1i}^2
 \end{aligned}$$

So, the pressure exerted by the particle on this wall

$$= \frac{\text{Force}}{\text{Area}} = \frac{mC_{1i}^2}{l^2} = \frac{mC_{1i}^2}{V}$$

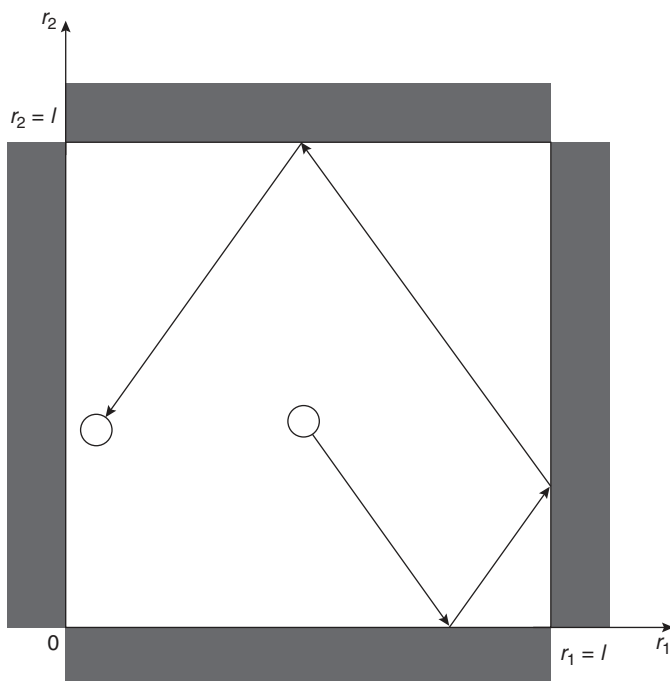


Figure 1.6 Trajectory of a typical particle.

Now, the total pressure exerted on this wall by all the particles in the gas is then

$$p_1 = \frac{1}{V} \sum_{i=1}^N m_i C_{1i}^2 \quad (1.3)$$

This is the result for the pressure exerted by the gas in the r_1 direction. Corresponding equations hold for the pressure calculated on the faces in the r_2 and r_3 directions. The average gas pressure is evaluated by taking the sum of these equations for the three coordinate directions and dividing by 3, to obtain

$$p = \frac{1}{3V} \sum_{i=1}^N m_i (C_{1i}^2 + C_{2i}^2 + C_{3i}^2) = \frac{1}{3V} \sum_{i=1}^N m_i C_i^2 \quad (1.4)$$

(iii) Translational Energy and Temperature

Each particle has *translational energy* due to its kinetic motion:

$$(\epsilon_{tr})_i = \frac{1}{2} m_i C_i^2 = \frac{1}{2} m_i (C_1^2 + C_2^2 + C_3^2)_i \quad (1.5)$$

and the *total translational energy* of the gas is simply the sum over all particles:

$$E_{\text{tr}} = \sum_{i=1}^N (\epsilon_{\text{tr}})_i \quad (1.6)$$

Using Eq. 1.4, we can write

$$E_{\text{tr}} = \frac{3}{2} pV \quad (1.7)$$

Recall the ideal (perfect) gas law: $p = \rho RT = \frac{N'}{V} \hat{R}T$, where \hat{R} is the universal gas constant (8314 J/kg-mol-K), R is the ordinary gas constant, N' is the number of moles in volume V , and T is the translational temperature. Using these results, we may write the total translational energy of the gas as

$$E_{\text{tr}} = \frac{3}{2} N' RT \quad (1.8)$$

A related property is the *average translational energy per particle*:

$$\langle \epsilon_{\text{tr}} \rangle \equiv \frac{E_{\text{tr}}}{N} = \frac{3}{2} \frac{N'}{N} \hat{R}T = \frac{3}{2} \frac{\hat{R}}{\hat{N}} T = \frac{3}{2} kT \quad (1.9)$$

Here, we have introduced a new universal constant:

$$\hat{N} = \frac{N}{N'} \quad (1.10)$$

that is Avogadro's constant, 6.022×10^{26} per kg-mol, which leads to another universal constant widely used in kinetic theory:

$$k \equiv \frac{\hat{R}}{\hat{N}} \quad (1.11)$$

that is Boltzmann's constant, 1.38×10^{-23} J/K. Another related property is the *specific translational energy*

$$e_{\text{tr}} \equiv \frac{E_{\text{tr}}}{\sum_{i=1}^N m_i} = \frac{3}{2} \frac{N'}{M} \hat{R}T = \frac{3}{2} RT \quad (1.12)$$

where the total mass is given by

$$M = \sum_{i=1}^N m_i \quad (1.13)$$

From these results, we can derive an expression for the *translational temperature* of the gas based on the properties of a collection of particles:

$$T = \frac{2}{3R} \frac{E_{\text{tr}}}{M} = \frac{2}{3R} \frac{\sum_{i=1}^N \frac{1}{2} m_i C_i^2}{\sum_{i=1}^N m_i} = \frac{\langle C^2 \rangle}{3R} \quad (1.14)$$

Note: the ordinary gas constant $R = \frac{\hat{R}N'}{M} = \frac{\hat{R}}{M_w}$ where M_w is the molecular weight.

Under our earlier assumption that the particles have no internal structure, the translational energy constitutes the only mode of energy of the gas. In this case, Eq. 1.12 therefore provides the specific energy that is an important variable in thermodynamics, and we will consider further aspects in more detail in Chapter 3. For now, we can evaluate related thermodynamic properties using standard definitions.

The *specific heat at constant volume* for a gas without internal structure:

$$c_v \equiv \left(\frac{\partial e}{\partial T} \right)_V = \frac{de_{\text{tr}}}{dT} = \frac{3}{2}R \quad (1.15)$$

The *specific heat at constant pressure* for a thermally perfect gas:

$$c_p = c_v + R = \frac{5}{2}R \quad (1.16)$$

Since our assumed gas model has constant specific heats, it is calorically as well as thermally perfect. The *ratio of specific heats* is defined as

$$\gamma \equiv \frac{c_p}{c_v} = \frac{5}{3} = 1.67 \quad (1.17)$$

This value is confirmed by experimental data measured at room temperature for monatomic gases such as helium, argon, and xenon.

Many common gases, such as N_2 , O_2 , and NO , are not monatomic, and we will later include additional forms of internal energy to describe fully their associated thermodynamics. However, in terms of their translational motion, kinetic theory does not require us to consider the internal energy modes, and, except for the thermodynamic properties, all of the relations provided in this section apply equally well to atoms and molecules.

(iv) Velocity and Speed

The average gas *velocity* vector is simply the mean over all particles:

$$\langle \vec{C} \rangle = \frac{1}{N} \sum_{i=1}^N \vec{C}_i = \vec{u} \quad (1.18)$$

and is also called the *flow* or *bulk velocity*. Similarly, the mean square speed is defined by

$$\langle C^2 \rangle = \frac{\sum_{i=1}^N m_i C_i^2}{\sum_{i=1}^N m_i} = 3RT \quad (1.19)$$

where we have used Eqs. 1.2 and 1.4, and the ideal gas law.