

1

Molecular Description

1.1

Mechanics of Continuous Media and Its Restriction

Rarefied gas flows can be modeled by many methods dependent on the flow regime. Under certain conditions, a gas can be considered as a continuous medium and then the hydrodynamic equations (see Section 6.1) are successfully applied. These equations provide a description of gas flows in terms of the so-called macroscopic quantities such as density, pressure, temperature, and velocity. Analytical and numerical methods of the mechanics of continuous media are well elaborated and described in numerous books, handbooks, and textbooks so that they are widely used in practical calculations. However, the consideration of gas as a continuous medium imposes some conditions and, consequently, restricts the application of the hydrodynamic equations. What are these restrictions?

The first restriction is based on the assumption that a characteristic size of gas flow (or macroscopic size) must be significantly larger than the so-called molecular mean-free-path (or microscopic size), that is, a path that a gaseous particle flies between two successive intermolecular collisions. What is the characteristic size? When macroscopic variables change slowly and smoothly, the characteristic size is a typical distance between boundaries of the gas flow. However, the macroscopic variables can change significantly over the mean-free-path, and then the assumption on the continuousness of the medium is broken at least in the region of the significant change. For instance, if a gas has a stepwise temperature distribution, continuous mechanics does not work near the temperature step.

The second restriction is related to nonstationary flows, namely, the continuous mechanics is valid if a significant change of macroscopic variable happens during a time interval significantly larger than the mean-free-time of gaseous particles. For instance, if an oscillation frequency of solid surface is close to the intermolecular collision frequency, a gas flow near this surface cannot be described by continuous mechanics even if the first assumption is fulfilled. Another example when the second assumption is not fulfilled is a sudden motion of a solid surface or sudden variation of its temperature.

Thus, if at least one of the above-mentioned assumptions is not fulfilled, continuous mechanics cannot be applied, but a modeling should be done at a microscopic level, that is, a gas must be considered as rarefied. This branch of fluid mechanics is called rarefied gas dynamics. The aim of this field is to obtain macroscopic characteristics based on microscopic behavior of gaseous particles. Such a behavior involves two kinds of interactions, namely, intermolecular collisions and gas–surface interaction. In this chapter, basic information about the intermolecular interaction is given.

1.2

Macroscopic State Variables

In this section, we will define main macroscopic quantities used in fluid mechanics. Consider a portion of gas occupying a volume \mathcal{V} . The amount of the gas can be measured by its mass M or by the number of particles N . The mass of one particle is given as

$$m := \frac{M}{N}. \quad (1.1)$$

If the number of particles is equal to the Avogadro number N_A (see Table A.1), then the amount of gas is one mole. The mass of one mole is called atomic weight and is calculated as

$$\mathcal{M} := mN_A. \quad (1.2)$$

The atomic weight is usually given in grams per mole. Its values for the noble gases are given in Table A.2. The gas amount can also be measured in the number of moles as

$$\nu := \frac{N}{N_A} = \frac{M}{\mathcal{M}}. \quad (1.3)$$

The quantities characterizing the gas amount, for example, volume \mathcal{V} , mass M , the number of particles N , or the number of moles, are called extensive. It is common to write equations in terms of specific variable given as a ratio of two extensive quantities. For instance, the specific mass, or mass density, is defined as

$$\rho := \frac{M}{\mathcal{V}}. \quad (1.4)$$

The number of particles per gas volume, or number density, is defined as

$$n := \frac{N}{\mathcal{V}}. \quad (1.5)$$

The mass density and number density are related via the molecular mass as

$$\rho = mn, \quad (1.6)$$

which follows from Eqs. (1.1), (1.4), and (1.5).

Any gas occupying a container of volume \mathcal{V} produces a pressure p on its walls, which is defined as a force F acting on an area A unity

$$p := \frac{F}{A}. \quad (1.7)$$

The unit of pressure in the International System of Units (SI) is given by newtons (N) per square meter (m^2) and is called pascal (Pa).

The pressure of gas depends on its amount, volume, and also on its temperature T , which is measured in kelvins (K). The definition of this quantity in the frame of equilibrium thermodynamics can be found in many textbooks, for example, Ref. [1]. Later the temperature definition will be given via the velocity distribution function.

1.3

Dilute Gas

A relation of gas pressure to its amount, volume, and temperature is called state equation. This book is restricted only to the so-called diluted gas obeying the following state equation:

$$p\mathcal{V} = \nu R_g T, \quad (1.8)$$

where R_g is the molar (or universal) gas constant (see Table A.1). The state equation in the form (1.8) is given in most of textbooks on thermodynamics, but in statistical physics it is usually written in terms of the number density n or mass density ρ as

$$p = nk_B T, \quad p = \frac{\rho}{m} k_B T, \quad (1.9)$$

where k_B is the Boltzmann constant (see Table A.1), which is related to the molar gas constant R_g and Avogadro number N_A as

$$k_B = \frac{R_g}{N_A}. \quad (1.10)$$

The combination of this equation with (1.2) yields the relation

$$\frac{k_B}{m} = \frac{R_g}{\mathcal{M}}, \quad (1.11)$$

which is quite useful because the kinetic theory deals with the molecular mass m , while in many practical fields, the atomic weight \mathcal{M} is more preferable.

A relation of internal energy E of gas to its state variables is called the energy equation. For a dilute monatomic gas, the internal energy is proportional to its temperature and is given as

$$E = \frac{3}{2} N k_B T, \quad \text{or} \quad E = \frac{3}{2} \nu R_g T. \quad (1.12)$$

The specific internal energy e , or energy per mass unity, is defined as

$$e := \frac{E}{M} \quad (1.13)$$

so by using (1.1) the energy equation (1.12) is transformed to

$$e = \frac{3}{2} \frac{k_B T}{m}. \quad (1.14)$$

The state equation (1.9) and energy equation (1.14) work well for the atmospheric pressure and for any lower pressure. Consequently, all results of the book are valid for this range of the pressure.

1.4

Intermolecular Potential

1.4.1

Definition of Potential

In case of dilute gas, the intermolecular interactions do not affect the state and energy equations, but they are important to describe the transport phenomena in gases, like mass, heat, and momentum transfers. In this section, main models of intermolecular interactions are given.

The intermolecular potential $U(r)$ is defined so that the potential energy of two particles separated by a distance r is equal to U . If this potential is known, then the interaction force F between these two particles is calculated as

$$F(r) = -\frac{dU(r)}{dr}. \quad (1.15)$$

An exact calculation of the potential $U(r)$ is a very hard task, that is why many simplified models were proposed.

1.4.2

Hard Sphere Potential

The most simple potential is the hard sphere (HS) model given as

$$U(r) = \begin{cases} \infty & \text{at } r < d, \\ 0 & \text{at } r > d, \end{cases} \quad (1.16)$$

where d is the sphere diameter. Physically, it means that two particles cannot be closer than their diameter, but when they are separated by a distance $r > d$ then the interaction force is zero. In many applications, this model works pretty well, that is why it is widely used in practical calculations. The molecular diameter can be extracted from the transport coefficients such as viscosity and thermal conductivity. However, if one calculates the diameter d from the gas viscosity at two different temperatures, one obtains two different values of the diameter. It means

that we cannot calculate the diameter once at one temperature and then use it for any other temperature.

1.4.3

Lennard-Jones Potential

As will be shown later, see Section 6.4.1, the dynamic viscosity μ of gas composed of hard spheres is proportional to the square root of the temperature T , $\mu \propto \sqrt{T}$, while empirical data, see for example, the review by Kestin *et al.* [2], indicate a different dependence of viscosity on the temperature. Such a discrepancy is explained by the neglect of attractive force between particles when they are separated by a distance $r > d$. Moreover, the repulsive force arising at a short distance is really large but not infinite as for the HS potential. These two factors are taken into account by the Lennard-Jones (LJ) potential given as

$$U(r) = 4\epsilon \left[\left(\frac{d}{r} \right)^{12} - \left(\frac{d}{r} \right)^6 \right], \quad (1.17)$$

where ϵ is the potential well depth. This potential contains two fitting parameters d and ϵ that allow us to describe better the dependence of transport coefficients on the temperature. The values of d and ϵ vary from one bibliography source to another because they are extracted from different coefficients. Some numerical values of the LJ potential parameters extracted from viscosity experimental data reported in the book by Hirschfelder *et al.* [3] are given in Table 1.1. The books in [4, 5] provide very similar data.

1.4.4

Ab initio Potential

Recently, a calculation of the potential *ab initio* (AI) became possible. A technique to calculate the AI potentials is well elaborated and the corresponding data for

Table 1.1 Parameters ϵ/k_B and d for LJ and AI potentials.

Gas	ϵ/k_B (K)		d (nm)	
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>
He	10.22	10.997898	0.2576	0.2640950
Ne	35.7	41.152521	0.2789	0.27612487
Ar	124.0	143.123	0.3418	0.335741
Kr	190	193	0.361	0.363
Xe	229		0.4055	

a) LJ, extracted from viscosity, Ref. [3].

b) AI, Refs [6–9].

Table 1.2 Parameters of *ab initio* potential given by (1.18).

Param.	Unit	Value	
		Ne, Ref. [7]	Ar, Ref. [8]
A	K	$4.02915058383 \times 10^7$	4.61330146×10^7
a_1	$(\text{nm})^{-1}$	$-4.28654039586 \times 10^1$	-2.98337630×10^1
a_2	$(\text{nm})^{-2}$	-3.33818674327	-9.71208881
a_3	nm	$-5.34644860719 \times 10^{-2}$	$2.75206827 \times 10^{-2}$
a_4	$(\text{nm})^2$	$5.01774999419 \times 10^{-3}$	$-1.01489050 \times 10^{-2}$
b	$(\text{nm})^{-1}$	$4.92438731676 \times 10^1$	4.02517211×10^1
C_6	$\text{K} (\text{nm})^6$	$4.40676750157 \times 10^{-2}$	$4.42812017 \times 10^{-1}$
C_8	$\text{K} (\text{nm})^8$	$1.64892507701 \times 10^{-3}$	$3.26707684 \times 10^{-2}$
C_{10}	$\text{K} (\text{nm})^{10}$	$7.90473640524 \times 10^{-5}$	$2.45656537 \times 10^{-3}$
C_{12}	$\text{K} (\text{nm})^{12}$	$4.85489170103 \times 10^{-6}$	$1.88246247 \times 10^{-4}$
C_{14}	$\text{K} (\text{nm})^{14}$	$3.82012334054 \times 10^{-7}$	$1.47012192 \times 10^{-5}$
C_{16}	$\text{K} (\text{nm})^{16}$	$3.85106552963 \times 10^{-8}$	$1.17006343 \times 10^{-6}$

many gases and mixtures can be found in numerous works, see for example, Refs [6–14]. The main advantage of the AI potentials is the absence of any parameters to be extracted from experimental data. Numerical results on the AI potential usually are given in terms of interpolating formulas. One of them has a form: [7, 8]

$$\frac{U(r)}{k_B} = A \exp \left[a_1 r + a_2 r^2 + \frac{a_3}{r} + \frac{a_4}{r^2} \right] - \sum_{n=3}^8 \frac{C_{2n}}{r^{2n}} \left(1 - e^{-br} \sum_{k=0}^{2n} \frac{(br)^k}{k!} \right). \quad (1.18)$$

The numerical values of the interpolating coefficients for neon and argon reported in Refs [7, 8] are reproduced in Table 1.2. The expressions of the potential $U(r)$ for helium and krypton have slightly different form and can be found in Refs [6] and [9], respectively.

The well depth ϵ for the AI potentials and the distance corresponding to the zero point

$$U(d) = 0, \quad (1.19)$$

are compared with those for the LJ potential extracted from viscosity in Table 1.1. As is expected, the values obtained by two quite different methodologies are close to each other. Both LJ and AI potentials are plotted on Figure 1.1, which shows that they are only slightly different, but qualitatively they are quite similar to each other. Thus, the LJ potential with the parameters ϵ and d extracted from viscosity provides very reliable description of the intermolecular interaction.

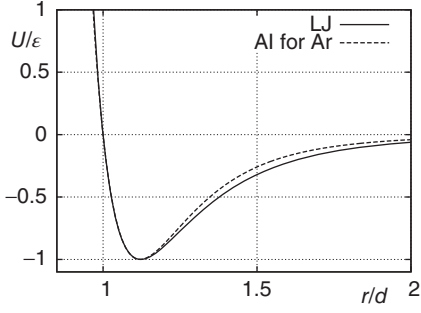


Figure 1.1 Potential U versus intermolecular distance r .

1.5 Deflection Angle

Once the intermolecular potential is known, the binary collision problem can be solved. Let us consider two particles of the same mass m moving with velocities \mathbf{v} and \mathbf{v}_* before collisions and changing their velocities to \mathbf{v}' and \mathbf{v}'_* after the collision. The relative velocities before and after the collision are denoted as

$$\mathbf{g}_r = \mathbf{v} - \mathbf{v}_*, \mathbf{g}'_r = \mathbf{v}' - \mathbf{v}'_*, \quad (1.20)$$

respectively. If the collision is elastic, the vector of their relative velocity changes only its direction, that is, $|\mathbf{g}'_r| = |\mathbf{g}_r|$. The angle χ between the vectors \mathbf{g}_r and \mathbf{g}'_r is called the deflection angle. Thus, when this angle is known, the post-collision velocities \mathbf{v}' and \mathbf{v}'_* are easily related to the pre-collisions velocities \mathbf{v} and \mathbf{v}_* .

To calculate the angle χ , a binary collision is considered in the reference frame related to one of the particles, while the other particle moves with a velocity \mathbf{g}_r as is shown in Figure 1.2. From this scheme, one can easily calculate the deflection angle χ for the HS potential determined by the impact parameter b as

$$\chi = 2 \arccos(b/d). \quad (1.21)$$

For an arbitrary potential $U(r)$, the deflection angle is determined not only by the parameter b but also by the kinetic energy of the relative motion related to the relative motion speed g_r as

$$E_r = \frac{mg_r^2}{4}. \quad (1.22)$$

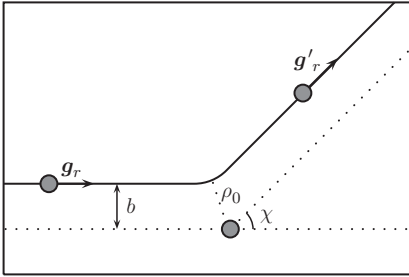


Figure 1.2 Scheme of binary collision.

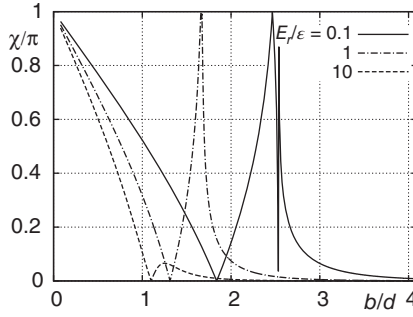


Figure 1.3 Deflection angle χ versus impact parameter b for LJ potential.

The calculation of χ can be performed numerically following a procedure described in many textbooks on classical mechanics, see for example, Ref. [15], and those on kinetic theory [3–5, 16–20]. Some details on the numerical scheme is given in Ref. [21].

In case of the LJ potential, the deflection angle χ is usually calculated in terms of the dimensionless quantities E_r/ϵ and b/d because the function $\chi(E_r/\epsilon, b/d)$ once calculated can be used for the LJ potential with any numerical values of the parameters d and ϵ . It is not possible to do the same with the AI potential, which requires calculations of the deflection angle χ for each combination of E_r and b . Typical plots of χ on b/d based on the data reported in Ref. [21] are depicted on Figure 1.3 for three values of the energy ratio $E_r/\epsilon = 0.1, 1$, and 10 . In contrast to the hard spheres (1.21), the dependence of χ on b/d for the LJ potential is not monotone, but it reaches zero, then it increases and then vanishes at $b/d \rightarrow \infty$.

1.6

Differential Cross Section

The kinetic equation will be given on terms of the so-called differential cross section (DCS) $\sigma_d(E_r, \chi)$. If we imagine a beam of particles uniformly distributed in the space and moving with the same velocity equal to g_r relative to a fixed target particle, then the number of the beam particles scattered into the angle interval $[\chi, \chi + d\chi]$ will be proportional to $\sigma_d(E_r, \chi) \sin \chi d\chi$. On the other hand, for a given energy E_r , the deflection angle is determined only by the impact parameter b . Since the particles are distributed uniformly, the number of particles having the impact parameter in the interval $[b, b + db]$ is proportional to b so that the DCS can be defined as

$$\sigma_d(E_r, \chi) \sin \chi d\chi = b db. \quad (1.23)$$

If the parameter b is expressed in terms of χ , the DCS can be calculated from (1.23). For the HS potential, the function $b = d \cos(\chi/2)$ is obtained from (1.21) and the DCS takes the form

$$\sigma_d(E_r, \chi) = \frac{b}{\sin \chi} \frac{db}{d\chi} = \frac{d^2}{4} \quad \text{for HS.} \quad (1.24)$$

For a potential such as LJ, several values of b can correspond to the same value of χ , see Figure 1.3, so that all these values must be included in the expressions of the DCS, that is, more generally it is defined as

$$\sigma_d(E_r, \chi) := \frac{1}{\sin \chi} \sum_i b_i \left| \frac{\partial b_i}{\partial \chi} \right|, \quad (1.25)$$

where b_i are all values of the impact parameter corresponding to the deflection angle χ . A detailed information about the DCS and its calculation for the LJ potential is given in the paper [21].

1.7

Total Cross Section

The total cross section (TCS) σ_t is defined via the integration of the DCS over the whole interval of the deflection angle variation

$$\sigma_t := 2\pi \int_0^\pi \sigma_d(E_r, \chi) \sin \chi \, d\chi. \quad (1.26)$$

Substituting (1.24) into (1.26), the TCS for the hard spheres is obtained as the area of circle with a radius d

$$\sigma_t = \pi d^2 \quad \text{for HS.} \quad (1.27)$$

The TCS also can be treated as the area of the circle around the target particle containing only those beam particles that undergo a collision.

If a potential is not zero at any distance, the TCS is infinite because all beam particles undergo collision with the target particle. In order to avoid such a non-sense result, an angle cut-off should be done, that is, we assume that a deflection within the small interval $[0, \chi_0]$ ($\chi_0 \ll 1$) is not considered as a collision, then the TCS becomes a finite value given as

$$\sigma_t(E_r) = 2\pi \int_{\chi_0}^\pi \sigma_d(E_r, \chi) \sin \chi \, d\chi, \quad (1.28)$$

which depends on the energy E_r of the relative motion.

Using the definition (1.23), the TCS can be calculated by integrating with respect to the impact parameter b . Again, to avoid the infinite TCS, the potential should be cut-off. Let us assume that $U(r) = 0$ if $r > b_M$, that is, a collision happens only if the impact parameter is smaller than b_M , then the TCS is given as

$$\sigma_t = 2\pi \int_0^{b_M} b \, db = \pi b_M^2 \quad (1.29)$$

that is the area of circle of a radius b_M . In this case, the TCS is independent of the collision energy E_r .

1.8

Equivalent Free Path

The concept of mean-free-path (MFP) is quite important in rarefied gas dynamics. It is defined as a mean distance traveled by a particle between two successive collisions and inversely proportional to the number density n and TCS σ_t so that

$$\text{MFP} \propto (n\sigma_t)^{-1}. \quad (1.30)$$

A more exact calculation of the MFP made for a gas being in equilibrium leads to the expression

$$\text{MFP} = \left(\sqrt{2}n\sigma_t \right)^{-1}. \quad (1.31)$$

The derivation of this formula can be found, for example, in Section 2.4 of the book [4] or in Section 4.3 of the book [17].

According to Eq. (1.27), the TCS of hard sphere is determined by their diameter d so that the MFP is a quite definite quantity for this potential. However, for a potential without a cut-off, the TCS is infinite and hence the MFP calculated by (1.31) is zero. Evidently, if a potential is nonzero at any distance theoretically, all particles are always colliding with each other. In other words, they never move freely. If a potential is cut-off at some distance b_M , then according to Eqs. (1.29) and (1.31), the MFP will be inversely proportional to b_M^2 . On the other hand, macroscopic properties of gas should not depend on the cut-off distance b_M , but they should converge by increasing b_M . Thus, the use of the MFP concept to describe nonequilibrium phenomena in gases is not appropriate, but some equivalent free path (EFP) independent of the cut-off should be used.

The gas viscosity μ when calculated for the LJ potential or for some similar one converges to a fixed value by increasing the cut-off distance b_M . Therefore, the EFP defined via the viscosity coefficient μ as

$$\ell := \frac{\mu v_m}{p} \quad (1.32)$$

is not affected by the cut-off distance and is suitable to treat transport phenomena calculated for different intermolecular potentials. Here, v_m is the most probable molecular speed defined in Section 2.4.

1.9

Rarefaction Parameter and Knudsen Number

In order to choose an appropriate numerical or analytical method to calculate rarefied gas flows, the rarefaction regime should be checked. Let us denote a characteristic size of gas flow as a , then the regime of flow is determined by the ratio

$$\text{Kn} := \frac{\text{MFP}}{a}, \quad (1.33)$$

which is called Knudsen number. However, it is very usual to use the rarefaction parameter to characterize the gas rarefaction defined via the EFP as

$$\delta := \frac{a}{\ell} = \frac{ap}{\mu v_m}. \quad (1.34)$$

The rarefaction parameter is inversely proportional to the Knudsen number because EFP is proportional to MFP. Since most of theoretical papers report the results in terms of the rarefaction parameter, it will be used in this book to characterize the gas rarefaction.

It is possible to distinguish several regimes of gas flows with respect to the rarefaction parameter. When $\delta \rightarrow 0$, the EFP becomes significantly larger than the characteristic size, $\ell \gg a$, and molecules move without any collision between them. This regime is called free-molecular or collisionless. It is relatively easy for numerical or analytical calculations. The book by Saksaganskii [22] contains a lot of examples of solutions for many problems of rarefied gases in this regime. Few examples of free-molecular flows will be considered in Chapters 11–16.

In the opposite limit $\delta \rightarrow \infty$, the EFP is quite smaller than a characteristic size of gas flow, $\ell \ll a$. Under this condition, the continuous mechanics equations are applicable that is why this regime is usually called continuous or hydrodynamic. There are numerous books dedicated to this regime, see for example, Refs [23, 24], so that this regime will be described very briefly in this book. Several examples of hydrodynamic flows given in Chapters 11–16 demonstrate the use of the so-called velocity slip and temperature jump boundary conditions, which extend an application of the hydrodynamic equations to lower values of the rarefaction δ .

Our main interest will be the so-called transitional regime when the rarefaction parameter is not small to neglect the intermolecular collisions, but it is not so large in order to apply the hydrodynamic equations, that is, when $\delta \sim 1$.

Exercises

- 1.1** Verify that Eq. (1.9) is equivalent to Eq. (1.8).

Hint: Use Eqs. (1.3), (1.5), and (1.10).

- 1.2** Calculate the mass of one atom of helium and xenon.

Solution: Using (1.2), we obtain $m = \mathcal{M}/N_A$. Then $m = 6.646 \times 10^{-27}$ kg for helium and $m = 2.180 \times 10^{-25}$ kg for xenon.

- 1.3** Estimate the EFP ℓ of helium ($v_m = 1.1 \times 10^3$ m/s, $\mu = 19$ μ Pa s) and xenon ($v_m = 1.9 \times 10^2$ m/s, $\mu = 21$ μ Pa s) under standard conditions, that is, $T = 273.15$ K and $p = 1$ atm (see Table A.1).

Solution: Substituting the given data into Eq. (1.32), we obtain $\ell = 0.21$ μ m for helium and $\ell = 0.039$ μ m for xenon.

Comments: Two different species of gas can have quite different EFPs under the same conditions. If one deals with a macroscopic size of flow of about few centimeters, the mechanics of continuous medium is applicable, but for a microflow, when its size is about few microns, the flow is transitional.

- 1.4** Estimate the EFP ℓ for helium under typical conditions of rough vacuum $p = 1$ Pa and high vacuum $p = 10^{-7}$ Pa. Assume $T = 273.15$ K.

Solution: Substituting the given data into Eq. (1.32), we obtain $\ell = 2.1$ cm at $p = 1$ Pa; $\ell = 2.1 \times 10^5$ m at $p = 10^{-7}$ Pa.

Comments: Assuming a typical size in vacuum systems to be about few centimeters, it can be said that the flow regime is transitional for rough vacuum and it is free molecular for high vacuum.

- 1.5** Calculate the Loschmidt constant, that is, the number of particles per cubic meter under standard conditions, using the state equation (1.9). Compare it with the value given in Table A.1.

Solution: $N_L = 2.69 \times 10^{25} \text{ m}^{-3}$.

Comments: The number is huge so that the statistical approach is justified.

- 1.6** Calculate the number of particles contained in 1 m^3 under the ultrahigh vacuum condition $p = 10^{-10}$ Pa at $T = 300$ K.

Solution: $N = 2.4 \times 10^{10}$.

Comments: Even for the high vacuum conditions, the number of particles is still huge.