Chapter 1
Elementary kinetic theory of gases

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1.1. Introduction. Molecular description of gases

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1.1. Introduction. Molecular description of gases

Subject of kinetic theory. What are we going to study?

- **Kinetic theory of gases** is a part of **statistical physics** where flows of gases are considered on the **molecular level**, i.e. on the level of individual molecules, and described in terms of changes of probabilities of various states of gas molecules in space and time based on known laws of interaction between individual molecules.

  Word "Kinetic" came from a Greek verb meaning "to move" or "to induce a motion."

- **Rarefied gas dynamics (RGD)** is often used as a synonymous of the kinetic theory of gases. In the narrow sense, the kinetic theory focuses on the general methods of statistical description of gas flows, while the rarefied gas dynamics focuses on solutions of practical gas dynamics problems based on methods of kinetic theory.
- **Non-equilibrium gas dynamics** combines methods of rarefied gas dynamics and continuum gas dynamics for description of non-equilibrium gas flows.
- **Direct simulation Monte Carlo (DSMC) method** is a stochastic Monte Carlo method for simulation of dilute gas flows on the molecular level. To date, DSMC is the state-of-the-art numerical tool for the majority of applications in the kinetic theory of gases and rarefied gas dynamics.
- **Monte Carlo (MC) method** is a general numerical method for a variety of mathematical problems based on computer generation of (pseudo) random numbers and probability theory.

1.1. Introduction. Molecular description of gases

Historical perspective

Historically, kinetic theory of gases evolves from the molecular theory of heat, which derives, e.g., gas laws from thermal (chaotic) motion of individual gas molecules.

Ludwig Eduard Boltzmann
(1844 –1906)
Austrian physicist and philosopher

The breakthrough was performed by Ludwig Boltzmann, the father of the kinetic theory, who derived the **Boltzmann kinetic equation** (Chapter 3), a equation that describes any dynamic process in gases in terms of motion and interaction of gas molecules.

The kinetic theory, however, attracted huge attention only in the middle of XX century as a practical tool for studying low-density gas flows in aerospace applications.

Applications of the approach developed by L. Boltzmann go far beyond the kinetic theory of gases. Numerous generalizations of his equation are used in various branches of physics. For example, the **Boltzmann transport equation (BTE)** is used in the solid-state physics to describe transport properties (e.g., thermal conductivity) of materials with crystalline lattices.

L. Boltzmann is famous not only for his kinetic equation. He was one of founders of the statistical physics in general and established a relationship between entropy S and probability of states of a physical system W, $S = k_B \log W$.

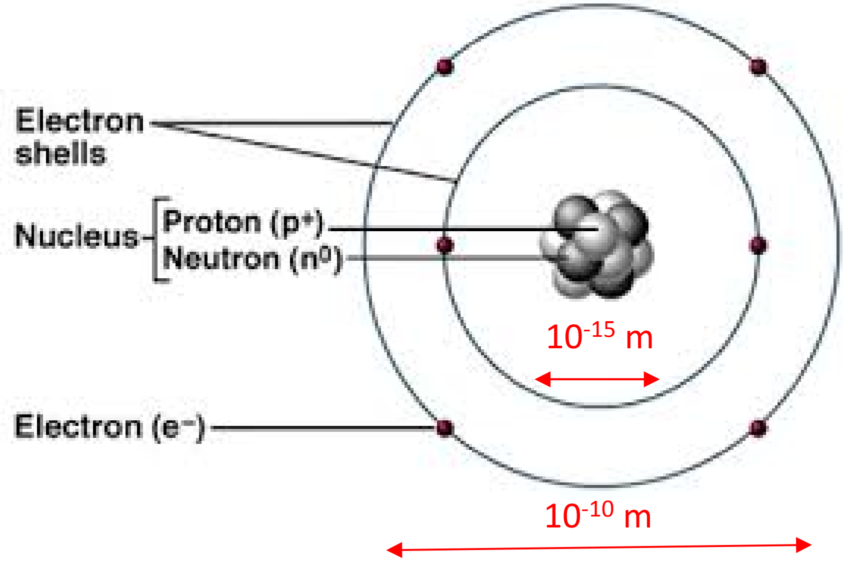
1.1. Introduction. Molecular description of gases

Hypothesis of molecular structure of gases

Kinetic theory of gases is a part of statistical physics where flows of *gases are considered on the molecular level* and described in terms of changes of probabilities of various states of gas molecules in space and time based on known laws of interaction between individual molecules.

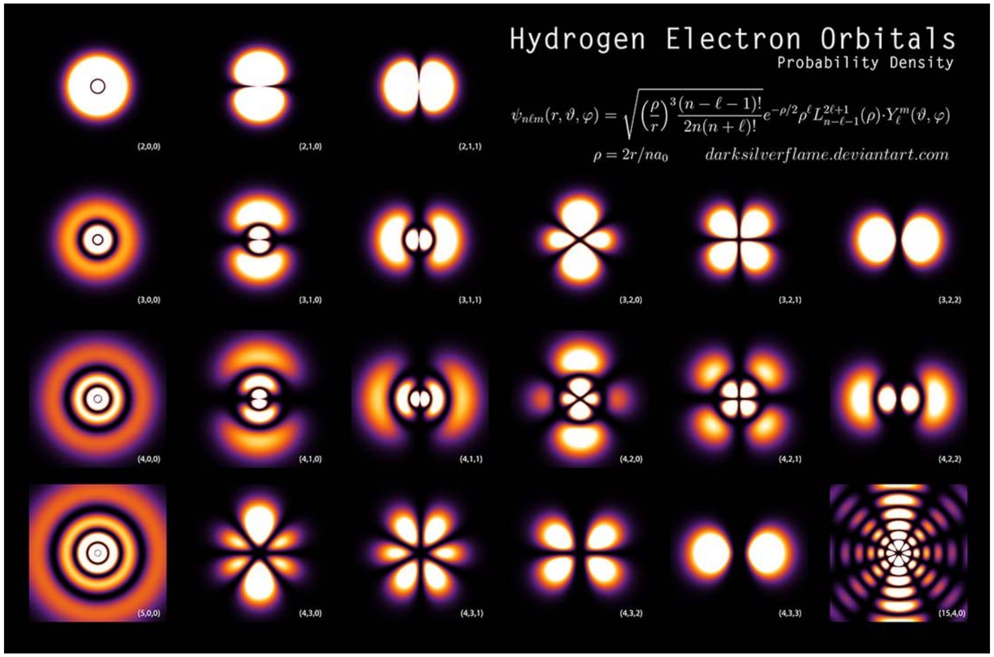
The starting point of the kinetic theory is the **hypothesis of the molecular structure of gases**: Any gas consists of distinct individual particles – molecules. Modern kinetic theory considers not only electrically neutral and chemically inert monatomic gases (e.g., **noble gases**), but also gases composed of charged ions and electrons (**plasma**), molecules (**molecular gases**) and chemically reactive gas mixtures, as well as **granular gases** composed of macroscopic solid particles.

Sizes of atoms and molecules



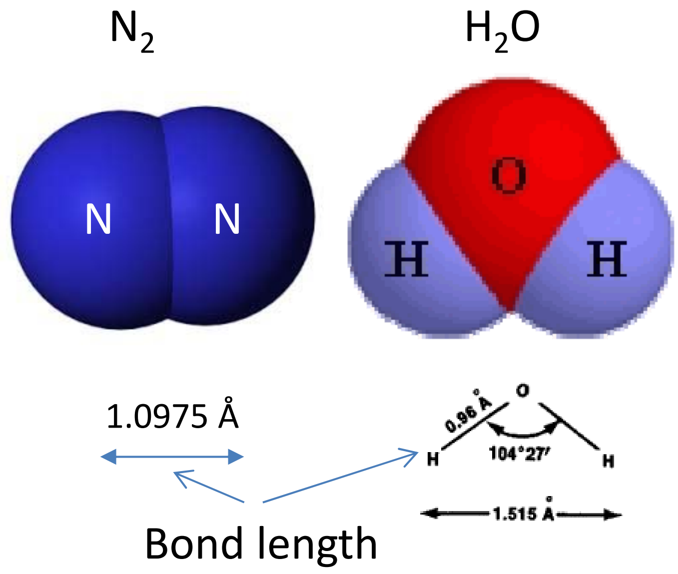
- Molecules consist of one or multiple atoms.
- Every atom has a **nucleus** that is surrounded by a "cloud" of negatively charged **electrons**.
- A nucleus consist of **nucleons**: positively charged **protons** and electrically neutral **neutrons.**
- The characteristic diameter of the nucleus is about 1 Fermi (10^{-15} m), while the diameter of the electron cloud is about 1 Angstrom (Å, 10^{-10} m).

1.1. Introduction. Molecular description of gases



According to quantum mechanics, atoms do not have any "natural" size, because electrons surrounding nuclei cannot be considered as point masses. Every electron (or electron pair) is characterized by an **electron orbital**, which is a mathematical function describing the probability to find electron in different points around the nucleus.

- Individual atoms compose a molecule when chemical **bonds** form due to the overlap of electron orbitals belonging to different atoms.
- Therefore, the distance between neighbor atoms in a molecule (**bond length**) has an order of the atomic diameter.
- Sizes of molecules of **diatomic** (O_2, N_2) and **triatomic** (CO_2, water vapor) gases have the same order of magnitude as the sizes of individual atoms.



1.1. Introduction. Molecular description of gases

In different applications, the sizes of atoms and molecules can be chosen based on different considerations in order to match the most important (in the particular field/problem) experimental characteristics.

In the kinetic theory, the size of atoms and molecules is usually characterized by so-called **gaskinetic** or **kinetic diameters** d, which are chosen to match values of gas viscosity predicted by a theory to experimentally measured values.

Masses of atoms and molecules

- Mass of a molecule is the sum of masses of individual atoms composing molecules.
- Mass of an atom is a sum of masses of the nucleus and electrons.
- The mass of a nucleus is not precisely equal to the sum of masses of individual nucleons because of relativistic effects (transformation of mass into binding energy between nucleons).
- The rest mass of a proton is m_p= 1.67×10^{-27} kg = 1.007 Da
- The rest mass of an electron is m_e =9.11×10^{-31} kg = 5.486×10^{-4} Da ~ 0.001 of proton mass, so the major mass of an atom is concentrated in its nucleus.
- Since masses of atoms and molecules are small in kg, it is convenient to measure them in specific atomic mass units. The **unified atomic mass unit** (symbol **u**) or **Dalton** (symbol **Da**) is the standard unit that is used for measuring masses on the atomic or molecular scale. One u is *approximately* equal to the mass of one nucleon (either a proton or neutron).

1.1. Introduction. Molecular description of gases

One **unified atomic mass unit** is defined as one twelfth of the mass of an unbound neutral atom of carbon-12 (C^{12}) in its nuclear and electronic ground state, and has a value of

$$1\text{ u} = 1\text{ Da} = m_u = \frac{m_{C^{12}}}{12} = 1.660539040\times10^{-27}\text{ kg}.$$

The **amu** without the "unified" prefix is an obsolete unit that was based on oxygen. Many sources still use the term "amu," but now define it in the same way as u (i.e., based on C^{12}). In this sense, the majority of uses of the terms "atomic mass units" and "amu" today actually refer to the unified atomic mass unit.

The definition of u is related to the definition of a mole. The **mole** (symbol **mol**) is the amount of substance, which contains as many elementary entities (particles) as there are atoms in 12 g of C^{12}. The notion of mole is used to count the number of particles, not the mass. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles. The number of particles in 1 mole is the *universal* constant that relates the number of entities to the amount of substance for any sample and called the **Avogadro constant**

$$N_A = \frac{12\ g}{m_{C^{12}}} = 6.022140857\times10^{23}\text{ mol}^{-1}\text{ (entities per mole).}$$

The **molar mass**, **molecular mass** or **molecular weight** of a species is the mass of its one mole

$$\mu_A = m\ N_A$$

where m is the mass of an individual particle. The **relative atomic mass** (**atomic weight**) has traditionally been a relative scale, but currently it is measured in u.

1.1. Introduction. Molecular description of gases

Let's assume that we know the molar mass of a gas μ_A in gram. What is the mass of individual molecule m of this gas in Da?

$$m\,[\mathrm{Da}] = \frac{\mu_A\,[\mathrm{g}]}{N_A}\Bigg/\frac{m_{C^{12}}\,[\mathrm{g}]}{12} = \frac{\mu_A\,[\mathrm{g}]}{12[\mathrm{g}]\,/\,m_{C^{12}}[\mathrm{g}]}\Bigg/\frac{m_{C^{12}}\,[\mathrm{g}]}{12} = \mu_A\,[\mathrm{g}]$$

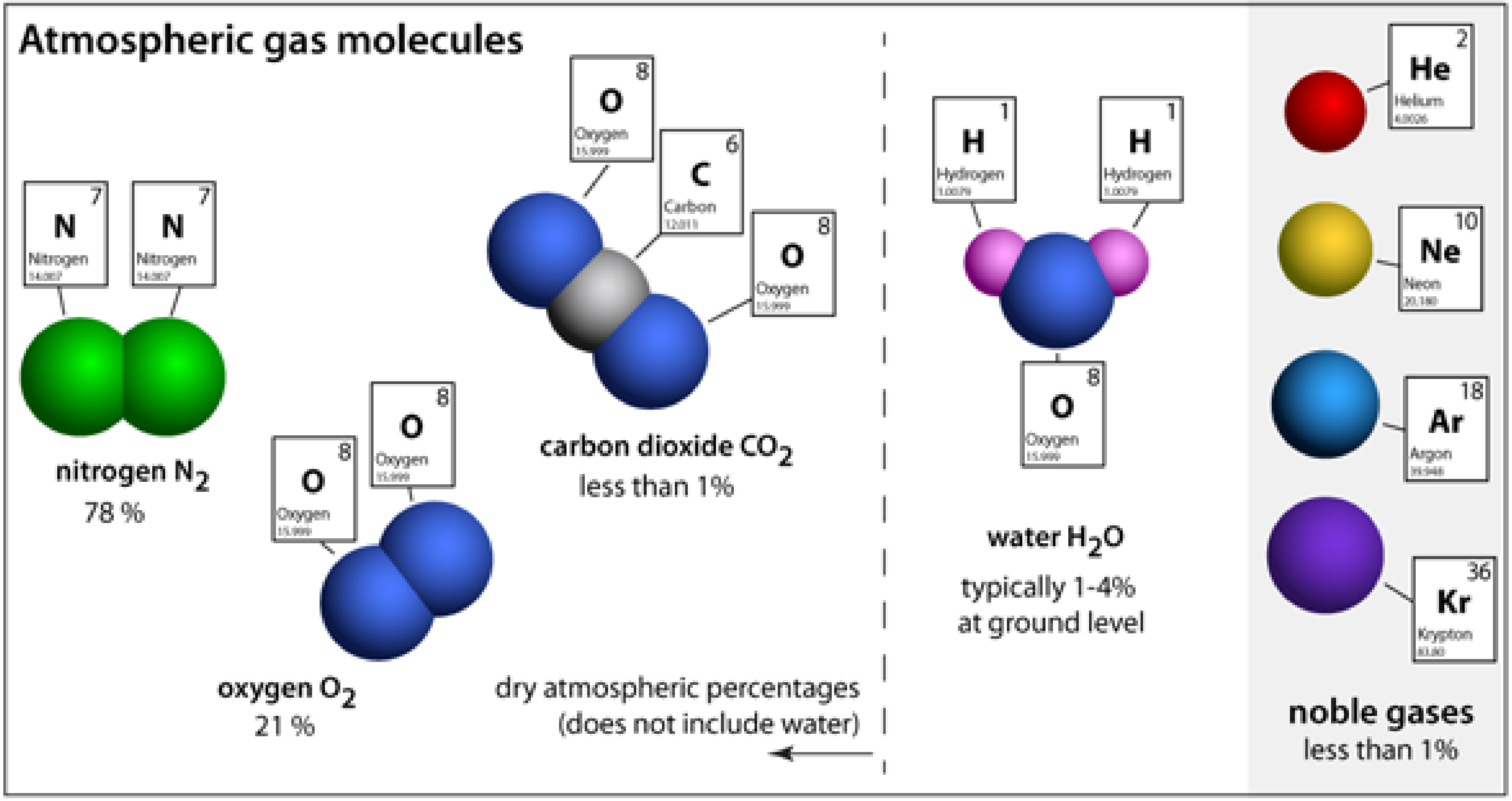
Thus, the mass of a molecule in Da is numerically equal to the molar mass in gram.

Properties of major components of atmospheric air and other gases

Species	Volume fraction in air	$d \times 10^{-10}$, m	$m \times 10^{-27}$, kg
Nitrogen N_2	0,7809	3,7 (4,17)	46,5
Oxygen O_2	0,2095	3,56 (4,07)	53,12
Carbon dioxide CO_2	0,0003	4,5 (5,62)	73,1
Carbon monoxide CO	–	(4,19)	46,5
Helium He	–	(2,33)	6,65
Neon Ne	–	(2,77)	33,5
Argon Ar	0,0093	3,9 (4,17)	66.3
Krypton Ke	–	(4,76)	139,1
Xenon Xe	–	(5,74)	218
Carbon vapor C	–	1,55	20
Silicon vapor Si	–	2,64	46,7

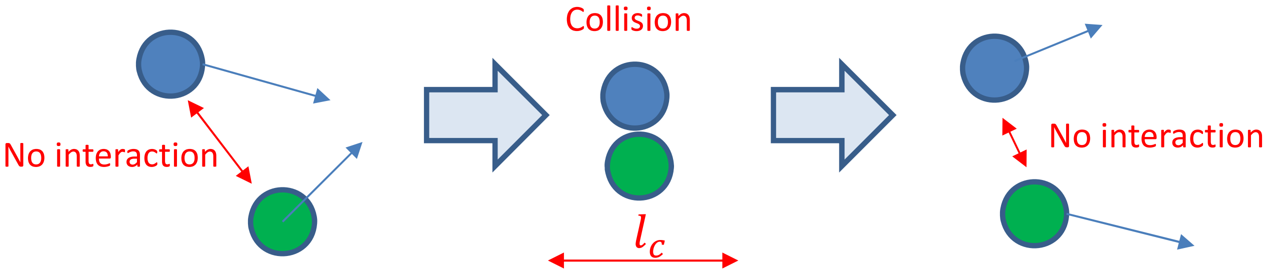
1.1. Introduction. Molecular description of gases

Species of the atmospheric air



1.1. Introduction. Molecular description of gases

Length and time scale of inter-molecular collisions



Individual interaction between a pair of gas molecules is called the **binary collision**.

Interatomic forces are short-range and molecules strongly interact with each other only if the distance between them is in the order of the molecular size. Then the **length scale of intermolecular collisions**, l_c, i.e. the characteristic length of a path of a molecule during collision, is in the order of the kinetic diameter of molecules

$$l_c \sim d \sim 1\ \text{Å}.$$

As we will see later on, the characteristic chaotic velocity of gas molecule $C = \sqrt{3RT}$ has the order of the sound speed or $\sqrt{\gamma RT}$ (R is the **gas constant**, γ is the **isentropic index**). With typical values of R ~ 300 J/K/kg and T ~ 300 K , C ~ 300 m/s. Then the **time scale of intermolecular collisions**, t_c, i.e. the characteristic duration of the binary collision, is equal to

$$t_c \sim \frac{l_c}{C} \sim 10^{-12}\ \mathrm{s} = 1\ \mathrm{ps}$$

The kinetic theory studies processes is gases evolving on length and time scales that are much larger that the length and time scale of an individual collision. For this reason, we will systematically neglect the displacement of molecules during collision and treat any collision as an instant change of molecular velocities taking place in a given point.

1.1. Introduction. Molecular description of gases

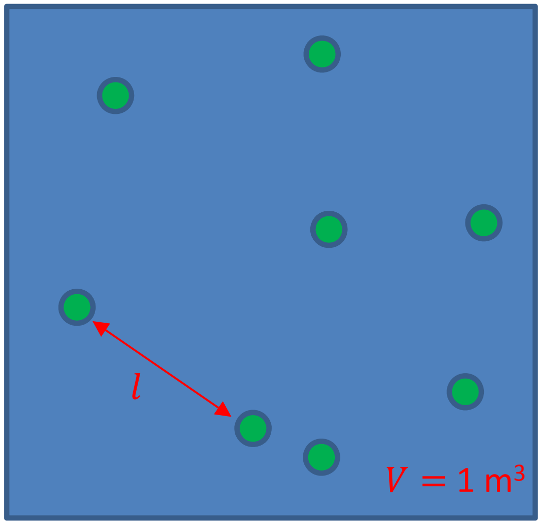
Characteristic distance between molecules in gases

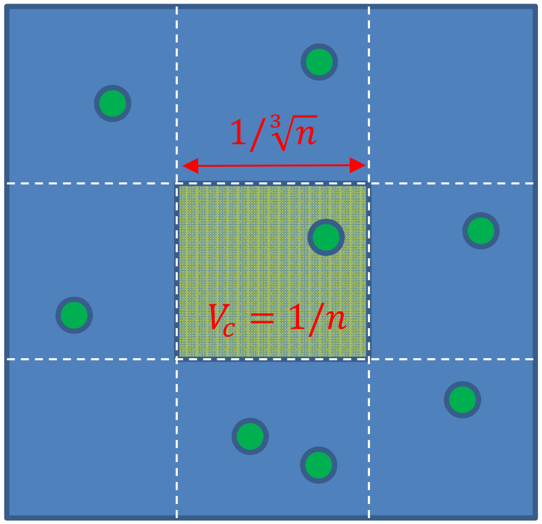
Number density of a gas n is the number of molecules in a unite volume $[n]$=1/m^3. If we know n then the number of molecules in volume V of a homogeneous gas is equal to $N = nV$.

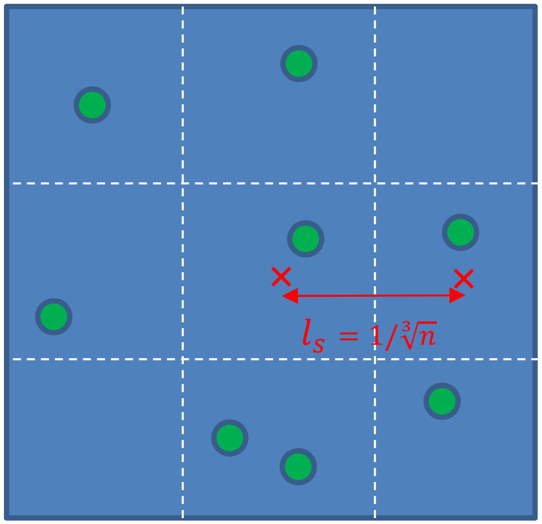
Let's assume that a gas has number density n is known and calculate (estimate) the **characteristic** (average, mean) **distance (spacing) between molecules** l_s?

If a unit volume (1 m^3) contains n molecules, then in average one molecule occupies the volume $1/n$, which we can consider as a cube of size $1/\sqrt[3]{n}$. Since in every such "cell" in average we have only one molecule, then the average distance between neighbor molecules is equal to the distance between "cell" centers, i.e.

$$l_s = 1/\sqrt[3]{n}$$







1.1. Introduction. Molecular description of gases

Example: The number of molecules in 1 cubic meter of an ideal gas (e.g., atmospheric air) at **standard conditions** (pressure 101325 Pa or 1 atm, temperature 273.15 K or 0° C) is called the **Loschmidt constant** and is equal to

$$n_L = 2.6868 \cdot 10^{25} \ \ 1/\mathrm{m}^3$$

Then the average distance between molecules is equal to $\bar{l} = 1/\sqrt[3]{n_L}$~3.3 nm $\gg \ d$.

Density parameter. Dilute and dense gases

Let's represent l_s in the form

$$l_s = \frac{1}{\sqrt[3]{n}} = \frac{d}{d\sqrt[3]{n}} = \frac{d}{\sqrt[3]{d^3 n}} = \frac{d}{\sqrt[3]{\epsilon}},$$

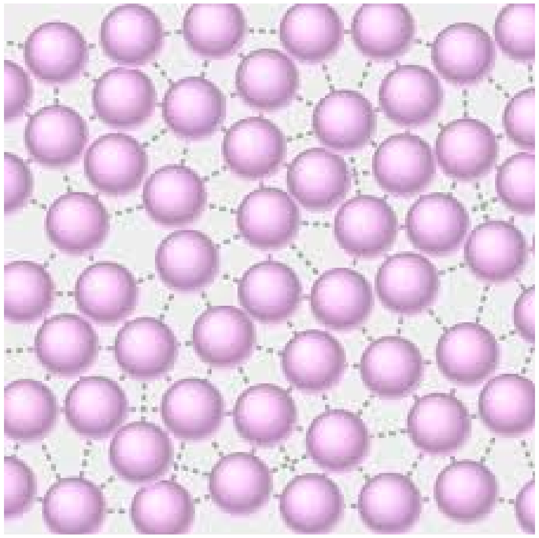
where $\epsilon = d^3 n$ is called the **density parameter**. The density parameter characterizes the volume occupied by molecules themselves. If every molecule is viewed as a sphere of diameter d, then the **volume fraction of molecules** (fraction of a unit volume occupied by molecules)

$$\alpha = \frac{\pi d^3}{6} n \sim \epsilon.$$

Dilute gas is a gas, where $\epsilon \ll 1$, i.e. the fraction of volume occupied by molecules is negligible compared to the volume occupied by the gas. In the dilute gas, distance between molecules l_s is much larger than the size of molecules d or length scale of collisions l_c, so that *at every particular time, the majority of molecules move without interaction with other molecules*. We will study the kinetic theory of only dilute gases.

1.1. Introduction. Molecular description of gases

It will be shown later on (see Section 1.4) that *in dilute gases, it is sufficient to account for only binary collisions between molecules*, while collective interactions between multiple molecules are so infrequent that they can be completely neglected.



Dense gas is a gas, where $\epsilon \sim 1$, and distance between molecules l_s is about the size of molecules d. Two major effects in dense gases:

- Smaller compressibility: The degree of compressibility is constrained by the volume fraction of molecules.
- Collective interactions between molecules: Every individual molecule interacts simultaneously with multiple surrounding molecules.

These effects make the dense gases similar to liquids. The dense gas is a "boundary" state of matter between "true" (dilute) gases and liquids.

At standard conditions in Earth's atmosphere,

$$\epsilon = d^3 n_L = (3.7 \cdot 10^{-10})^3 \times 2.6868 \cdot 10^{25} = 1.4 \cdot 10^{-3},$$

so that the atmospheric air can be considered as a dilute gas in the full range of pressures specific for Earth's atmosphere. However, if density increase in 10-100 time (up to pressure of 10-100 atm at temperature 0° C), then effects of the dense gas become important.

The kinetic theory is mostly successful in description of properties of dilute gases.

1.1. Introduction. Molecular description of gases

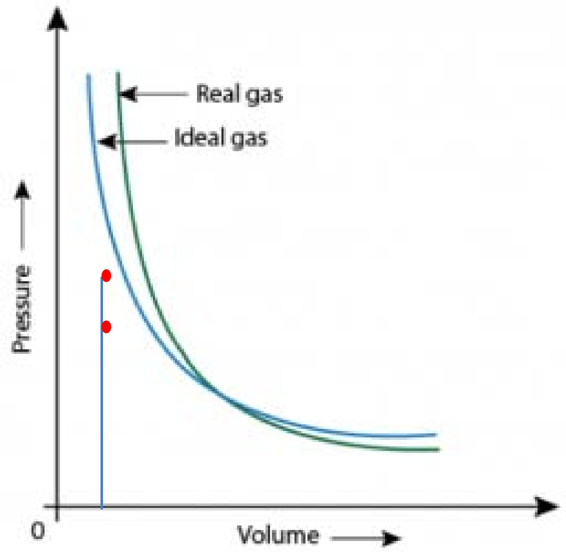
In thermodynamics, the model of an **ideal gas** corresponds to the model of dilute gas in the kinetic theory.

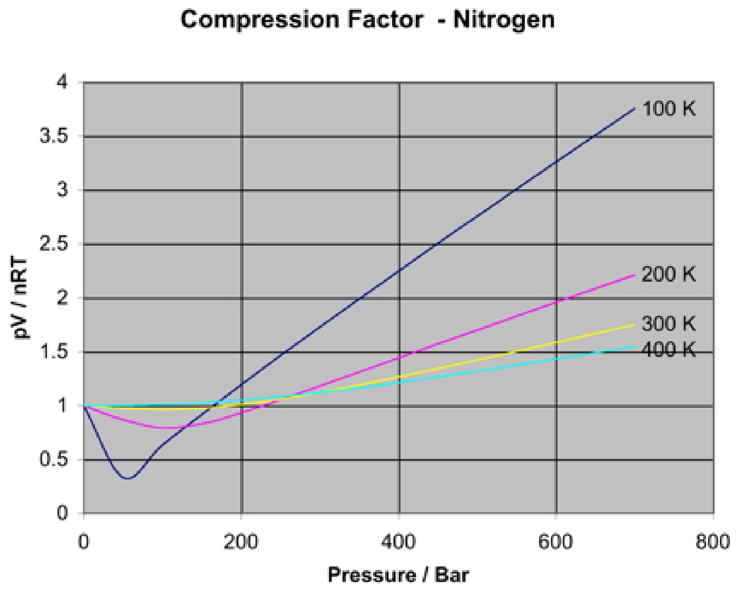
Any deviation from the ideal gas behavior is called the **real-gas effect**.

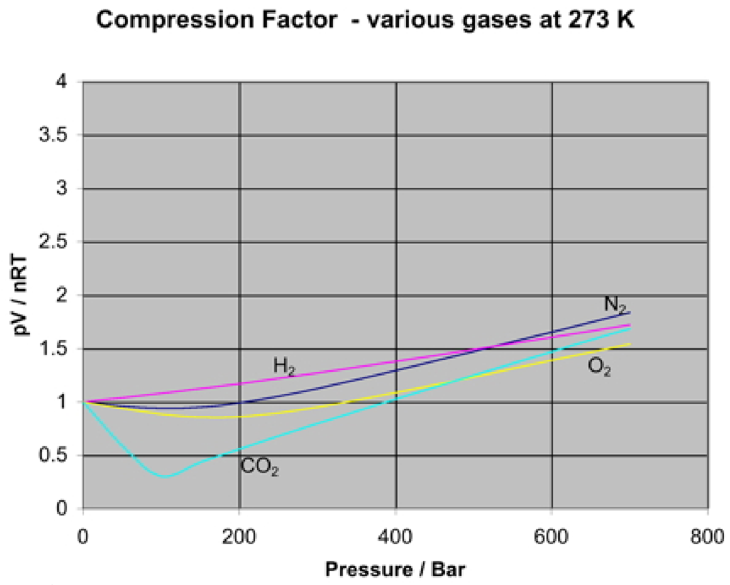
Real-gas effects exhibit themselves, in particular, in deviation from the ideal gas laws (see Section 1.3):

$$pV = Nk_BT = const \text{ at } N, T = const$$

(Here p, V, and N are the pressure, volume, and number of molecules, k_B is the Boltzmann constant). In real gases, pressure rises with decreasing V faster than it is predicted for the ideal gas.







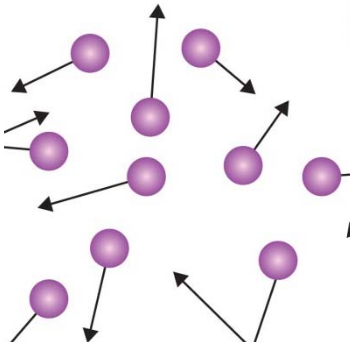
1 bar = 10^5 Pa ~ 1 atm

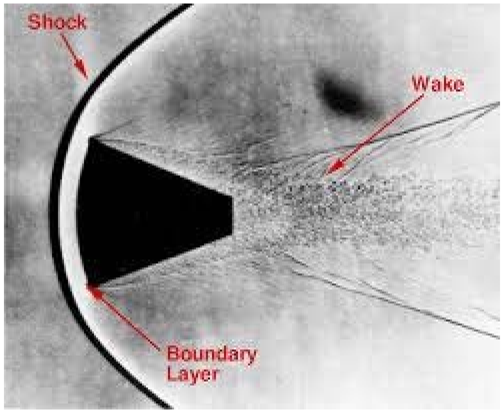
1.1. Introduction. Molecular description of gases

Purpose of the kinetic theory

Kinetic theory of gases is a part of statistical physics where *flows* of gases *are considered* on the molecular level and described in terms of changes of probabilities of various states of gas molecules in space and time *based on known laws of interaction between individual molecules*.

Input:
Law of interaction between molecules





Output:
Any flow property

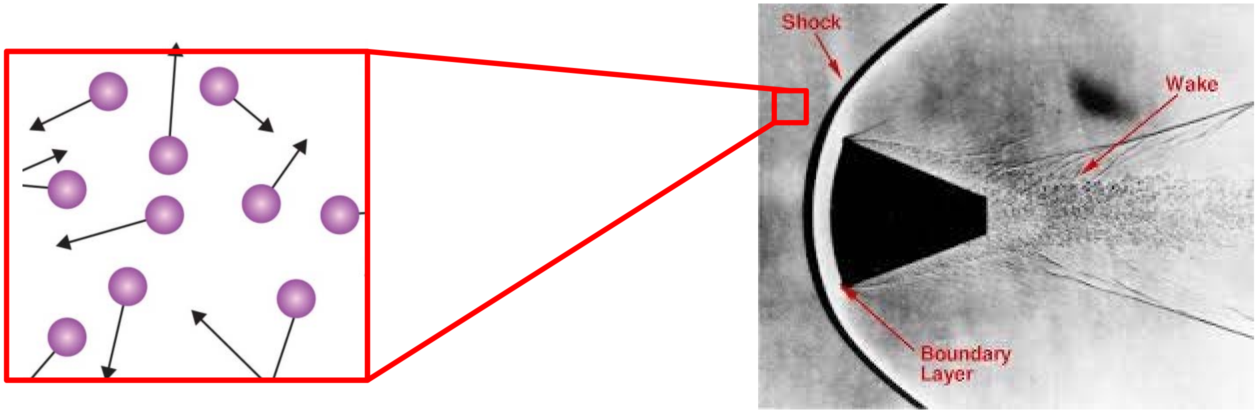
The major purpose of the kinetic theory is to derive mathematical description of a gas flow from a law of interaction between individual gas molecules.

- ➢ As a result, in kinetic theory, any gas property (e.g. viscosity) or parameter (e.g. pressure), is completely defined by physical parameters of intermolecular interaction law and parameters of motion of individual molecules (velocity, etc.).
- ➢ Kinetic theory itself, however, cannot predict the intermolecular interaction laws. These laws must be establish by the methods of quantum mechanics or experimentally.

1.1. Introduction. Molecular description of gases

Chaotic motion of molecules. Major approach of the kinetic theory

Kinetic theory of gases is a part of statistical physics where *flows* of gases *are* considered on the molecular level and *described in terms of changes of probabilities of various states of gas molecules* in space and time based on known laws of interaction between individual molecules.



Too many molecules

In the majority of practical problems, the number of individual molecules in gas flows is too large in order to trace every individual molecule.

Example: The number of molecules in 1 cubic meter of atmospheric air) at standard conditions

$$n_L = 2.6868 \cdot 10^{25}\ \ 1/\mathrm{m}^3.$$

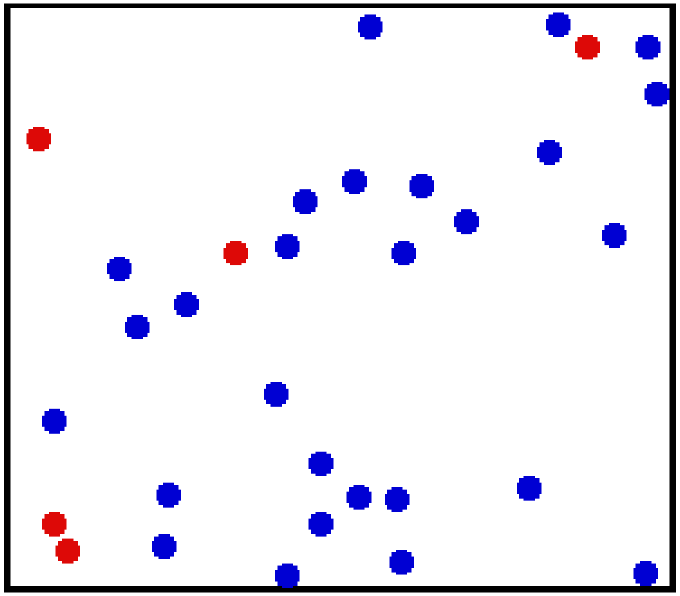
If we want to trace every molecule in such volume, then we need to store in computer memory $6 \times n_L$ real numbers (3 coordinates, 3 velocity component for every molecule) and to use

$$6 \times n_L \times 8\ \ 2^{30} \sim 10^{16}\ \mathrm{GByte}.$$

of computer memory. This is an unviable approach even in the very long run!

1.1. Introduction. Molecular description of gases

The major foundation of the kinetic theory is the well-established experimental fact that individual molecules in gases move chaotically, i.e. individual molecules in any small volume of a gas flow have vectors of velocity that are different from each other in magnitude and direction.



Chaotic motion of molecules is also called **thermal motion** since, as will see later on, temperature is a measure of magnitude of chaotic velocities of individual molecules

Then one can use the methods of mathematical theory of probability and statistics in order to study distributions of chaotic velocities of gas molecules without considering motion of all molecules composing a gas flow.

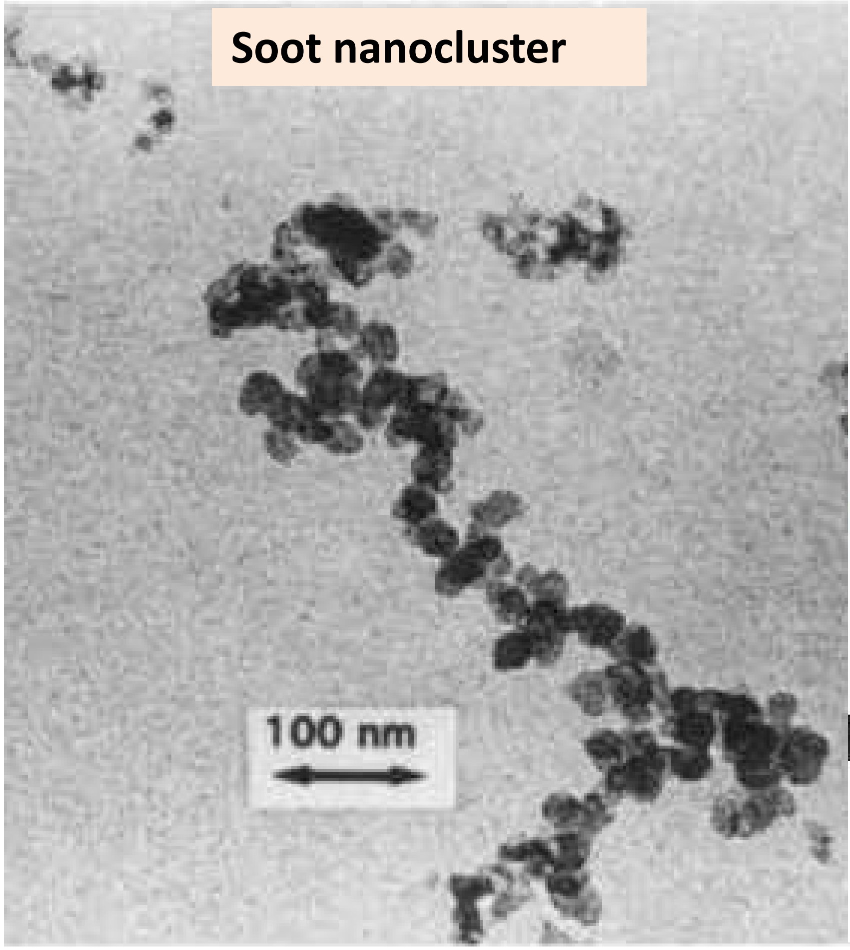
The major approach of the kinetic theory is to consider coordinates, velocities (and, may be other parameters describing internal motion of individual atoms within molecules) as random variables. Such statistical approach allows one to study systems composed of extremely large number of gas molecules N without explicit restrictions on N.

1.1. Introduction. Molecular description of gases

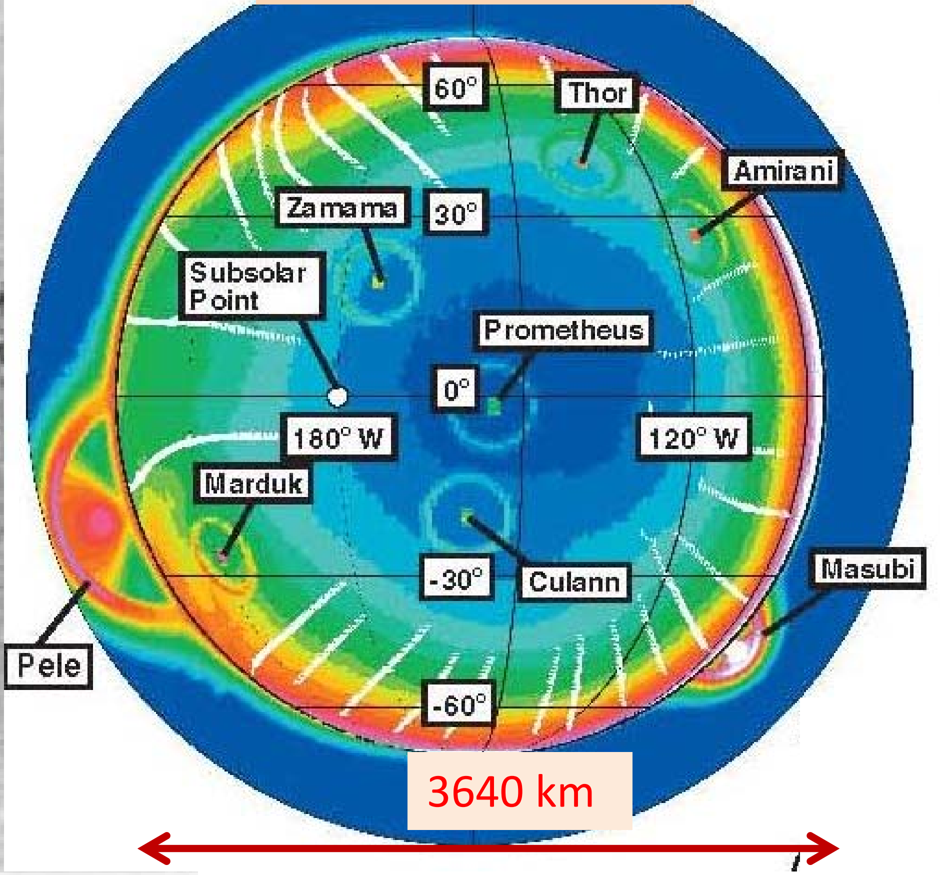
As a result,

- Kinetic theory has no intrinsic restrictions on the number of molecules in the flow and flow length scale.
- It can be used for problem from nano- to planetary scale.

Soot nanocluster



Atmosphere of Io

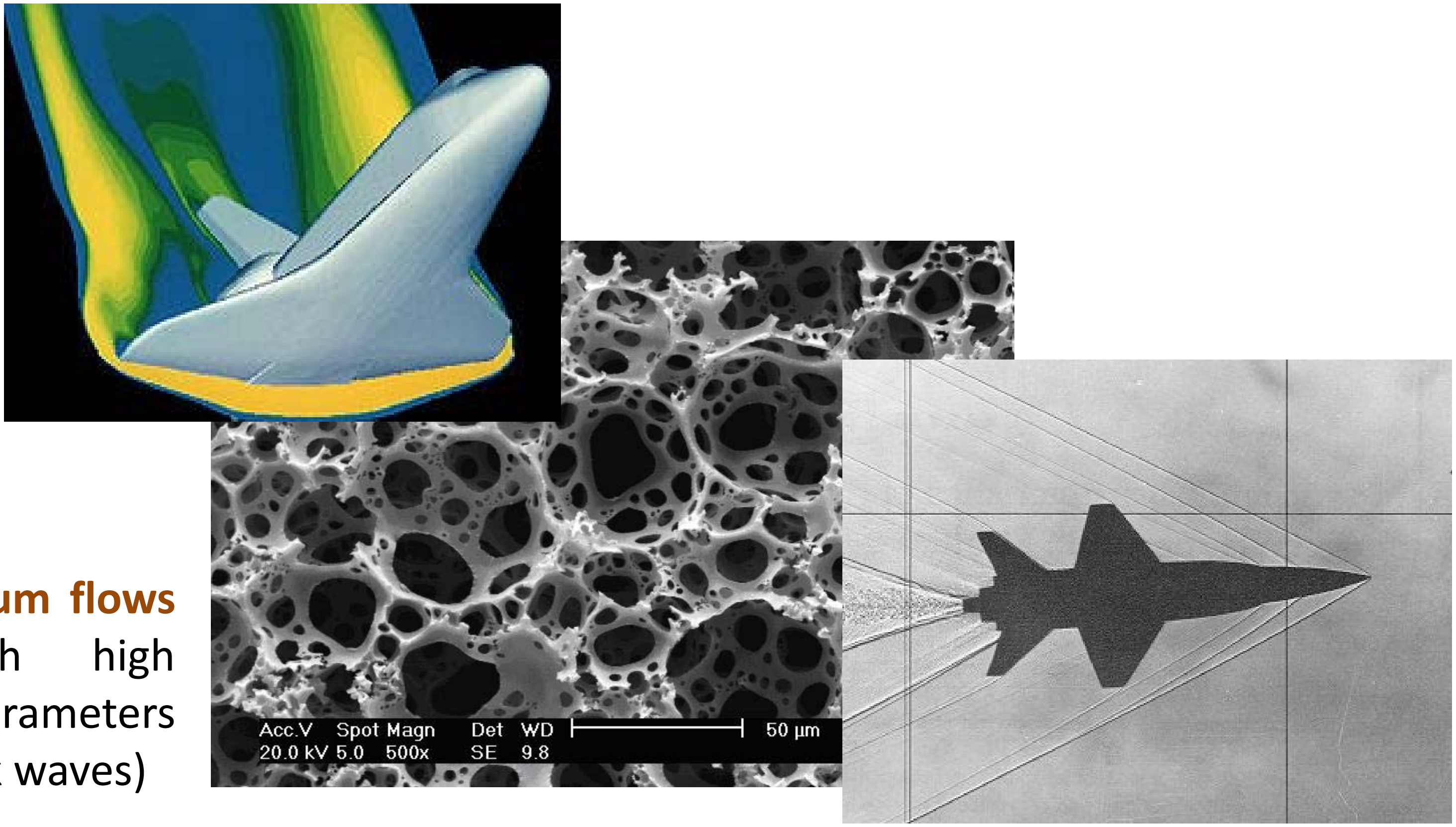


1.1. Introduction. Molecular description of gases

Specific goals of the kinetic theory

- To provide a kinetic foundation of the continuum gas dynamics, i.e. to derive gas dynamics equations from equations of motion of individual molecules
- To generalize continuum gas dynamics, i.e. to develop approaches for mathematical descriptions of gas flows in conditions when continuum gas dynamics is not applicable

Examples of conditions when the kinetic description of gas flows in required:



- **Low-density flow**
- **Small-scale flow**
- **Fast, non-equilibrium flows** and flows with high gradients of gas parameters (evaporation, shock waves)

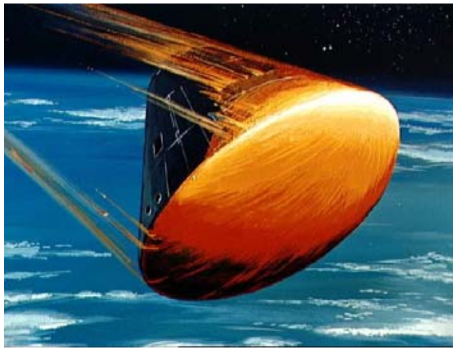
1.1. Introduction. Molecular description of gases

Applications of the kinetic theory of gases and RGD

- **Aerospace applications: Flows in upper atmosphere and in vacuum**

Satellites and spacecrafts
on LEO and in deep space

Re-entry vehicles in
upper atmosphere



Nozzles and jets
in space environment

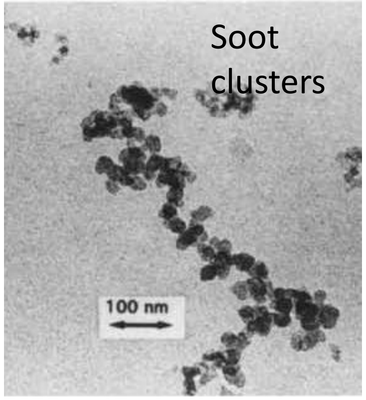
- **Vacuum devices, microchannels, microparticles and clusters**

Vacuum pumps,
vacuum chambers

Microelectronic devices
and MEMS

Microchannels

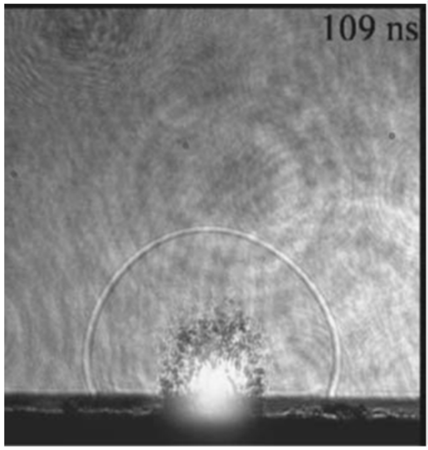
Microparticles
and clusters

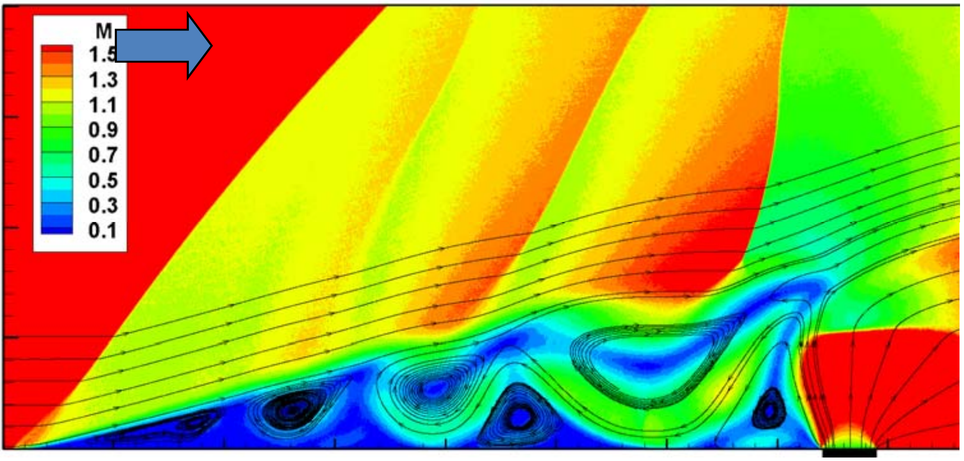


1.1. Introduction. Molecular description of gases

Applications of the kinetic theory of gases and RGD

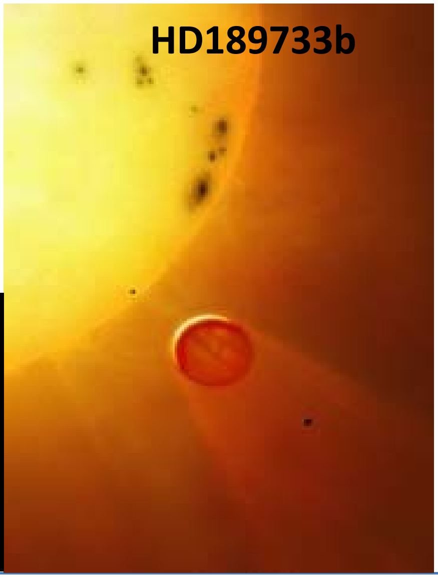
- **Fast, non-equilibrium gas flows (laser ablation, evaporation, vapor deposition)**



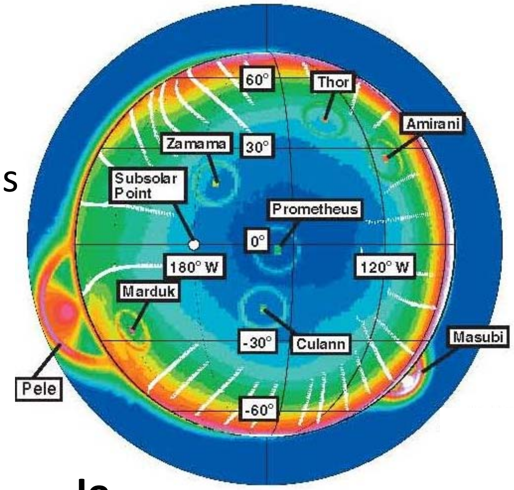


- **Natural phenomena in planetary science and astrophysics**

Dynamics of upper planetary atmospheres: Solar system, exoplanets

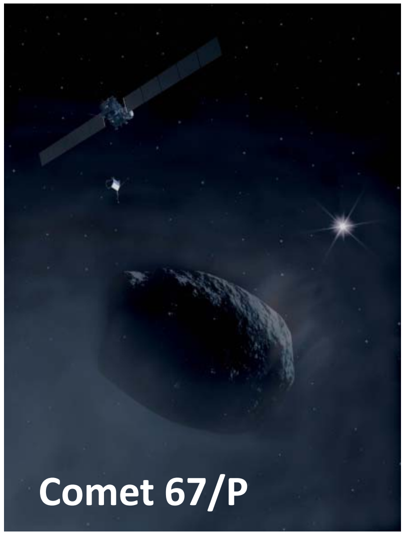


Global atmospheric evolution of distant bodies in the solar systems (Io, Enceladus, Pluto, etc.)



Io

Atmospheres of comets



1.2. Molecular quantities and macroscopic gas parameters

- Macroscopic gas parameters in continuum mechanics
- Molecular quantities
- Macroscopic gas parameters as volume-averaged molecular quantities
- Macroscopic gas velocity and velocity of chaotic motion of molecules
- Total and internal energies
- Restrictions of the continuity hypothesis

1.2. Molecular quantities and macroscopic gas parameters

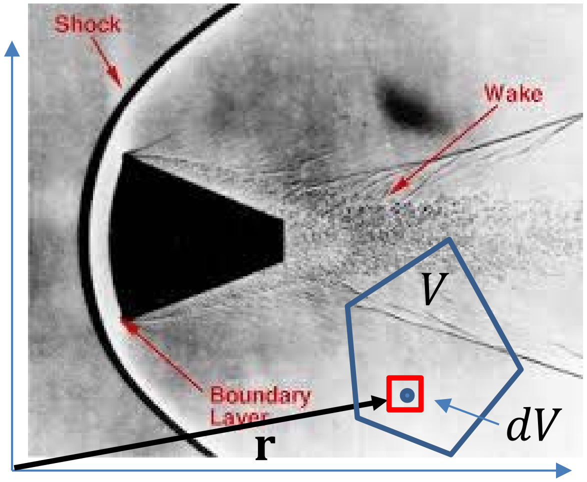
In Section 1.1 we discussed two major specific goals of the kinetic theory:

- To provide a kinetic foundation of the continuum gas dynamics, i.e. to derive gas dynamics equations from equations of motion of individual molecules
- To generalize continuum gas dynamics, i.e. to develop approaches for mathematical descriptions of gas flows in conditions when continuum gas dynamics is not applicable

In order to achieve these goals we, first of all, need to establish a relationship between physical quantities assigned to individual gas molecules and macroscopic gas parameters. Such parameters should have the same meaning as gas parameters in continuum mechanics.

Macroscopic gas parameters in continuum gas dynamics

In continuum gas dynamics, the molecular structure of a gas is neglected. The gas is viewed as a matter that is *continuously* distributed and fills the entire region of space it occupies. Various physical quantities associated with the this matter (**continuum**) are characterized by continuous fields of densities of mass, momentum, energy, etc.



$E(\mathbf{r},t)$, density of the energy in point $\mathbf{r}$, $[E]$ = J/m^{3};

$dE = E(\mathbf{r},t)dV$, gas energy in the infinitesimal volume around point $\mathbf{r}$;

The gas energy E_V in a finite volume V is equal to

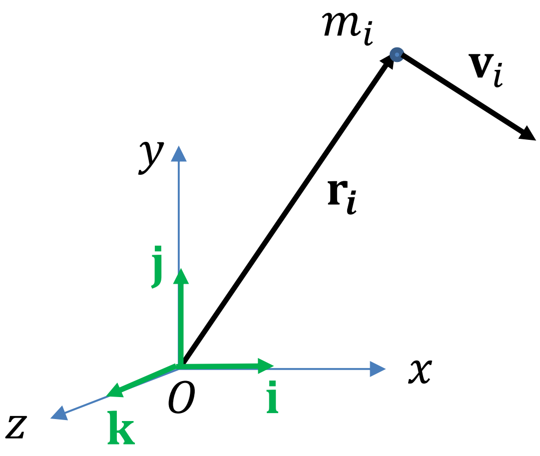
$$E_V(t) = \int_V E(\mathbf{r},t)dV \,.$$

1.2. Molecular quantities and macroscopic gas parameters

From the point of view of molecular structure of gases, any gas is a system of molecules. Then *any macroscopic gas quantity is a function of corresponding molecular quantities* associated with individual gas molecules. For example, the total energy of the gas in volume V is just a sum of energies of individual molecules.

Molecular quantities

Let's denote different molecules by the subscript i ($i = 1,2, \ldots$) and assume that every molecule is a point mass particle of mass m_i. The state of molecule i at time t is completely defined by its position vector $\mathbf{r}_i$ and velocity vector $\mathbf{v}_i$. We can also introduce a number of other physical quantities that are associated with molecule i.



$$\mathbf{r}_i = x_i\mathbf{i} + y_i\mathbf{j} + z_i\mathbf{k}$$

$$\mathbf{v}_i = v_{xi}\mathbf{i} + v_{yi}\mathbf{j} + v_{zi}\mathbf{k}$$

1, quantity that serves to count the number of molecules;

m_i, molecule mass;

$\mathbf{p}_i = m_i\mathbf{v}_i$, linear momentum of molecule;

$E_i = m_i\mathbf{v}_i^2/2$, translational (kinetic) energy of molecule;

$\mathbf{L}_i = m_i(\mathbf{r}_i \times \mathbf{v}_i)$, angular momentum of molecule;

Any such physical quantity $\Phi_i = \Phi_i(\mathbf{r}_i, \mathbf{v}_i, t)$ associated with an individual gas molecule is called the **molecular quantity**.

One can introduce many different molecular quantities, but the most important of them correspond to physical quantities that *conserve* their values in a **closed system** of molecules, i.e. a system, where molecules are not affected by any external force.

1.2. Molecular quantities and macroscopic gas parameters

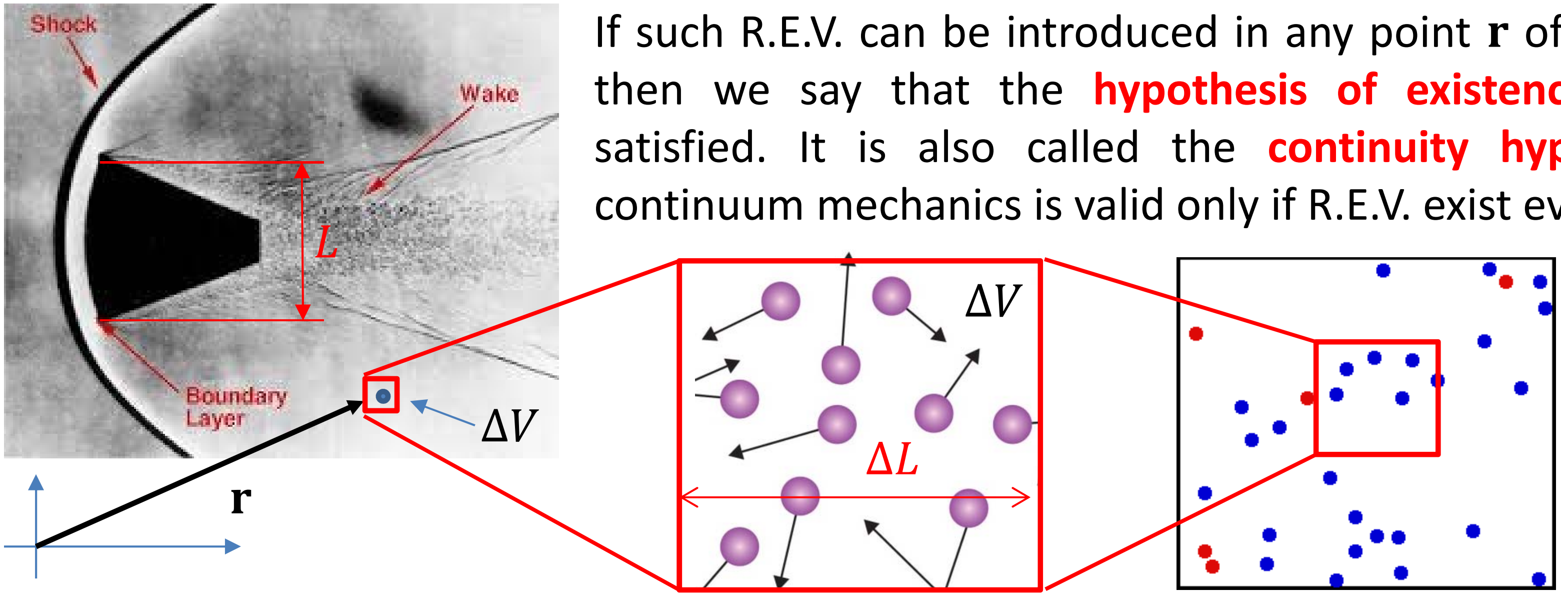
Representative elementary volume and continuity hypothesis

Macroscopic gas parameters (macroparameters) can be introduced as averaged values of corresponding individual molecular quantities. Their definition is based on the **hypothesis of existence of a representative elementary volume** (R.E.V.).

Representative elementary volume ΔV around some point in the flow is such a volume that

- Linear size of this volume ΔL is negligibly small compared to the flow length scale L, $\Delta L \ll L$, so that we can neglect inhomogeneity of the gas flow inside ΔV and mathematically consider ΔV as an infinitesimal volume.
- This volume contains very large number of molecules, $\Delta N \gg 1$, so that the total value of any physical quantity for the whole system of molecules inside this volume exhibit negligible fluctuations because of the chaotic motion of molecules.

If such R.E.V. can be introduced in any point $\mathbf{r}$ of the flow field, then we say that the **hypothesis of existence of R.E.V.** is satisfied. It is also called the **continuity hypothesis**, since continuum mechanics is valid only if R.E.V. exist everywhere.



1.2. Molecular quantities and macroscopic gas parameters

Macroscopic gas properties as volume-averaged molecular quantities

If R.E.V. exists in point $\mathbf{r}$, then we can introduce the macroscopic gas parameter $\overline{\Phi}$ of physical quantity Φ in this point as a volume-averaged value of corresponding molecular quantities $\Phi_i(\mathbf{r}_i, \mathbf{v}_i, t)$ for all molecules in R.E.V

(1.2.1) $$\overline{\Phi}(\mathbf{r}, t) = \frac{1}{\Delta N} \sum_{i=1}^{\Delta N} \Phi_i(\mathbf{r}_i, \mathbf{v}_i, t) \qquad [\overline{\Phi}] = [\Phi]$$

If $\Phi_i = 1$, then $\overline{\Phi} = \overline{1}$;

If $\Phi_i = m_i$, then $\overline{\Phi} = \overline{m_i}$ is the average mass of molecules;

If $\Phi_i = m_i \mathbf{v}_i$, then $\overline{\Phi} = \overline{m_i \mathbf{v}_i}$ is the average linear momentum of molecules;

If $\Phi_i = m_i \mathbf{v}_i^2/2$, then $\overline{\Phi} = \overline{m_i \mathbf{v}_i^2/2}$ is the average kinetic energy of molecules.

If the continuity hypothesis is satisfied then $\overline{\Phi}$ must have the following properties:

1. $\overline{\Phi}$ does not depend on the choice of the particular shape and size of R.E.V.

2. If we introduce a new molecular quantity, $\Psi_i = \overline{\Phi_i}(\mathbf{r}_i, t)$ then

(1.2.2) $$\overline{\Psi_i} = \overline{\overline{\Phi_i}} = \overline{\Phi_i}.$$

3. The averaging is a linear operation in a sense that, if we introduce a molecular quantity in the form of a linear combination, $a\Phi + b\Psi$, of quantifies Φ and Ψ, then $(a, b = const)$

(1.2.3) $$\overline{a\Phi + b\Psi} = a\overline{\Phi} + b\overline{\Psi}.$$

1.2. Molecular quantities and macroscopic gas parameters

In addition to $\overline{\Phi}$, we can define the **density of physical quantity** per unit volume

(1.2.4) $$\overline{\Phi_V}(\mathbf{r},t) = \frac{1}{\Delta V}\sum_{i=1}^{\Delta N}\Phi_i(\mathbf{r}_i,\mathbf{v}_i,t) = \frac{\Delta N}{\Delta V}\overline{\Phi}(\mathbf{r},t)\,, \qquad [\overline{\Phi_V}] = \frac{[\Phi]}{m^3}$$

and **specific gas macroscopic parameter**, i.e. physical quantity per unit mass

(1.2.5) $$\overline{\Phi_M}(\mathbf{r},t) = \frac{1}{\Delta M}\sum_{i=1}^{\Delta N}\Phi_i(\mathbf{r}_i,\mathbf{v}_i,t) = \frac{\Delta V}{\Delta M}\overline{\Phi_V}(\mathbf{r},t)\,, \qquad [\overline{\Phi_M}] = \frac{[\Phi]}{kg}$$

where

$$\Delta M = \sum_{i=1}^{\Delta N} m_i$$

is the total mass of molecules in R.E.V.

If $\Phi_i = 1$, then $\overline{\Phi_V} = n$ is the gas **number density** (number of molecules in a unit volume);

If $\Phi_i = m_i$, then $\overline{\Phi_V} = \rho$ is the gas **mass density** (mass of molecules in a unit volume);
If $\Phi_i = m_i\mathbf{v}_i^2/2$, then $\overline{\Phi_M} = e_{tot}$ is the gas **specific translational energy** (total kinetic energy of molecules per unit mass).
Since $n = \Delta N/\Delta V$ and $\rho = \Delta M/\Delta V$, there is a simple relationship between three types of macroscopic parameters (per unit molecule, per unit volume, and per unit mass):

(1.2.6) $$\overline{\Phi_V}(\mathbf{r},t) = n\overline{\Phi}(\mathbf{r},t) = \rho\overline{\Phi_M}(\mathbf{r},t).$$

1.2. Molecular quantities and macroscopic gas parameters

Macroscopic gas velocity and velocity of chaotic motion of molecules

Macroscopic gas velocity (bulk velocity) $\mathbf{u}$ is the center-of-mass velocity of molecules in R.E.V.

(1.2.7)
$$\mathbf{u}(\mathbf{r},t) = \frac{1}{\Delta M}\sum_{i=1}^{\Delta N} m_i \mathbf{v}_i = \frac{\overline{(\mathbf{v}_i m_i)_V}}{\rho} = \frac{\overline{m_i \mathbf{v}_i}}{\overline{m_i}}.$$

Gas velocity can be also viewed as the gas specific linear momentum.

If all molecules have the same mass, then $\mathbf{u}$ is the average velocity of molecules in R.E.V.:

(1.2.8)
$$\mathbf{u}(\mathbf{r},t) = \frac{1}{m\Delta N}\sum_{i=1}^{\Delta N} m \mathbf{v}_i = \frac{\overline{(\mathbf{v}_i)_V}}{n} = \bar{\mathbf{v}}_i.$$

Velocity $\mathbf{c}_i$ of chaotic motion of molecule i is the velocity of the molecule with respect to center-of mass velocity or gas velocity in the point where the molecule is located:

(1.2.9)
$$\mathbf{c}_i = \mathbf{v}_i - \mathbf{u}(\mathbf{r}_i, t).$$

The chaotic velocity is defined by $\mathbf{v}_i$, $\mathbf{r}_i$, and t.

The mean square velocity C, where $C^2 = \overline{(\mathbf{c}_i)^2}$, is called the **gas thermal velocity** and used as a numerical measure of chaotic motion. For a gas of identical molecules ($m_i = m = const$),

$$C^2 = \overline{(\mathbf{v}_i - \mathbf{u})^2} = \overline{(\mathbf{v}_i)^2 - 2\mathbf{v}_i \cdot \mathbf{u} + \mathbf{u}^2} = \overline{(\mathbf{v}_i)^2 - 2\mathbf{v}_i \cdot \bar{\mathbf{v}}_i + \bar{\mathbf{v}}_i{}^2} = \overline{(\mathbf{v}_i)^2} - 2\bar{\mathbf{v}}_i \cdot \bar{\bar{\mathbf{v}}}_i + (\bar{\bar{\mathbf{v}}}_i)^2$$

or

(1.2.10)
$$C^2 = \overline{(\mathbf{v}_i)^2} - \mathbf{u}^2.$$

Here we use properties given by Eqs. (1.2.2) and (1.2.3).

1.2. Molecular quantities and macroscopic gas parameters

Total and internal energies

The total translational energy of a gas is the sum of kinetic energies of its molecules. **The specific total translational energy** e_{tot} and **density of total translational energy** E_{tot} are

(1.2.11) $$e_{tot}(\mathbf{r},t) = \frac{1}{\Delta M}\sum_{i=1}^{\Delta N}\frac{m_i \mathbf{v}_i{}^2}{2}, \qquad E_{tot}(\mathbf{r},t) = \frac{1}{\Delta V}\sum_{i=1}^{\Delta N}\frac{m_i \mathbf{v}_i{}^2}{2} = \rho e_{tot}.$$

The internal or **thermal energy** of a monatomic gas is the kinetic energy of chaotic or thermal motion of molecules. **The specific internal energy** e is the internal energy of a unit mass and **density of the internal energy** E is the internal energy of unit volume:

(1.2.12) $$e(\mathbf{r},t) = \frac{1}{\Delta M}\sum_{i=1}^{\Delta N}\frac{m_i(\mathbf{v}_i-\mathbf{u})^2}{2}, \qquad E(\mathbf{r},t) = \frac{1}{\Delta V}\sum_{i=1}^{\Delta N}\frac{m_i(\mathbf{v}_i-\mathbf{u})^2}{2} = \rho e.$$

In the case of molecules of the identical mass, $m_i = m = const$:

(1.2.13) $$e(\mathbf{r},t) = \frac{1}{m\Delta N}\frac{m}{2}\sum_{i=1}^{\Delta N}\frac{(\mathbf{v}_i-\mathbf{u})^2}{2} = \frac{\overline{(\mathbf{v}_i-\mathbf{u})^2}}{2} = \frac{C^2}{2}, \qquad E(\mathbf{r},t) = mne = n\frac{mC^2}{2},$$

and, if we use Eq. (1.2.10),

(1.2.14) $$e_{tot} = e + \frac{\mathbf{u}^2}{2}, \qquad E_{tot} = E + \frac{\rho\mathbf{u}^2}{2}.$$

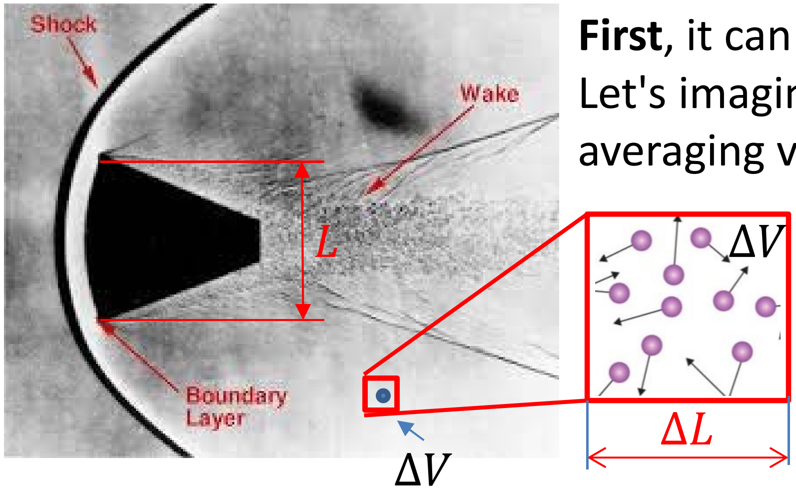
Thus, total specific energy is the sum of the specific internal energy and kinetic energy $\mathbf{u}^2/2$ of the gas macroscopic motion per unit mass.

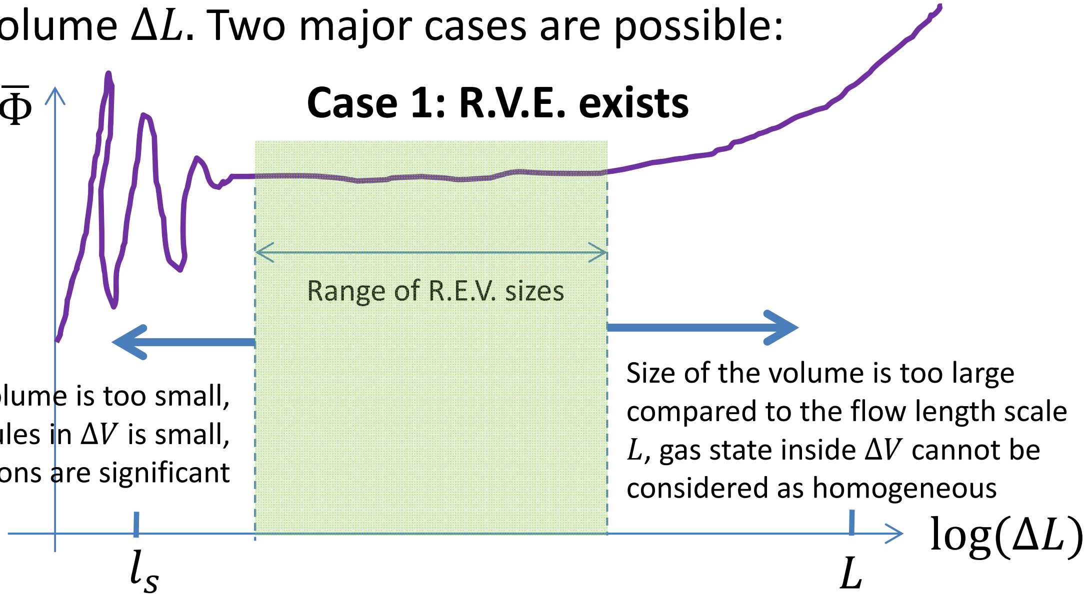
1.2. Molecular quantities and macroscopic gas parameters

Restrictions of the continuity hypothesis

The definition of macroparameters as volume-averaged quantities has two major drawbacks:

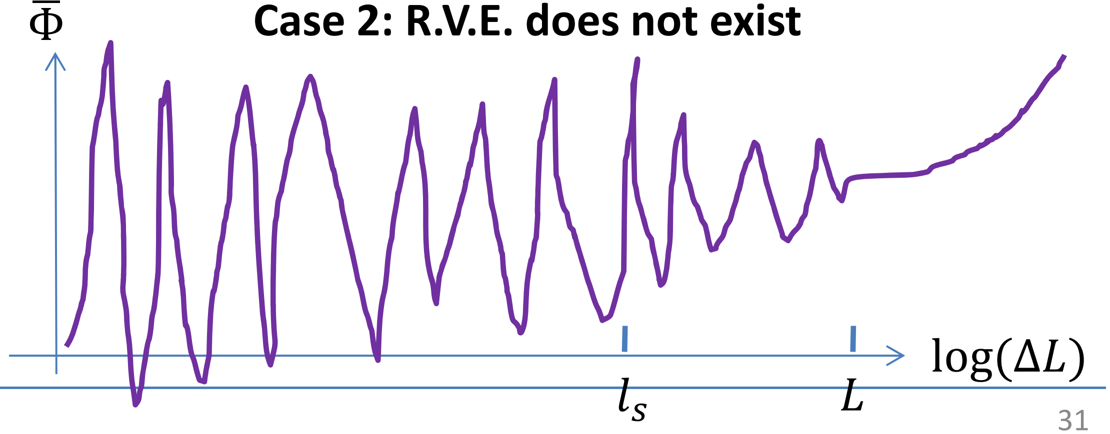
First, it can be applied only if the continuity hypothesis is satisfied. Let's imagine what can happen to $\bar{\Phi}$ when we vary the size of averaging volume ΔL. Two major cases are possible:





Size of the volume is too small, number of molecules in ΔV is small, fluctuations are significant

Size of the volume is too large compared to the flow length scale L, gas state inside ΔV cannot be considered as homogeneous



Transition from case 1 to case 2 occurs if we gradually decrease the number density of molecules (and increase l_s), i.e. if we consider more and more rarefied gas flows. Thus, *the continuity hypothesis and our definition of $\bar{\Phi}$ fail in rarefied gas flows, which is the major subject of the kinetic theory.*

1.2. Molecular quantities and macroscopic gas parameters

Second, the definition of $\overline{\Phi}$ in the form of Eq. (1.2.1) can be used for real calculations only if we know position vectors $\mathbf{r}_i$, velocities $\mathbf{v}_i$, and quantities $\Phi_i(\mathbf{r}_i, \mathbf{v}_i, t)$ for all molecules in the gas flow.

The definition of macroscopic gas parameters given in this section is well-suited, e.g., for **atomistic** (**molecular dynamics**) **simulations** of matter (including gases), where positions and velocities of all atoms are explicitly tracked by solving equation of motions for every atom in the system.

In applications of the kinetic theory, the number of gas molecules is so huge that we cannot trace all of them. Later on, an alternative, kinetic (statistical) definition of macroscopic gas parameters will be given (Section 3.2). Eq. (1.3.1), however, will be in agreement with that new definition in the case when the continuity hypothesis is satisfied.

1.3. Gas laws

- Ideal gas equation of state
- Equation of state of calorically perfect gas
- Assumptions of elementary kinetic theory
- Kinetic foundation of the ideal gas equation of state
- Kinetic foundation of the equation of state of a calorically perfect gas
- Kinetic definition of gas temperature
- Brownian motion
- Equipartition of energy

1.3. Gas laws

Ideal gas equation of state

Physicists of XVIII century (Boyle, Charles, Gay-Lussac, Avogadro, etc) experimentally established a number of **gas laws**, i.e. relationships between basic thermodynamic gas parameters such as mass M, volume V, number density n, mass density ρ, pressure p, and **absolute thermodynamic temperature** T. Many of these laws can be reduced to a single equation

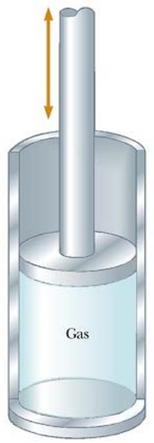
(1.3.1) $$\frac{p}{\rho T} = R = \frac{\bar{R}}{\mu_A} = const$$

where gas-specific constant R is called the **gas constant,** $\bar{R} = 8.3144598$ J/mol/K is the **universal gas constant**, and μ_A is the molar mass. All parameters in the left-hand side of Eq. (1.3.1) can be directly measured: $\rho = M/V$ (M is the mass of the gas, V is the occupied volume) with scale, p with manometer, and T with thermometer. Then the gas constant R can be determined from experiment, [R]=J/kg/K. The molar mass can be established without knowing molecule mass m and Avogadro constant in chemistry by measuring the relative masses of species that participate in chemical reactions. Then one can find value of $\bar{R}$.

Although initially Eq. (1.3.1) was established for particular processes like compression of a fixed mass of a gas ($M = const$) in a cylinder, it was found that *this equation holds for any process*, where pressure and temperature vary within "reasonable" ranges. Therefore, this equation, often re-written in the form

(1.3.2) $$p = \rho R T,$$

is called the gas **equation of state** (**EOS**) or **Clapeyron equation**. A gas, whose thermodynamic parameters satisfy the Clapeyron equation, is called the **ideal gas**.



1.3. Gas laws

Equation of state of calorically perfect gas

Another series of experiments resulted in the relationship between the **specific internal energy** u of the gas and its temperature T

(1.3.3)
$$\frac{e}{T} = c_V = const.$$

where the gas-specific constant c_V is called the **gas specific heat at fixed volume**, $[c_V]$=J/kg/K. Absolute value of e in Eq. (1.3.3) can not be directly measured, but the change of u in, e.g., **adiabatic process** $(dQ = 0)$ can be measured through the work performed by the gas using the first law of thermodynamics,

$$dQ = de + pdV = 0\,,$$

i.e. $de = -pdV$ and

$$c_V = \frac{de}{dT} = -p\frac{dV}{dT}.$$

In the right-hand side of the last equation, all quantities (p, dV, and dT) can be directly measured experimentally. Similarly to Eq. (1.3.1), it was shown that *Eq. (1.3.3) holds for any process*, where pressure and temperature vary within "reasonable" ranges. Therefore, this equation, often re-written in the form

(1.3.4)
$$e = c_V T,$$

is called the gas **equation of state**. The gas, whose thermodynamic parameters satisfy Eq. (1.3.4), is called **calorically perfect**.

1.3. Gas laws

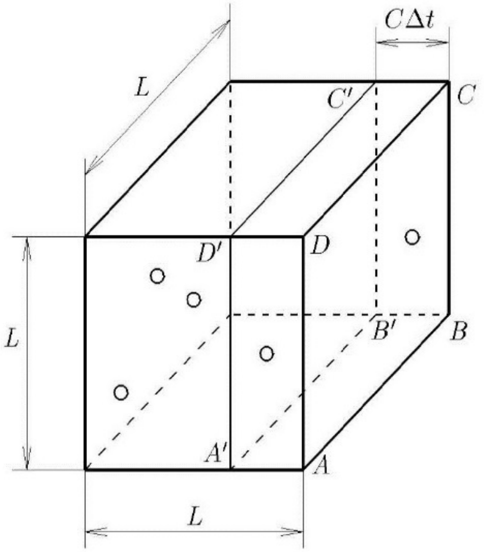
The **model of ideal and thermodynamically perfect gas** is the model of gas, whose thermodynamic parameters satisfy two equations of state, (1.3.2) and (1.3.4). It is quite often, e.g., in gas dynamics, that the *ideal and thermodynamically perfect gas is shortly called the ideal gas*. For example, the closed system of Euler equations is usually obtained in gas dynamics specifically for the gas satisfying both Eqs. (1.3.2) and (1.3.4).

Equations of state are used in thermodynamics as *empirical*, i.e. established in experiments. Our goal is to show that these equations can be derived theoretically based on the assumptions of the molecular structure of a gas and chaotic motion of gas molecules. In addition, we will establish a relationship between temperature and thermal velocity of individual molecules.

Assumptions of elementary kinetic theory

For derivations, we will use only an elementary approach based on the following assumptions:

1. We will consider a volume (vessel) V occupied by a *dilute* **homogeneous** gas, where there is no gradients of macroscopic parameters and macroscopic parameters are the same in any point of volume V. For simplicity we consider a vessel in the form a cube of size L, $V = L^3$ containing N molecules at number density $n = N/V$.
2. Every gas molecule is a "billiard" ball of diameter d without internal structure. Position of a molecule can be described by 3 Cartesian coordinates, i.e. a molecule has 3 **translational degrees of freedom**.



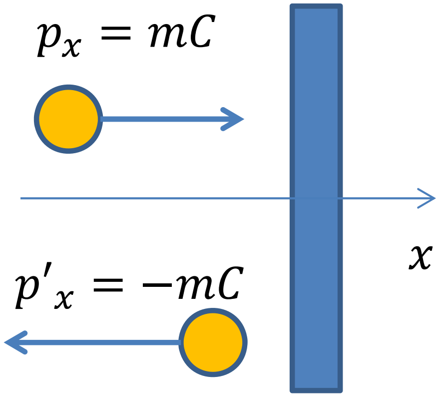
1.3. Gas laws

3. Gas in volume V is kept under fixed external conditions (e.g., fixed temperature of the vessel wall) for very long time. It is known from thermodynamics that in this case the gas reaches an **equilibrium state**, which does not change unless external conditions change (e.g., change of the wall temperature or volume). We consider only the equilibrium state.
4. We will assume that the vessel is at rest, i.e. macroscopic gas velocity is zero, and, thus, chaotic velocity of every molecule $\mathbf{c}_i$ is equal to its velocity in an inertial framework, $\mathbf{c}_i = \mathbf{v}_i$.
5. We will not account for the real distribution of chaotic velocities of individual molecules. We will assume that that all molecules moves with the same averaged thermal velocity $|\mathbf{c}_i| = C$ and $N/6$ molecules at every time move toward any of 6 faces of cubic volume V.

The theory that can be derived based on these assumptions is called **elementary kinetic theory**.

Kinetic foundation of the ideal gas equation of state

Let F be the force exerted on any face of vessel along normal to the face. **Pressure** p is force exerted on a unit area, i.e. $p = F/S = F/L^2$. Force F appeares because individual molecules rebound from the face and exchange the momentum with the vessel. If gas and vessel are in equilibrium, then absolute value of average velocity of a molecule before and after the impact is the same. The only result of interaction is the change of velocity direction to the opposite one. If before the impact the molecule moves with momentum mC towards a wall, then after the "reflection", the molecule has momentum $-mC$. During the impact the molecule transfers momentum Δp_1 to the wall.



$$\Delta p_1 = mC - (-mC) = 2mC$$

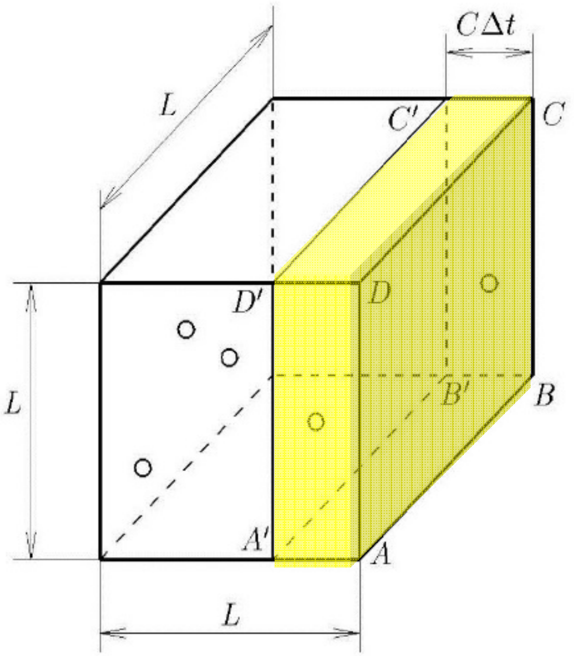
1.3. Gas laws

Now let's consider the forces F exerted on the face $ABCD$.

In order to find F let's consider some interval of time Δt and determine how many molecules ΔN interact with the face $ABCD$ during this time. Such molecules must be located in the layer $ABCDA'B'C'D'$ of thickness $C\Delta t$ and volume $\Delta V = C\Delta t L^2$ and move towards the wall, otherwise they will not reach the wall during Δt . Then $\Delta N = (1/6) n \Delta V$.

The total momentum transferred to the wall during Δt is equal to

$$\Delta P = \Delta N \cdot \Delta p_1 = \left(\frac{1}{6} n C \Delta t L^2\right) \cdot (2mC) = \frac{1}{3} nmC^2 \Delta t L^2$$



According to Newton's second law of motion, force is the rate of change of momentum, $F = \Delta P/\Delta t$, and the pressure is the equal to ($\rho = mn$)

(1.3.5)
$$p = \frac{\Delta P}{\Delta t L^2} = \rho \frac{C^2}{3}$$

Let's compare Eq. (1.3.5) with the ideal gas EOS: These equations coincide if we assume that the thermodynamic temperature is defined by the average chaotic velocity of molecules as

(1.3.6)
$$RT = \frac{C^2}{3} \quad \text{or} \quad \frac{mRT}{2} = \frac{mC^2/2}{3}$$

1.3. Gas laws

Kinetic foundation of the equation of state of a calorically perfect gas

If gas is dilute, then collisions between molecules are instant events and the number of interacting molecules an any particular time is negligibly small, so we can neglect contribution of the potential energy of interaction between gas molecules to the total gas energy. Then the total internal energy of gas in volume V is the sum of kinetic energies of individual molecules $mC^2/2$. Then the specific internal energy (per unit mass) is equal to

(1.3.7) $$e = \frac{N(mC^2/2)}{mN} = \frac{C^2}{2}.$$

Eq. (1.3.7) coincides with the EOS of calorically perfect gas (1.3.4) if

(1.3.8) $$c_V T = \frac{C^2}{2} \quad \text{or} \quad \frac{m c_V T}{3} = \frac{mC^2/2}{3}.$$

Eqs. (1.3.6) and (1.3.8) result in

$$c_V = \frac{3}{2} R,$$

equation which is known from thermodynamics.

Thus, we see that both EOSs can be explained from the point of view of molecular structure of gases if we assume that *the gas temperature is a measure of averaged kinetic energy of chaotic motion of individual gas molecules*.

1.3. Gas laws

Kinetic definition of gas temperature

In order to make the final step towards the kinetic definition of temperature let's use the relationship between the gas constant and universal gas constant given by Eq. (1.3.1): $R = \bar{R}/\mu_A$. Then Eq. (1.3.6) reduces to

(1.3.9)
$$\frac{(\bar{R}/N_A)T}{2} = \frac{mC^2/2}{3}.$$

The new *universal* constant

(1.3.10)
$$k_B = \frac{\bar{R}}{N_A} = 1.38064852 \times 10^{-23} \ \frac{\mathrm{J}}{\mathrm{K}}$$

is called the **Boltzmann constant**. With the Boltzmann constant, Eq. (1.3.9) can be re-written as

(1.3.11)
$$\frac{k_B T}{2} = \frac{1}{3}\frac{mC^2}{2},$$

i.e. absolute thermodynamic temperature is such a measure of chaotic motion of molecules that $k_B T/2$ is equal to the average energy of chaotic motion of a single molecule per one **degree of freedom**. This is the kinetic definition of temperature.

This definition is very general: In statistical physics, *for any system in the equilibrium state*, temperature is defined as such parameter that $k_B T/2$ is equal to the average energy of chaotic motion of a single molecule per one degree of freedom.

1.3. Gas laws

With the Boltzmann constant, the gas constant can be defined as

$$R = \frac{\bar{R}}{\mu_A} = \frac{k_B N_A}{m N_A} = \frac{k_B}{m},$$

and the EOSs of ideal and calorically perfect gas can be re-written as follows

(1.3.11) $$p = \rho R T = m n \frac{k_B}{m} T \quad \text{or} \quad p = n k_B T,$$

(1.3.12) $$e = \frac{3}{2} R T = \frac{3}{2} \frac{k_B}{m} T,$$

or, for the internal gas energy per molecule $e_1 = me$,

(1.3.13) $$e_1 = \frac{3}{2} k_B T.$$

Thus, the heat capacity of gas per unit molecule at constant volume is equal to $(3/2)k_B$. It means that $k_B/2$ is equal to the heat capacity of the gas per one degree of freedom of gas molecule.

The Boltzmann constant can be also considered as a scaling coefficient appeared in Eq. (1.3.11) because we used independent units to measure energy and temperature, that is why $[k_B]$ = J/K.

The Boltzmann constant establishes a proportionality between energy and temperature.

1.3. Gas laws

Equipartition of energy

In statistical physics, an **equipartition theorem** is formulated and proven. This theorem implies that, for any physical system in the equilibrium state, the energy is equally distributed between all degrees of freedom in this system, so that $k_B T/2$ is equal to the average energy of *any* degree of freedom. Then, Eq. (1.3.11) for an equilibrium system with energy E and N degrees of freedom can be re-written as follows:

(1.3.14)
$$\frac{k_B T}{2} = \frac{E}{N}.$$

If we consider a gas at equilibrium in a unit volume with number density n, then $N = 3n$ (every molecule has 3 translational degrees of freedom) and $E = n(mC^2/2)$, so that Eq. (1.3.14) reduces to Eq. (1.3.11).

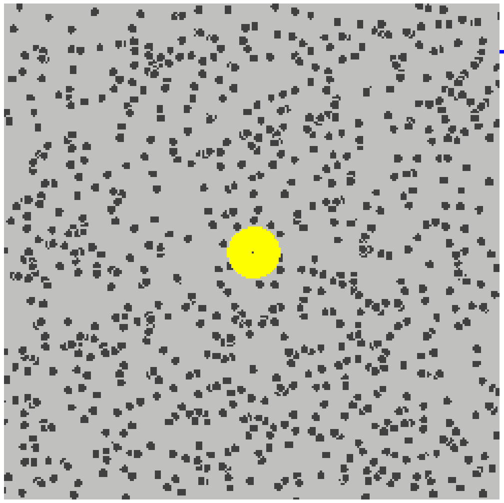
The equipartition theorem highlights the fact that, in both thermodynamics and statistical physics, temperature is a quantity that characterizes, strictly speaking, only equilibrium states. In non-equilibrium states, the temperature T can be introduced formally using Eqs. (1.3.11) or (1.3.14) as a measure of the internal energy, but different degrees of freedom have different average energies, and these energies are not characterized by T.

Differences between energies of individual degrees of freedom, e.g., corresponding to the translational motion of molecules in x, y, and z directions, can be used as measures of degree of non-equilibrium in gas flows (see Section 6.6).

1.3. Gas laws

Brownian motion

The Boltzmann constant was first introduced by Max Plank in 1900-1901. He also predicted the value of k_B using the **law of the blackbody radiation**. It was interesting, however, to measure k_B directly based on the chaotic motion of molecules. The Boltzmann constant can be easily defined only if we know N_A, but experimental determination of N_A is also very difficult, since we need to either count huge number of molecules or accurately define the molecule mass. For the first time, French physicist Jean Perrin measured k_B in 1908 by observing motion of Brownian particles and comparing observations with predictions of the kinetic theory.



See experimental video: Brownian motion of particles in water

Brownian motion is the chaotic (random) motion of small dust particles in gases and liquids. It was first observed by English botanist Robert Brown in 1827. The explanation of the Brownian motion is in the chaotic motion of surrounding molecules of liquid or gas. Variation of velocity of a Brownian particles is induced by impacts of individual gas molecules. Thus, *Brownian motion provided experimental evidences of two major hypothesis of kinetic theory: molecular structure and chaotic motion of molecules*.

The kinetic theory of the Brownian motion was developed by Albert Einstein (1905) and Marian Smoluchowski (1906). It predicts that the average displacement of a Brownian particle depends on its mass, gas temperature, and the Boltzmann constant. Jean Perrin experimentally confirmed this theory and found value of k_B . It was possible because the mass of a Brownian particle is much larger than the mass of individual molecule and could be directly measured.

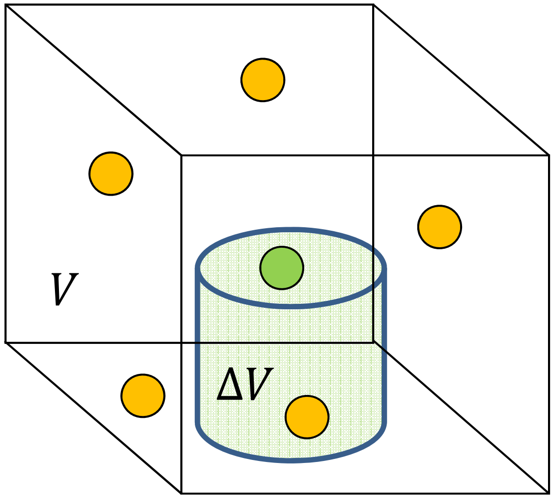
1.4. Collision frequency. Free molecular, transitional, and continuum flow regimes

- Homogeneous random distribution of molecules in space (in a volume)
- Probabilities of collisions with participation of various number of particles
- Collision frequency and mean free time
- Equilibrium and relaxation
- Knudsen number. Free molecular, transitional, and continuum flow regimes
- Local Knudsen number
- Local equilibrium. Summary on the length scales in dilute and dense gases

1.4. Collision frequency. Free molecular, transitional, and continuum flow regimes

The goal of the present section is to introduce major quantities characterizing the rate of collisions between molecules and to make conclusions on the effect of intermolecular collisions under various flow conditions. The first question is: Do we need to consider collective interactions between molecules or it is sufficient to take into account only binary collisions? To answer this question we need to study random distributions of molecules in space.

Homogeneous random distribution of molecules in space (in a volume)



Let's consider a volume V filled with N gas molecules at number density $n = N/V$, choose a subvolume of size ΔV inside V, and fix one (green) molecule. Since molecules move chaotically, we can observe the green molecule sometimes inside ΔV, sometimes outside. Let's assume that we determine position of our molecule with respect to ΔV K times ($K \gg 1$) and found that it was inside $K(\Delta V)$ times. Then the quantity

$$P_1 = P_1(\Delta V) = \lim_{K \to \infty} \frac{K(\Delta V)}{K}$$

is called the **probability** to find our green molecule inside ΔV. Any probability P of a random event is relative frequency of occurrence of this even among all possible outcomes ($0 \le P \le 1$). We say that molecules are distributed inside V **with equal probability** (or **homogeneously**) if, for any molecule,

(1.4.1) $$P_1(\Delta V) = \frac{\Delta V}{V}.$$

1.4. Collision frequency. Free molecular, transitional, and continuum flow regimes

Every time when we perform observations we can find more than one molecule inside ΔV. Let's calculate the probability $P_k(\Delta V)$ to find in ΔV (during one observation) k molecules assuming what positions of individual molecules are independent from each other (i.e. presence or absence of one molecule in ΔV does not affect presence or absence of any other molecule there). For this purpose we can use the solution of statistical problem called the **Bernoulli trial**.

In the Bernoulli trial (see Section 1.8), we perform N independent measurements (determination of positions of N particles with respect to ΔV). Every measurement has only two outcomes: Success (particle inside ΔV with probability P_1) or failure (particle outside ΔV with probability $1 - P_1$). The probability of k successes in a series of N measurements is equal to

$$P_k = P_k(\Delta V) = \frac{N!}{k!\,(N-k)!} \mathrm{P}_1^k (1 - P_1)^{N-k}. \quad (1.4.2)$$

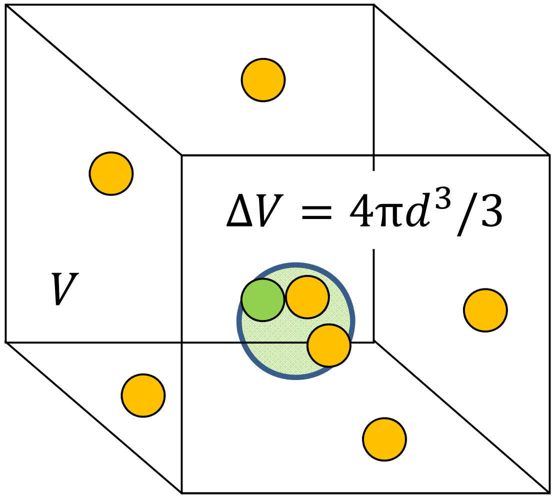
Probabilities of collisions with participation of various number of particles

Binary collision is a process of interaction between two molecules.

Triple collision is a process of interaction between three molecules.

Let's compare probabilities of collisions with different number of molecules.

If k particles interact with each other, then they should be close to each other, not farther than the characteristic length scale of collisions $l_c = d$. Then a collision with participation of k particles occurs if we can find k particles in a sphere of radius d and volume $\Delta V = 4\pi d^3/3$. Probability of such event is given by Eq. (1.4.2).



1.4. Collision frequency. Free molecular, transitional, and continuum flow regimes

Now let's compare probabilities of collisions between $k+1$ and k molecules using Eq. (1.4.2):

$$\frac{P_{k+1}}{P_k} = \frac{N-k}{k+1}\frac{P_1}{1-P_1} = \frac{N-k}{k+1}\frac{P_1}{1-P_1} = \frac{N-k}{k+1}\frac{\Delta V}{V-\Delta V}.$$

This equation can be simplified in the case when $\Delta V \ll V$ and $k \ll N$. Using additionally Eq. (1.4.1):

$$\frac{P_{k+1}}{P_k} = \frac{n\Delta V}{k+1} = \frac{4\pi/3}{k+1} n d^3 = \frac{4\pi/3}{k+1}\epsilon.$$

Thus, we see that

(1.4.3)
$$\frac{P_{k+1}}{P_k} \sim \epsilon.$$

In the dilute gas, the density parameter is small, $\epsilon \ll 1$, and it is sufficient to account only for binary collisions between molecules.

In the dense gas, interactions between multiple particles (collective interactions) must be taken into account.

In the kinetic theory of dilute gases, only binary collisions between molecules are accounted for.

1.4. Collision frequency. Free molecular, transitional, and continuum flow regimes

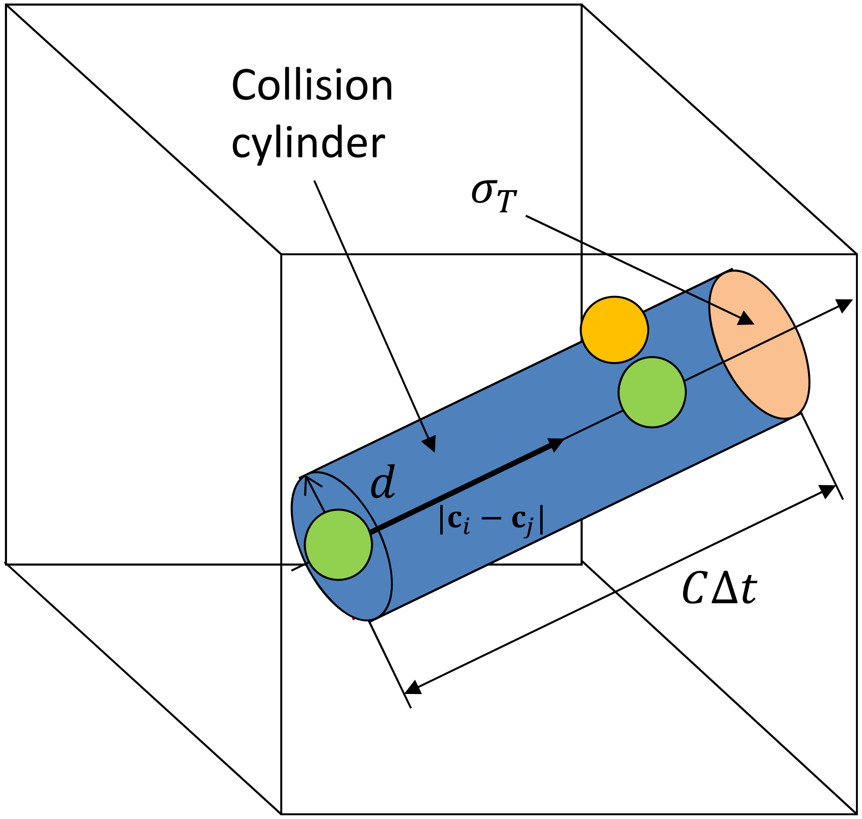
Collision frequency and mean free path

Collision frequency of a molecule z is the mean number of binary collisions which an individual molecule participates in per unit time.

In order to find z, let's first calculate the mean number of collisions Δz of a green molecule during time Δt. During this time the molecule will make a path $C\Delta t$. Any other orange molecule can participate in the collision with the selected molecule only if the center of the orange molecule is within the collisional cylinder of diameter d and height $C\Delta t$.

Area of cross section $\sigma_T = \pi d^2$ of the collisional cylinder is called the **total collision cross section**.

The volume of collision cylinder is $\Delta V = \sigma_T C\Delta t$.



Then the number of collisions Δz is equal to the average number of orange molecules in the collision cylinder, $\Delta z = n\Delta V = n\sigma_T C\Delta t$, and the collision frequency for a molecule is equal to

(1.4.4) $$z = \frac{\Delta z}{\Delta t} \approx \sigma_T n C.$$

Collision density or **collision frequency per unit volume** Z is the mean number of binary collisions in a unit volume per unit time. It can be easily found based on z: Every molecule per

1.4. Collision frequency. Free molecular, transitional, and continuum flow regimes

unit time participates in z collisions and we totally have n molecules in a unit volume. Then

(1.4.5)

$$Z = \frac{1}{2} n z \approx \frac{1}{2} \sigma_T n^2 C,$$

where coefficient $(1/2)$ appeared because two molecules participate in every binary collision.

The **mean free time** τ of a molecule is the mean interval of time between two sequential collisions of a given molecule with other molecules:

(1.4.6)

$$\tau = \frac{1}{z} \approx \frac{1}{\sigma_T n C}.$$

The **mean free path** λ of a molecule is the mean path a molecule travels between two sequential collisions with other molecules:

(1.4.7)

$$\lambda = \tau C \approx \frac{1}{\sigma_T n}.$$

More accurately, $\lambda = \tau v_*$, where the characteristic velocity v_* is not necessarily equal to C, but can be chosen based on different considerations.

The mean free path does not depend on thermal velocity C. This quantitative result, however, is valid only for billiard balls – molecules in the form of **hard spheres** of constant diameter d.

The obtained equations for z, Z, τ, and λ are not accurate (sign “$\approx$” is used) because we did not account for real distribution of chaotic velocities of individual molecules. The "accurate" theory, however, results in equations that are different only by some numerical coefficients. For instance, the "accurate" theory predicts that the mean free path of gas molecules in the form of billiard balls of diameter d in the equilibrium state is equal to

$$\lambda = \frac{1}{\sqrt{2} \sigma_T n}.$$

1.4. Collision frequency. Free molecular, transitional, and continuum flow regimes

Example: Basic collision properties in atmospheric air at standard conditions.

For N_2, the major component of air, $d = 3.7$ Å and $m = 46.5 \cdot 10^{-27}$ kg (slide 9) and the gas constant is equal to

$$R = \frac{k_B}{m} = \frac{1.38 \cdot 10^{-23}}{46.5 \cdot 10^{-27}} = 297 \ \frac{\mathrm{J}}{\mathrm{kg} \cdot \mathrm{K}}.$$

According to the kinetic definition of temperature, Eq. (1.3.11), at standard temperature of 273.15 K:

$$C = \sqrt{3RT} = \sqrt{3 \frac{k_B}{m} T} = 493 \ \frac{\mathrm{m}}{\mathrm{s}}.$$

Number density at standard conditions is equal to the Loschmidt constant $n_L = 2.6868 \cdot 10^{25} \ 1/\mathrm{m}^3$ (slide 13). Total collision cross section is equal to $\sigma_T = \pi d^2 = 43 \cdot 10^{-20}$ m². Then

Collision frequency of a molecule $z \approx \sigma_T n C = 5.7 \cdot 10^9$ 1/s.

Collision density in a unit volume $Z \approx \frac{1}{2} \sigma_T n^2 C = 7.7 \cdot 10^{34}$ 1/s/m³.

Mean free time $\tau \approx \frac{1}{\sigma_T n C} = 0.18 \cdot 10^{-9}$ s = 0.18 ns

Mean free path $\lambda \approx \frac{1}{\sigma_T n} = 0.086 \cdot 10^{-6}$ m = 0.086 μm.

1. Thermal velocity is of the order of sound speed, $a = \sqrt{\gamma R T}$, where γ is the isentropic index.
2. The smaller m, the larger thermal velocity at fixed temperature. The highest thermal velocities at given T are specific for hydrogen and helium.

1.4. Collision frequency. Free molecular, transitional, and continuum flow regimes

Equilibrium and relaxation

The major assumption (confirmed by observations) of thermodynamics is that every system (of molecules) under constant external conditions approaches with time an **equilibrium state**. The system stays in equilibrium forever unless external conditions are changed.

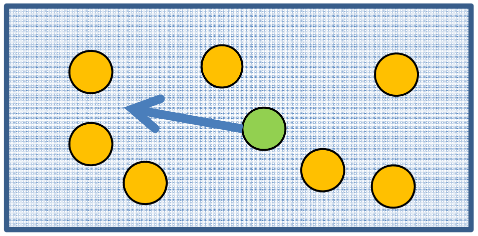
We cannot give a kinetic (statistical) definition of the equilibrium state right now, because it can be done only based on the analysis of statistical distribution of chaotic velocities of individual molecules in gases. We assume, however, that the kinetic theory must be in agreement with thermodynamics and any system of gas molecules in time should evolve towards the equilibrium state.

The process of transition of any volume of gas from arbitrary initial non-equilibrium state to equilibrium is called the **relaxation**. The characteristic time t_r required to reach the equilibrium state is called the **relaxation time**.

- The major (and often the only) physical mechanism leading to equilibrium are collisions between gas molecules. The relaxation occurs primarily due to intermolecular collisions.
- The larger number of collisions between molecules, the faster relaxation and shorter relaxation time, so collisional properties like z, τ, and λ can be used to characterize the rate of relaxation.
- For molecules - "billiard balls", equilibrium is established after a few collisions of every molecule, so that the relaxation time is usually assumed to be equal to the mean free time: $t_r = \tau$

Example of extreme non-equilibrium state:

One energetic molecule surrounded by molecules at rest



Such state cannot exist during long time: After multiple collisions between molecules, the initial energy of the green molecule will be re-distributed between all molecules

1.4. Collision frequency. Free molecular, transitional, and continuum flow regimes

Let's consider how collisions can affect properties of non-homogeneous flows. Any non-homogeneous flow has an intrinsic flow length scale(s) L that characterizes the magnitude of gradients of macroscopic gas parameters.

Knudsen number. Free molecular, transitional, and continuum flow regimes

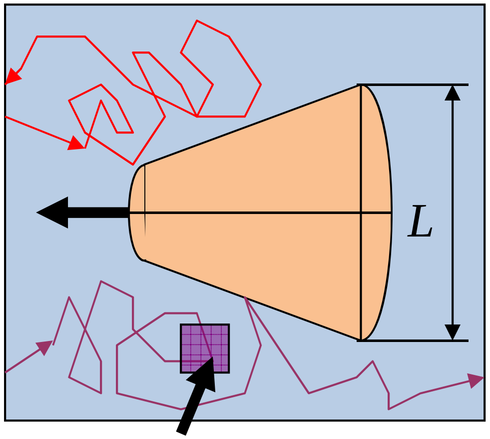
Knudsen number is the ratio of the characteristic mean free path λ_* to the flow length scale L :

$$Kn = \frac{\lambda_*}{L} \quad (1.4.8)$$

For example, in aerodynamics problems, L is usually chosen to be equal to the characteristic size of a body, and λ_* is defined by gas parameters in the undisturbed free stream around the body. Kn is measure of the importance of intermolecular collisions in the gas flow. Depending on the value of Kn, three major regimes of the dilute gas flow can be introduced:

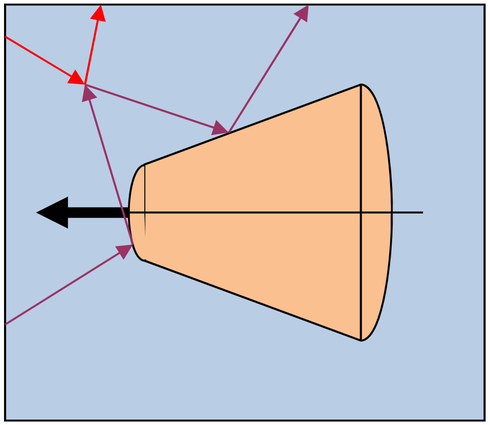
Continuum flow regime

$Kn \ll 1 \ (Kn < 0.03)$



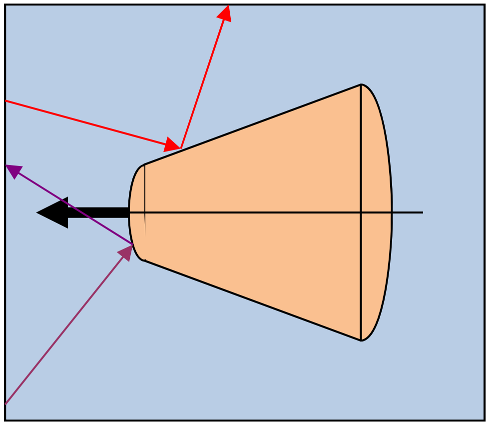
Transitional flow regime

$Kn \sim 1 \ (0.03 < Kn < 3-10)$



Free molecular flow regime

$Kn \gg 1 \ (Kn > 3-10)$



Locally equilibrium flows (CGD)

Non-equilibrium flows (RGD)

1.4. Collision frequency. Free molecular, transitional, and continuum flow regimes

Continuum flow regime is a regime at $Kn \ll 1$, when every molecule is a subject of multiple collisions inside the flow domain. Usually, in this case the continuity hypothesis is valid and, moreover, a system of molecules in any R.E.V. is in the state of local equilibrium, since the number of collisions is so large that it is sufficient for establishing equilibrium in R.E.V. This is the regime, when the gas flow can be satisfactory described by the continuum gas dynamics.

Transitional flow regime is a regime at $Kn \sim 1$, when every molecule participates only in a few collisions within the flow domain. The overall effect of collisions on the flow is non-negligible, but the flow is strongly non-equilibrium and continuum gas dynamics fails to describe such flows. Flows in this regime can be described by only the kinetic theory. Most of simulations of flows in the transitional regime is performed by the Direct Simulation Monte Carlo method.

Free molecular or collisionless flow regime is the regime at $Kn \gg 1$, when collisions are so infrequent that can be completely neglected. In this case the flow is primarily governed by the laws of interaction of individual molecules with walls or interfacial boundaries. Such flows are strongly non-equilibrium and computed based on the kinetic theory, but many free molecular flow problems admit theoretical solutions and do not require numerical simulations.

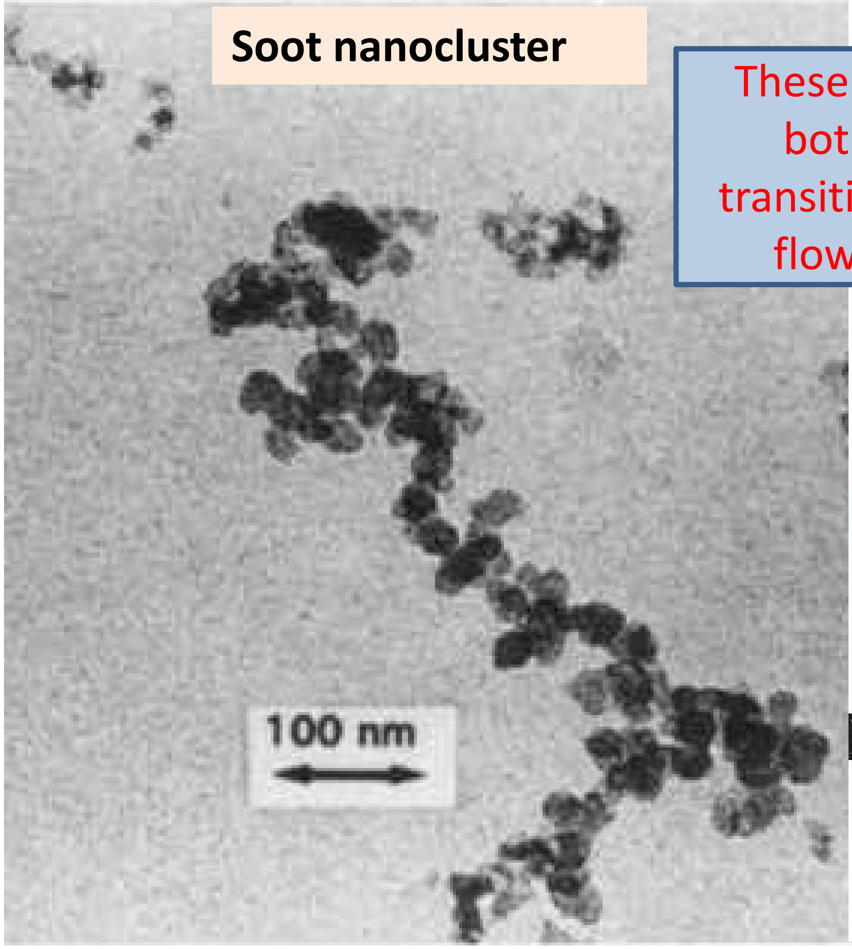
- The ranges of Kn for every regime shown in the previous slide are approximate: They *depend on the problem under consideration and on the adopted choice of* λ_* *and* L in the definition of Kn. Example: Flow over a sphere. Traditionally Kn is based on the sphere radius ($L = R$), but we can also define Kn based on the sphere diameter ($L = 2R$).
- There are *flows that cannot be characterized by a single value of* Kn *common for the whole flow*. Such flows can include local zones corresponding to different flow regimes.

1.4. Collision frequency. Free molecular, transitional, and continuum flow regimes

The degree of flow rarefaction depends not only on the properties of the gas itself (molecule size, number density, etc.), but it is also essentially determined by the flow length scale. The degree of rarefaction is the flow property, not the gas property!

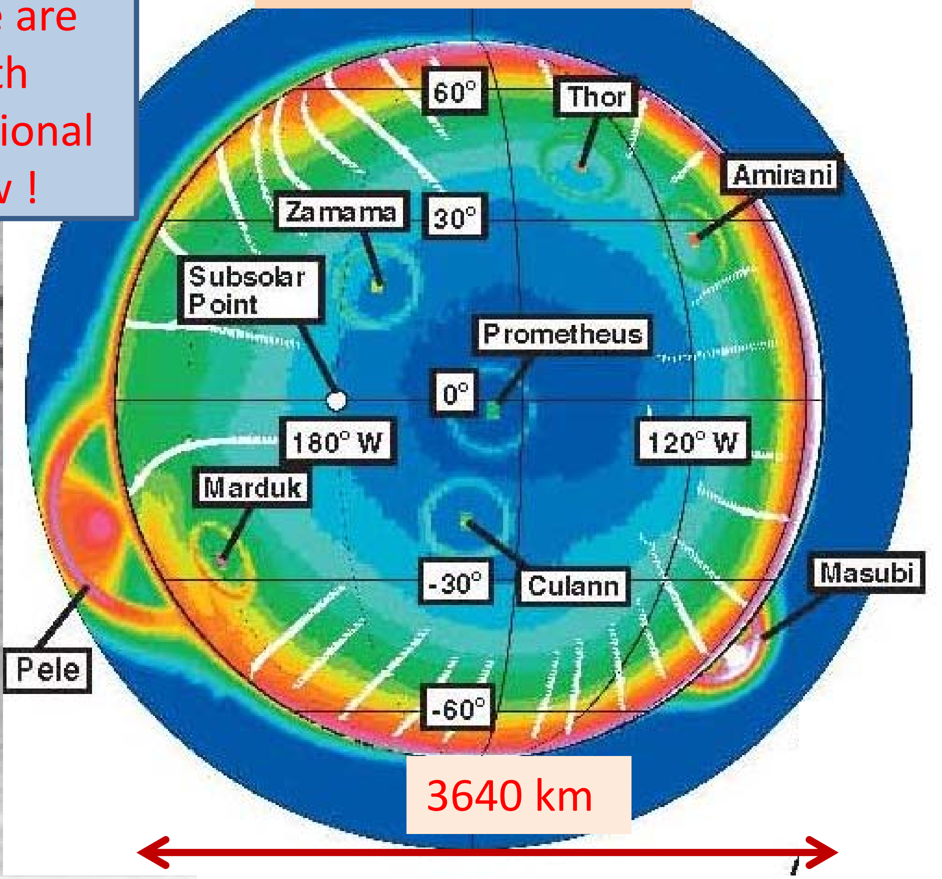
In the same gas, e.g., in air at standard conditions, one flow (on the scale of $L \sim 1$ m, $Kn \sim 10^{-7}$) can be continuum, while other (on the scale of $L \sim 1$ μm, $Kn \sim 0.1$) can be transitional or even free molecular.

Soot nanocluster



These are both transitional flow !

Atmosphere of Io



1.4. Collision frequency. Free molecular, transitional, and continuum flow regimes

Local Knudsen number

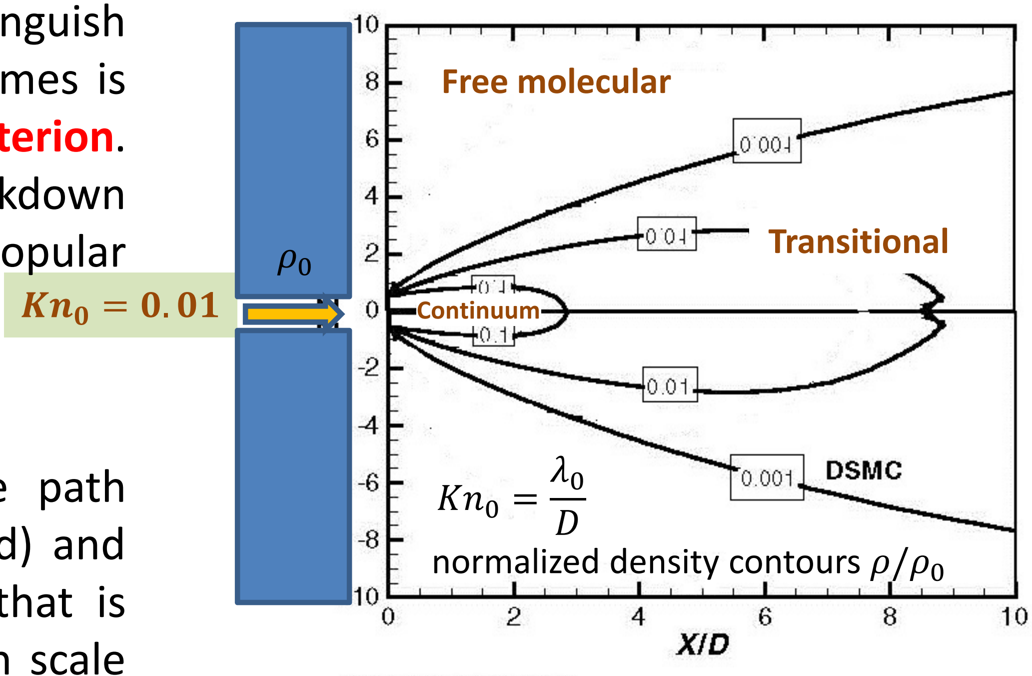
One of the major example of flows that could not be characterized by a single Knudsen number is the flow in a free jet expanding into vacuum or low-pressure background gas. Inside the nozzle or around it, the flow can be continuum, but then the gas density gradually drops to zero, so the jet flow field can include the zones of continuum, transitional, and free molecular flow.

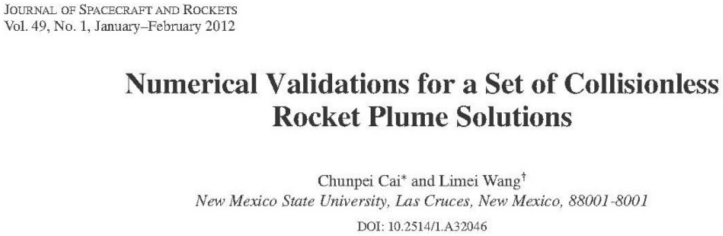
A criterion that allows one to distinguish between zoned with different flow regimes is called a **continuum breakdown criterion**. There are a lot of *empirical* breakdown criterions suggested, with the most popular based on the **local Knudsen number**

$$Kn(\mathbf{r},t)=\frac{\lambda(\mathbf{r},t)}{H(\mathbf{r},t)},$$

where $\lambda(\mathbf{r},t)$ is the local mean free path (defined in the point r of the flow field) and $H(\mathbf{r},t)$ is the local flow length scale that is often based on the characteristic length scale of the density variation (density gradient ∇n):

$$H=\frac{n}{|\nabla n|},\qquad \nabla n=\frac{\partial n}{\partial x}\mathbf{i}+\frac{\partial n}{\partial y}\mathbf{j}+\frac{\partial n}{\partial z}\mathbf{k}.$$

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Numerical Validations for a Set of Collisionless Rocket Plume Solutions

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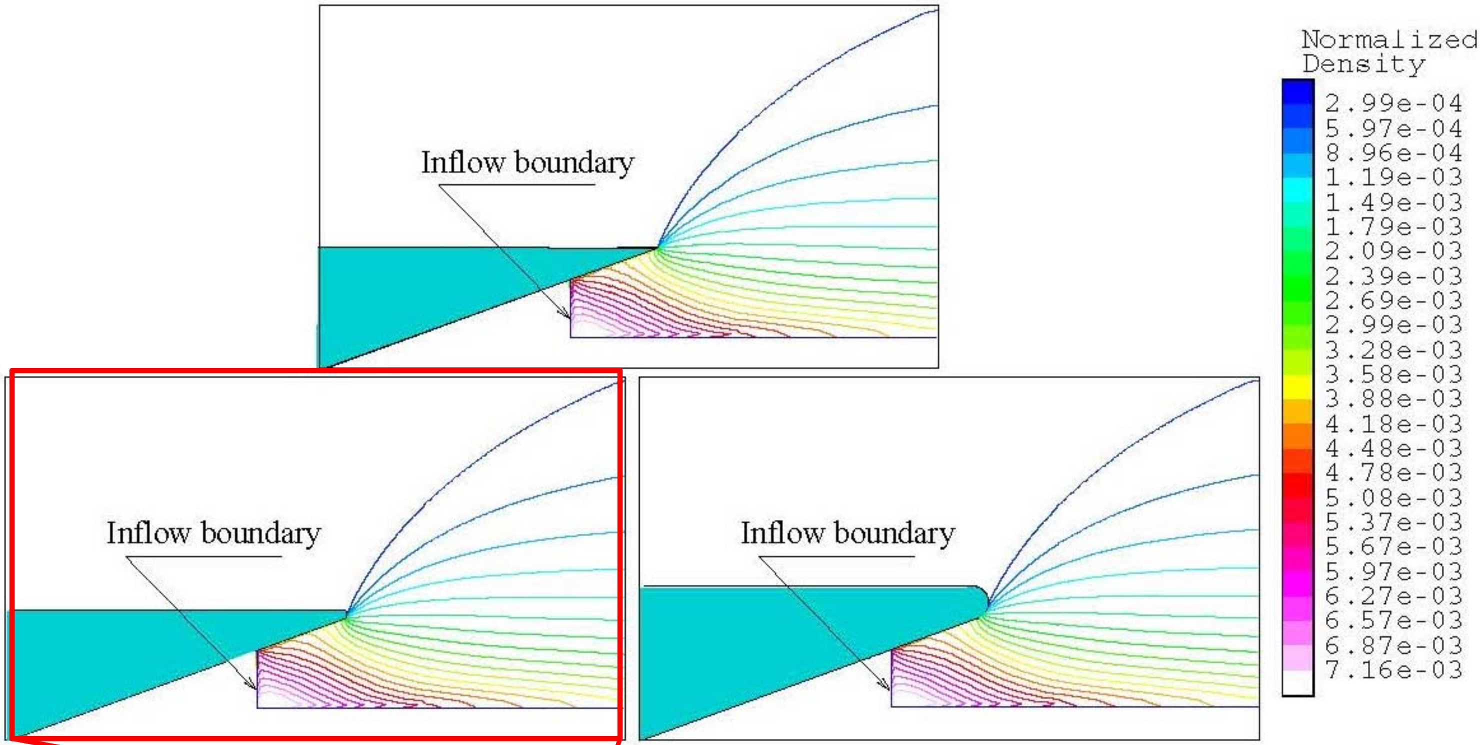
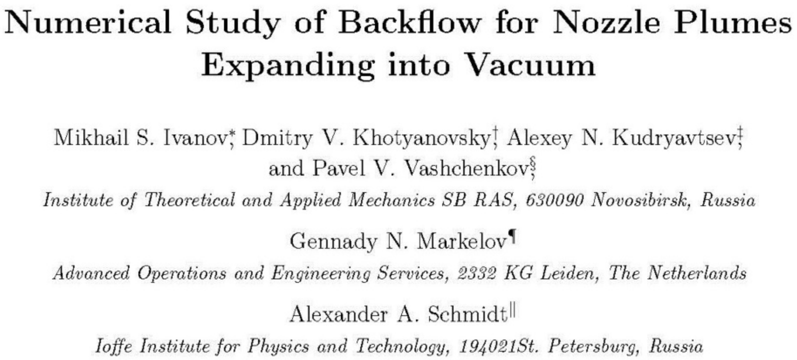
1.4. Collision frequency. Free molecular, transitional, and continuum flow regimes

Strong density drop occurs not only in the jet, but also in the diverging part of the Laval nozzle.



Density drops in more than order of magnitude



Numerical Study of Backflow for Nozzle Plumes Expanding into Vacuum

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1.4. Collision frequency. Free molecular, transitional, and continuum flow regimes

Relaxation length. Local equilibrium. "Extended" continuity hypothesis

if we consider a small volume of size λ^3, then every molecule travels through this volume during the relaxation time τ. And, thus, the total number of collisions in such volume is enough to turn the system of gas molecules in this volume into the **local equilibrium state**. Therefore the mean free path can be considered as the **relaxation length,** i.e. characteristic length scale of volumes in the gas flow, where the local equilibrium can be established due to collisions between molecules. Note, the Eq. (1.4.7) can be re-written as follows

$$\lambda \approx \frac{1}{\sigma_T n} = \frac{1}{\pi d^2 n} = \frac{d}{\pi n d^3} \sim \frac{d}{\epsilon}, \tag{1.4.9}$$

where $\epsilon = nd^3$ is the density parameter. Then let's estimate the number of molecules in λ^3:

$$N = n\lambda^3 = \frac{nd^3}{\epsilon^3} = \frac{1}{\epsilon^2}.$$

Assume that we have a continuum gas flow ($\lambda \ll L$) of a dilute gas ($\epsilon \ll 1$, practically $\epsilon < 10^{-3}$). Then the choice of a R.E.V. size equal to the relaxation length satisfies all requirements to R.E.V:

1. R.E.V. contains many particles (more than 10^6 according to Eq. (1.4.8)), so that the definition of macroscopic parameters as volume-averaged molecular quantities makes sense: It produces values that do not fluctuate because of chaotic motion of molecules.
2. R.E.V. is small compared to the flow length scale, providing homogeneous distribution of molecules in R.E.V.
3. Moreover, since the R.E.V. size is in the order of relaxation length, in every R.E.V. gas molecules are in local equilibrium, so that we can use multiple relationships established, e.g., in thermodynamics, for equilibrium systems.

1.4. Collision frequency. Free molecular, transitional, and continuum flow regimes

Thus, we see that in the continuum flow regime of a dilute gas an **"extended" continuity hypothesis**, which includes requirements 1, 2, and 3, is valid. Local equilibrium of gas flows in the continuum flow regime is intensively used in gas dynamics, where the **conservation laws** (mass, momentum, and energy equations) are supplied with multiple **closure equations** (equations of state, Newton's law for viscous stresses, Fourier's law for heat flux, etc.) that are necessary to obtained a **closed system** of equations (a system where the number of unknowns is equal to the number of equations), but valid only in conditions of local equilibrium.

Summary on the length scales in dilute and dense gases

We introduced four linear (and time) scales of processes in gases: collision length scale l_c, mean distance between molecules l_s, relaxation length – mean free path λ, and flow length scale L. Depending on the nature of the gas (dense/dilute) and flow regime (continuum/non-continuum) we have the following relationships between these scales

In a dense gas (density parameter $\epsilon = \pi d^3 \sim 1$):

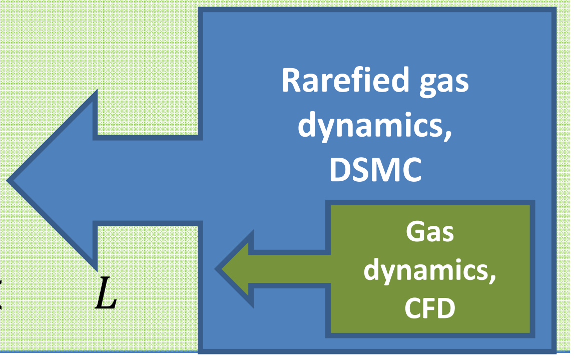
$$l_c \sim d \quad \sim \quad l_s \sim \frac{d}{\sqrt[3]{\epsilon}} \quad \sim \quad \lambda \sim \frac{d}{\epsilon}$$

In a dilute gas (density parameter $\epsilon = \pi d^3 \ll 1$):

$$l_c \sim d \quad \ll \quad l_s \sim \frac{d}{\sqrt[3]{\epsilon}} \quad \ll \quad \lambda \sim \frac{d}{\epsilon}$$

In continuum flows of a dilute gas ($\epsilon \ll 1, \lambda \ll L$):

$$l_c \sim d \quad \ll \quad l_s \sim \frac{d}{\sqrt[3]{\epsilon}} \quad \ll \quad \lambda \sim \frac{d}{\epsilon} \sim l_{R.E.V.} \quad \ll \quad L$$

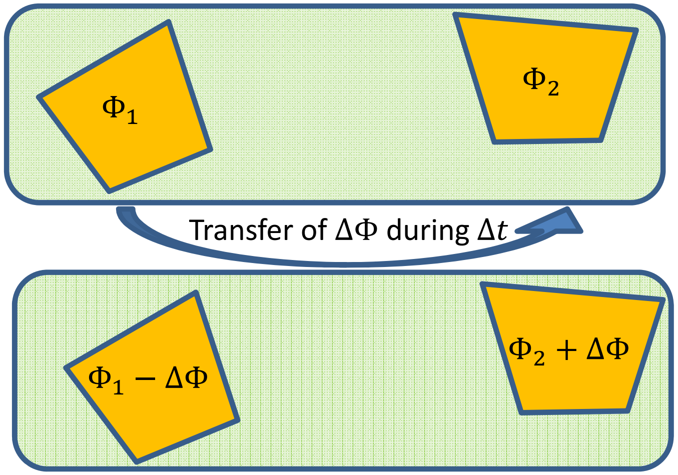


1.5. Transfer of molecular quantities

- Processes of transfer of physical quantities
- Fluxes and flux densities of physical quantities
- Convective and collisional transfer of molecular quantities

1.5. Transfer of molecular quantities

Processes of transfer of physical quantities



Let’s consider some **conservative physical quantity** Φ, i.e. a physical quantity which is conserved in a closed physical system. Examples of conservative quantities: Number of particles, mass, linear momentum, angular momentum, energy, etc.

Since such quantity cannot “appear” or “disappear’, a non-homogeneous distribution of such physical quantity in space can evolve only by means of re-distribution of this physical quantity in space. Physical processes of re-distribution of conservative physical quantities are called the **transfer processes**. From the point of view of molecular structure of matter, all transfer process are related to the motion and interaction of individual particles (electrons, atoms, molecules) or propagation of electromagnetic waves.

Example: **Diffusion** is the mixing of two matters that are brought in contact with each other. Diffusion is the particle number transfer process. Non-reversible mixing occurs as a result of chaotic motion of molecules. Diffusion happens in gases (fastest), liquids, and solids (slowest).

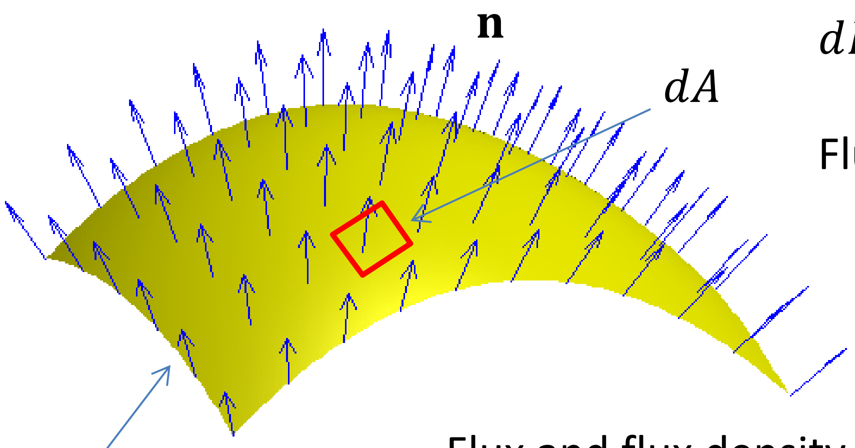
1.5. Transfer of molecular quantities

Fluxes and flux densities of molecular quantities

In continuum mechanics we systematically use such macroscopic parameters as fluxes and flux densities, e.g., heat flux, in order to describe transfer process of various molecular quantities.

For a given surface S and direction specified by the **unit normal vector** $\mathbf{n}$ to the surface, **flux** F_Φ of physical quantity Φ is the amount of this quantity which is transferred through surface S in the direction of $\mathbf{n}$ per unit time, $[F_\Phi]$=$[\Phi]$/s. For example, energy flux has unit of J/s.

The **flux density** $\mathbf{f}_\Phi$ of physical quantity Φ is such vector quantity that the flux dF_Φ through any surface of infinitesimal area dA with unit normal $\mathbf{n}$ is equal to $dF_\Phi = \mathbf{n} \cdot \mathbf{f}_\Phi dA$, so the flux density can be considered as the flux of Φ per unit area, $[\mathbf{f}_\Phi]$=$[\Phi]$/s/m^2. For example, energy density flux has unit of J/s/m^2.



$dF_\Phi = \mathbf{n} \cdot \mathbf{f}_\Phi dA$, flux through infinitesimal area dA;

Flux through the whole surface S is equal to

$$F_\Phi = \int_S \mathbf{n} \cdot \mathbf{f}_\Phi dA.$$

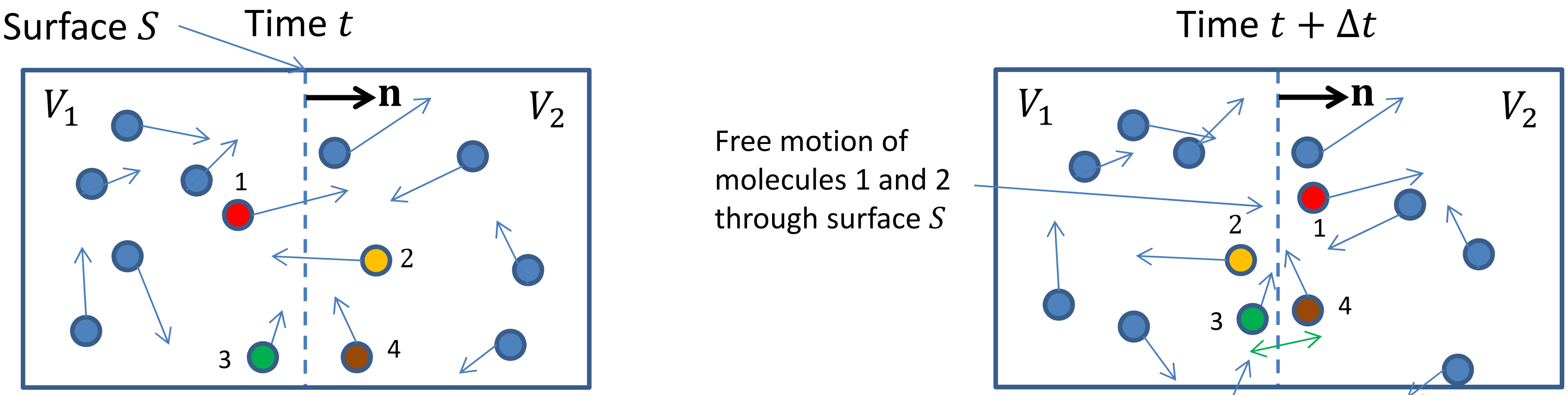
This is the **surface integral** (see calculus)

Flux and flux density can be both positive and negative. Negative value of the flux means that the corresponding physical quantity is preferentially transferred through surface S in the direction opposite to $\mathbf{n}$.

1.5. Transfer of molecular quantities

Convective and collisional transfer of molecular quantities

From the point of view of molecular structure of a gas, transport of any physical quantity through any surface is a result of motion and interaction of individual gas molecules.


Surface S

Time t

Time $t + \Delta t$

Free motion of molecules 1 and 2 through surface S

Interaction between molecules 3 and 4

Two mechanisms of transfer of molecular quantities:

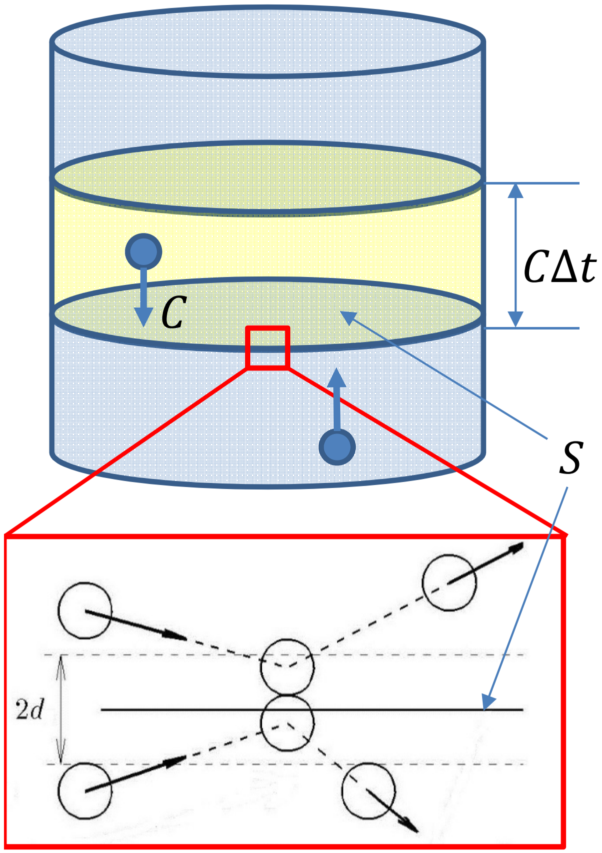
Free motion of molecules through surface S: If during time Δt a molecule (molecule 1) moves from volume V_1 to volume V_2 through surface S or vise versa (molecule 2) then amount of quantity Φ in V_1 decreases in V_1 and increases in V_2. This mechanisms of transfer of molecular quantities is called **convective**. Its contribution to the momentum flux is called **kinetic**.

Interaction of molecules at different sides of surface S: Total quantity of Φ in V_1 can change because some molecules in this volume (molecule 3) interact by forces with molecules (molecule 4) in V_2. This interaction will result in the redistribution Φ between V_1 and in V_2 during time Δt even if molecules do not cross the surface S. This mechanisms of transfer of molecular quantities is called **collisional**. Its contribution to the momentum flux is called **virial**.

1.5. Transfer of molecular quantities

Let's compare the relative contributions of convective and collisional transfer of molecular quantities in gas flows.

The rates of change of a conservative quantity due to convective and collisional transfer depend on the number of molecules that participate in every type of transfer processes. Let's consider some planar surface S of area A and estimate the number of molecules that participate in convective, ΔN_{free}, and collisional transfer, ΔN_{coll}, through S during time Δt.



Value of ΔN_{free} can be estimated like value of ΔN in slide 37

$$\Delta N_{free} = \frac{nC\Delta t A}{6}.$$

Molecules contribute to collisional transfer if they are located at different sides of S and participate in collisions. Then ΔN_{coll} can be estimated as the total number of collisions occurring in the layer of thickness $2d$ around surface S:

$$\Delta N_{coll} = Z(2dA)\Delta t = \sigma_T d n^2 C\Delta t A = \pi d^3 n^2 C\Delta t A.$$

Then

$$\frac{\Delta N_{coll}}{\Delta N_{free}} = 6\pi d^3 n \sim \epsilon$$

In a dilute gas, the density parameter is small, $\epsilon \ll 1$, and collisional transfer is small compared to the convective one. In the kinetic theory of dilute gases, collisional transfer is neglected.

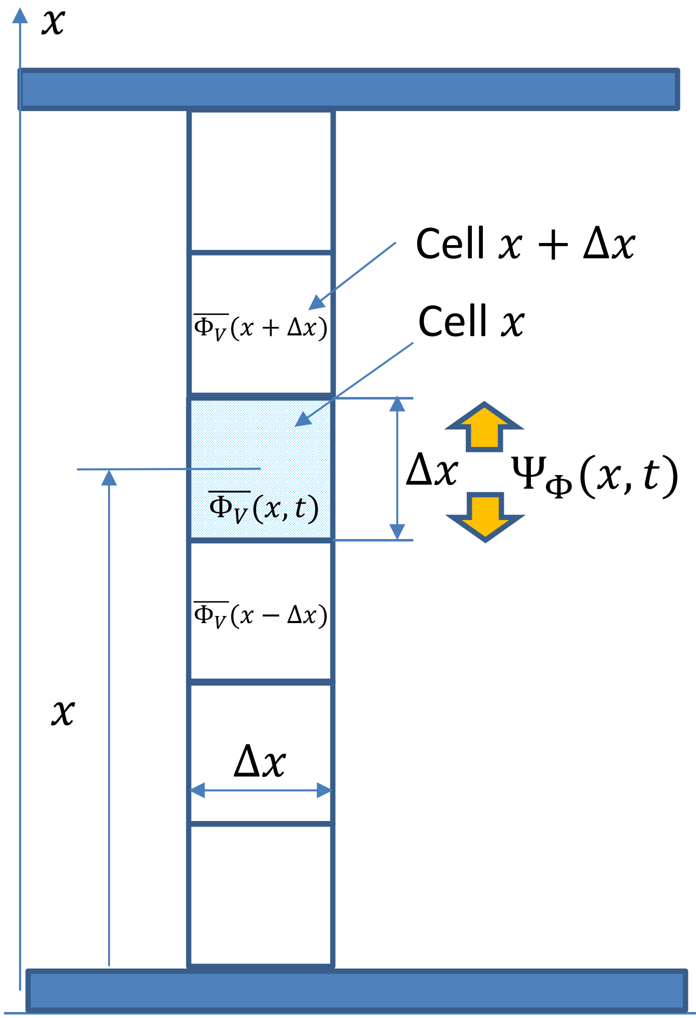
1.6. Transfer equation

- Simple transfer equation
- Homogenization of macroscopic parameters as a result of chaotic motion

1.6. Transfer equation

Simple transfer equation

Let's obtain a macroscopic transfer equation that describes transfer of some molecular quantity Φ due to chaotic motion of molecules under conditions when the "extended" continuity hypothesis is valid.



Let's assume that

- Convective transfer is the only reason for change of macroscopic gas parameters (no external forces, etc.)
- Transfer occurs in the direction of axis x and divide the flow into R.E.V. in the form of cubic cells of size Δx.

$\overline{\Phi_V}(x,t)$ is the density of Φ in the cell with center at x.

$\Psi_\Phi(x,t)$ is the density of flux of Φ that is transferred *from cell x into neighbor cells* with centers $x+\Delta x$ and $x-\Delta x$.

We assume that in every R.E.V. (every cell) gas is in local equilibrium, so that $\Delta x=\lambda$. The total quantity of Φ transferred from cell x to any neighbor cell during Δt is then equal to

$$\Delta\Phi=\Psi_\Phi(x,t)\Delta t\lambda^2=\frac{1}{6}C\Delta t\lambda^2 n\bar{\Phi}=\frac{1}{6}C\Delta t\lambda^2\overline{\Phi_V}$$

and

$$\Psi_\Phi(x,t)=\frac{1}{6}C\overline{\Phi_V}.$$

1.6. Transfer equation

Then we can write an **equation of balance** of total amount of Φ in cell x during time Δt:

$$\Delta x^3 \overline{\Phi_V}(x, t+\Delta t) - \Delta x^3 \overline{\Phi_V}(x, t) = [\Psi_\Phi(x+\Delta x, t) + \Psi_\Phi(x-\Delta x, t) - 2\Psi_\Phi(x, t)]\Delta x^2 \Delta t.$$

If we divide the equation by $\Delta x^3 \Delta t$, then we get

(1.6.1) $$\frac{\overline{\Phi_V}(x, t+\Delta t) - \overline{\Phi_V}(x, t)}{\Delta t} = -\frac{[\Psi_\Phi(x, t) - \Psi_\Phi(x+\Delta x, t)] - [\Psi_\Phi(x-\Delta x, t) - \Psi_\Phi(x, t)]}{\Delta x}$$

Here

(1.6.2) $$f_\Phi\left(x + \frac{\Delta x}{2}, t\right) = \Psi_\Phi(x, t) - \Psi_\Phi(x+\Delta x, t) = -\frac{C\lambda}{6} \frac{\overline{\Phi_V}(x+\Delta x) - \overline{\Phi_V}(x)}{\Delta x}$$

is the density of flux of Φ between cells x and $x + \Delta x$. Then

$$\frac{\overline{\Phi_V}(x, t+\Delta t) - \overline{\Phi_V}(x, t)}{\Delta t} = -\frac{f_\Phi(x+\Delta x/2, t) - f_\Phi(x-\Delta x/2, t)}{\Delta x}.$$

$f_\Phi > 0$ if transfer of Φ occurs in the positive direction of axis x.

Finally, let's consider Eqs. (1.6.1) and (1.6.2) in the limit when $\Delta x \to 0$ and $\Delta t \to 0$

(1.6.3) $$f_\Phi = -K_\Phi \frac{\partial \overline{\Phi_V}}{\partial x}, \qquad K_\Phi = \frac{C\lambda}{6},$$

(1.6.4) $$\frac{\partial \overline{\Phi_V}}{\partial t} = -\frac{\partial f_\Phi}{\partial x} \quad \text{or} \quad \frac{\partial \overline{\Phi_V}}{\partial t} = \frac{\partial}{\partial x}\left(K_\Phi \frac{\partial \overline{\Phi_V}}{\partial x}\right).$$

1.6. Transfer equation

Eq. (1.6.3) establishes a linear relationship between the flux density of molecular quantity and gradient of corresponding macroscopic parameter. The sign “-” in Eq. (1.6.3) means that the transport of molecular quantity preferentially occurs in the direction opposite to the direction of the gradient, i.e. from regions where density of Φ is large to regions where density of Φ is small. Coefficient of proportionally K_Φ in Eq. (1.6.3) is called the **transfer (transport) coefficient**. K_Φ is not a constant, since C depends on T ($C \sim \sqrt{RT}$), and λ depends on n and, in general, on T. Thus, the larger T, the larger K_Φ and the rate of the transfer process.

Equation (1.6.4) is the simple **transfer equation**. It can be applied to study transfer of various molecular quantities.

The question is: Where did we use in derivation of Eq. (1.6.4) the "extended" continuity hypothesis?

One can notice that me made a “trick” in derivation of Eq. (1.6.3) from Eq. (1.6.2). Namely, we first assumed $\Delta x = \lambda$, but then considered the case when $\Delta x \to 0$ at fixed λ:

$$F_\Phi = -\frac{C\lambda}{6}\frac{\overline{\Phi_V}(x+\Delta x) - \overline{\Phi_V}(x)}{\Delta x} \xrightarrow[\Delta x \to 0]{} -\frac{C\lambda}{6}\frac{\partial \overline{\Phi_V}}{\partial x}$$

This "trick" is in based on the assumption that the "extended" continuity hypothesis is valid. We cannot arbitrary change λ since it is given by physical properties of our flow, but, since $\lambda \ll L$, we can consider Δx as an infinitely small size compared with the flow length scale L.

1.6. Transfer equation

Homogenization of macroscopic parameters as a result of chaotic motion

Let's solve a boundary value problem for Eq. (1.6.4) assuming that $K_\Phi = const$

$$\frac{\partial \overline{\Phi_V}}{\partial t} = K_\Phi \frac{\partial^2 \overline{\Phi_V}}{\partial x^2}$$

with the initial distribution of $\overline{\Phi_V}$ in the form of a step function

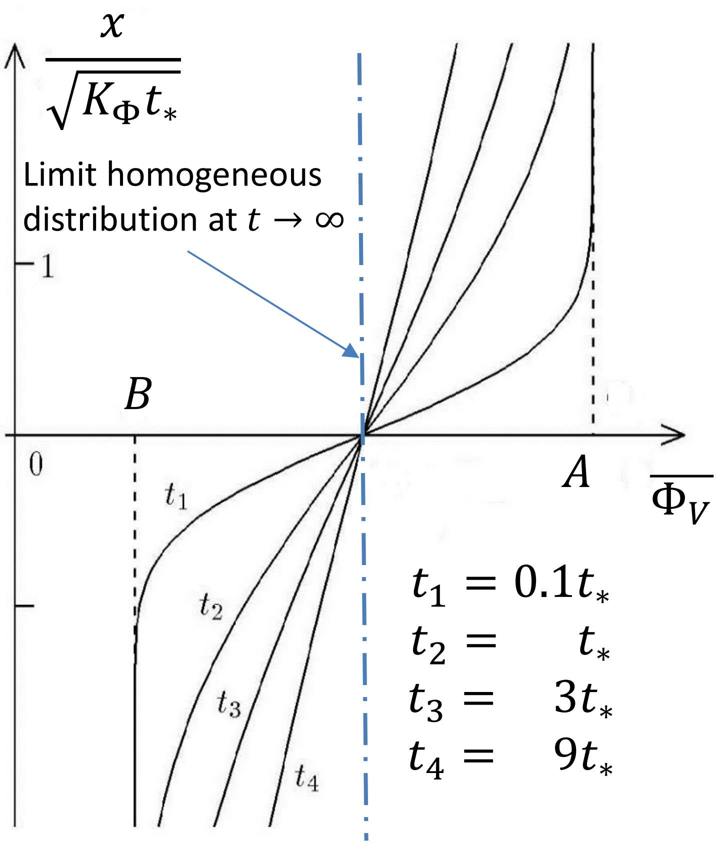
$$\text{At } t = 0: \qquad \overline{\Phi_V}(x,0) = \begin{cases} A, & x > 0; \\ B, & x < 0. \end{cases}$$

Solution takes the form (can be checked by substitution)

$$\overline{\Phi_V}(x,t) = \frac{A+B}{2} + \frac{A-B}{2}\,\mathrm{erf}\left(\frac{x}{2\sqrt{K_\Phi t}}\right), \qquad (1.6.5)$$

where $\mathrm{erf}(x)$ is the **error function**:

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt\,.$$



Limit homogeneous distribution at $t \to \infty$

$t_1 = 0.1 t_*$
$t_2 = t_*$
$t_3 = 3 t_*$
$t_4 = 9 t_*$

Chaotic motion results in non-reversible homogenization of initial non-homogeneous distribution of macroscopic parameter $\overline{\Phi_V}$*. As a result of chaotic motion, quantity* Φ *is transferred from layers with larger* $\overline{\Phi_V}$ *to layers with smaller* $\overline{\Phi_V}$. The rate of this process is defined by K_Φ.

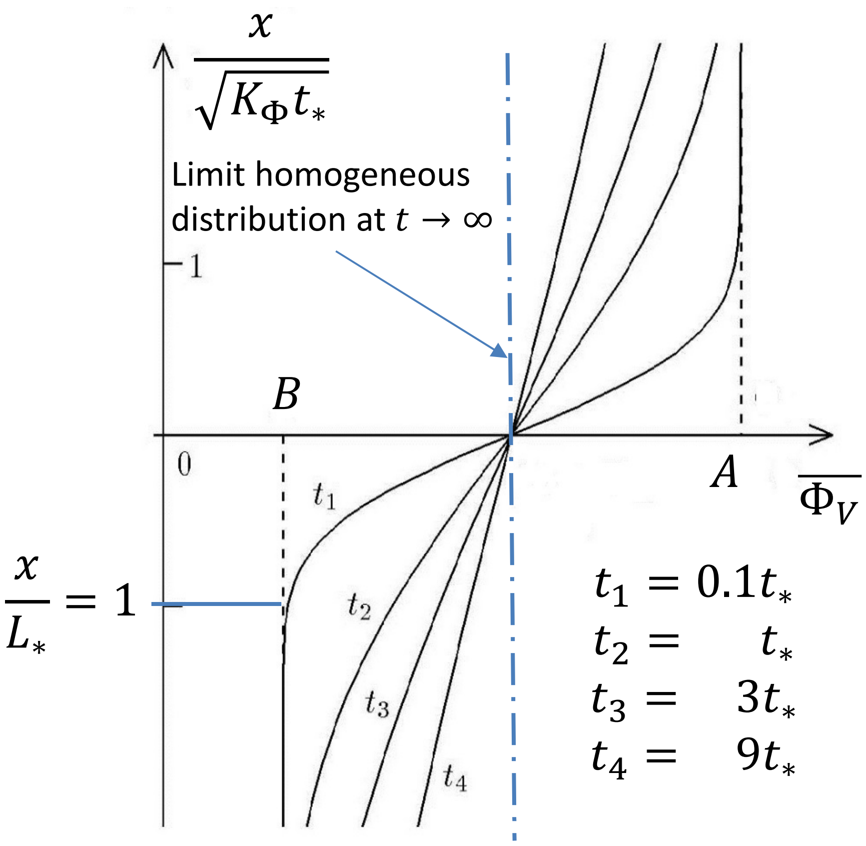
1.6. Transfer equation

Note that solution in the form of Eq. (1.6.5) depends not on individual values of x and t, but on the variable $\xi = x/\sqrt{K_\Phi t}$. It means that at any time t_*, the characteristic linear scale of the domain L_* affected by the transfer of molecular quantity is equal to

$$L_* = \sqrt{K_\Phi t_*}. \qquad (1.6.6)$$

This equation establishes a simple, but universal relationship between time , t_*, and length , L_*, scales of the transfer process.

This equation can be used as follows: If we know that the transfer process through some boundary occurs during time t_*, then the domain around this boundary, where macroscopic parameters are affected by this process, has the characteristic size L_* given by Eq. (1.6.6).



1.7. Diffusion, viscous drag, and heat conduction

- Diffusion
- Viscous drag
- Heat conduction

1.7. Diffusion, viscous drag, and heat conduction

Diffusion

Diffusion in gases is the physical process of redistribution of number of molecules by means of preferential motion of molecules from regions where molecules more abundant to regions where they are less abundant due to chaotic motion of molecules. In the important case of **binary diffusion**, two different gases are mixing with each other. Binary diffusion cannot be considered based on the simple transfer equation, because it was derived for a gas composed of identical molecules. Let’s apply the transfer equation

$$\frac{\partial \overline{\Phi_V}}{\partial t} = -\frac{\partial f_\Phi}{\partial x}, \qquad f_\Phi = -K_\Phi \frac{\partial \overline{\Phi_V}}{\partial x}, \qquad K_\Phi = \frac{C\lambda}{6}$$

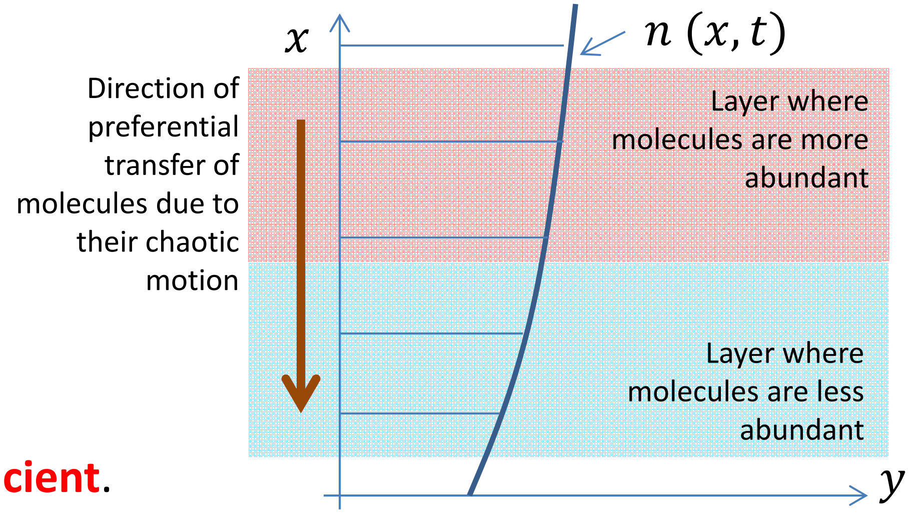
in order to describe **self-diffusion**, e.g. homogenization of distribution of number density in a gas of identical molecules. We consider $\Phi_i = 1$, $\overline{\Phi} = 1$, and assume that there is a non-homogeneous distribution of number density $\overline{\Phi_V} = n(x,t)$ along axis x. Then the number flux density in x direction is given by the equation

(1.7.1) $$J_x = -D \frac{\partial n}{\partial x},$$

where

(1.7.2) $$D = \frac{C\lambda}{6} = \frac{\sqrt{3}}{6\pi} \frac{1}{\sigma_T} \frac{1}{n} \sqrt{\frac{k_B}{m} T} \sim \frac{\sqrt{T}}{n}$$

is called the **self-diffusivity** or **self-diffusion coefficient**.



1.7. Diffusion, viscous drag, and heat conduction

The transfer equation takes the form

(1.7.3)
$$\frac{\partial n}{\partial t} = -\frac{\partial J_x}{\partial x} \quad \text{or} \quad \frac{\partial n}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial n}{\partial x}\right)$$

and is called the **diffusion equation**. The linear relationship between the diffusion flux density J_x and gradient of number density of molecules given by Eq. (1.7.1) is called **Fick's law of diffusion**. It was first established experimentally. We showed that this experimental law in gases is explained by the chaotic motion of molecules.

Eq. (1.7.2) is not accurate, but predicts correct functional dependence of D on n and T: The "accurate" kinetic theory predicts that for gas composed of **hard sphere** (**HS**) molecules

(1.7.4)
$$D = \frac{3\sqrt{\pi}}{8\pi}\frac{1}{\sigma_T}\frac{1}{n}\sqrt{\frac{k_B}{m}T}.$$

The experiments show that the (self-)diffusion coefficient varies as a function of n and T as

(1.7.5)
$$D \sim \frac{T^{\alpha}}{n},$$

where exponent α can be different from ½. The "accurate" kinetic theory shows that the dependence of D on T is determined by the model of interaction between gas molecules. Models that are more sophisticated that the HS model can accurately predict Eq. (1.7.5).

Note: In the kinetic theory, self-diffusion has a limited importance (contrary to diffusion of different species) and usually considered as a limit case of binary diffusion of two gases with similar m and σ_T.

1.7. Diffusion, viscous drag, and heat conduction

Viscous drag

Viscosity of a fluid (informally) is ability of fluid to resist the shear load. **Viscous drag** in gases is the physical process of redistribution of angular momentum in the direction perpendicular to the flow velocity from layers with higher gas velocity to layers with smaller gas velocity. Let's apply the transfer equation

$$\frac{\partial \overline{\Phi_V}}{\partial t} = -\frac{\partial f_\Phi}{\partial x}, \qquad f_\Phi = -K_\Phi \frac{\partial \overline{\Phi_V}}{\partial x}, \qquad K_\Phi = \frac{C\lambda}{6}$$

in order to describe viscous drag. We consider $\Phi_i = m_i v_{iy}$, then $\bar{\Phi} = m u_y$ and $\overline{\Phi_V} = n\bar{\Phi} = \rho u_y$, and assume that there is a non-homogeneous distribution of $u_y(x,t)$ along axis x, while $n = const$. Then the flux density τ_{xy} of y-component of angular momentum through a surface normal to axis x is given by the equation

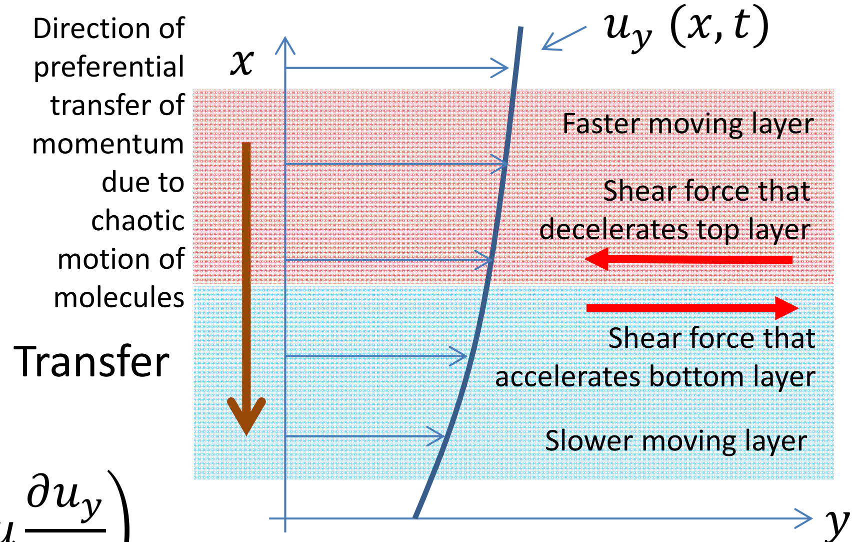
(1.7.6)
$$\tau_{xy} = -\mu \frac{\partial u_y}{\partial x}$$

is called the **shear stress** and

(1.7.7)
$$\mu = \frac{C\lambda}{6} mn = \frac{1}{2\sqrt{3}} \frac{m}{\sigma_T} \sqrt{\frac{k_B}{m} T} \sim \sqrt{T}$$

is called the (**dynamic**) (**shear**) **viscosity** (**coefficient**). Transfer equation takes the form

(1.7.8)
$$\frac{\partial}{\partial t}(\rho u_y) = -\frac{\partial \tau_{xy}}{\partial x} \quad \text{or} \quad \frac{\partial}{\partial t}(\rho u_y) = \frac{\partial}{\partial x}\left(\mu \frac{\partial u_y}{\partial x}\right)$$



1.7. Diffusion, viscous drag, and heat conduction

and is called the **viscous drag equation**.

The shear stress τ_{xy} has unit of kg·(m/s)/s/m^2 = N/m^2 = Pa since this is a force (flux of linear momentum) per unit area. The quantity τ_{xy} characterizes the **tangential** or **shear force** applied to a unit area on a surface with normal along axis x and acting along axis y. The linear relationship between the shear stress and gradient of macroscopic velocity, Eq. (1.7.6), is known as **Newton's law of viscosity**. It was first established experimentally. We showed that this experimental law in gases is explained by the chaotic motion of molecules.

Eq. (1.7.6) establishes two important facts about the viscosity coefficient:

1. *Viscosity of dilute gases does not depend on number density*. This fact is in accurate agreement with experiments.
2. Viscosity is proportional to $T^{1/2}$. Experimentally, it is know that the *dependence of viscosity on temperature in some limited range of temperature can be well-approximated by the power law*

(1.7.9)
$$\mu(T) = \mu_0 \left(\frac{T}{T_0}\right)^{\omega},$$

where the **viscosity index** ω varies between 1/2 and 1 with values 1/2 specific for higher T and 1 for lower T. The "accurate" kinetic theory predicts that value $\omega = 1/2$ is specific only for hard sphere molecules with the accurate value of viscosity equal to

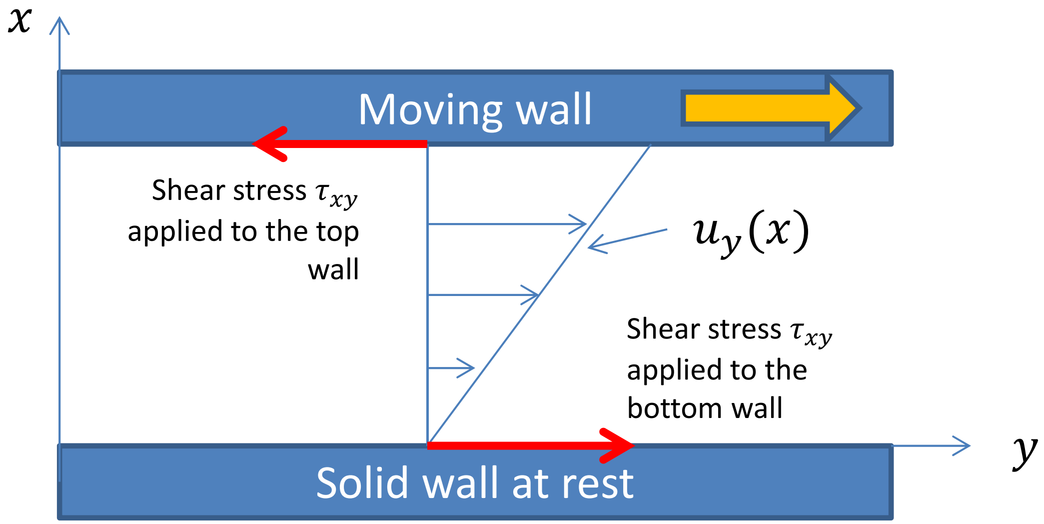
(1.7.10)
$$\mu = \frac{5\sqrt{\pi}}{16}\frac{m}{\sigma_T}\sqrt{\frac{k_B}{m}T}.$$

1.7. Diffusion, viscous drag, and heat conduction

The "accurate" kinetic theory also shows that the value of the viscosity index ω in Eq. (1.7.9) is defined by the adopted molecular model of interatomic collisions (Chapter 2). By using more sophisticated molecular models than the model of hard sphere molecules, it is possible to theoretically obtain the viscosity of gases varying as $\sim T^{\omega}$ and to bring the theory in accurate agreement with results of experimental measurements.

If viscosity of gases is known at some particular temperature, then one can use Eq. (1.7.9) in order to find the collision cross section $\sigma_T = \pi d^2$ and gas kinetic diameter d. This approach is systematically used in the kinetic theory in order to find d.

Viscosity and shear stresses in gases can be studies theoretically by considering a standard problem of flow between two parallel solid walls moving with respect to each other. The steady-state flow occurring in this problem in the gap between walls is called the **Couette flow**.



1.7. Diffusion, viscous drag, and heat conduction

Heat conduction

Heat conduction or **heat transfer** in gases is the physical process of redistribution of internal energy from hotter to colder regions due to chaotic motion of molecules. Let's apply the transfer equation

$$\frac{\partial \overline{\Phi_V}}{\partial t} = -\frac{\partial f_\Phi}{\partial x}, \qquad f_\Phi = -K_\Phi \frac{\partial \overline{\Phi_V}}{\partial x}, \qquad K_\Phi = \frac{C\lambda}{6}$$

in order to describe heat conduction. We consider $\Phi_i = m_i \mathbf{c}_i^2/2 = m_i \mathbf{v}_i^2/2$ (no bulk velocity), then $\overline{\Phi} = mC^2/2 = (3/2)k_B T$ (see Eq. (1.3.11)) and $\overline{\Phi_V} = n\overline{\Phi} = (3/2)n k_B T = \rho c_V T$, and assume that there is a non-homogeneous distribution of temperature $T(x,t)$ along axis x, while there is only minor inhomogeneity of n, so $n = const$ (see the comment on slide 78). Then the energy flux density in x direction, q_x, given by the equation

(1.7.11) $$q_x = -\kappa \frac{\partial T}{\partial x},$$

is called the **heat flux density** and

$$c_V = \frac{3}{2}\frac{k_B}{m}$$

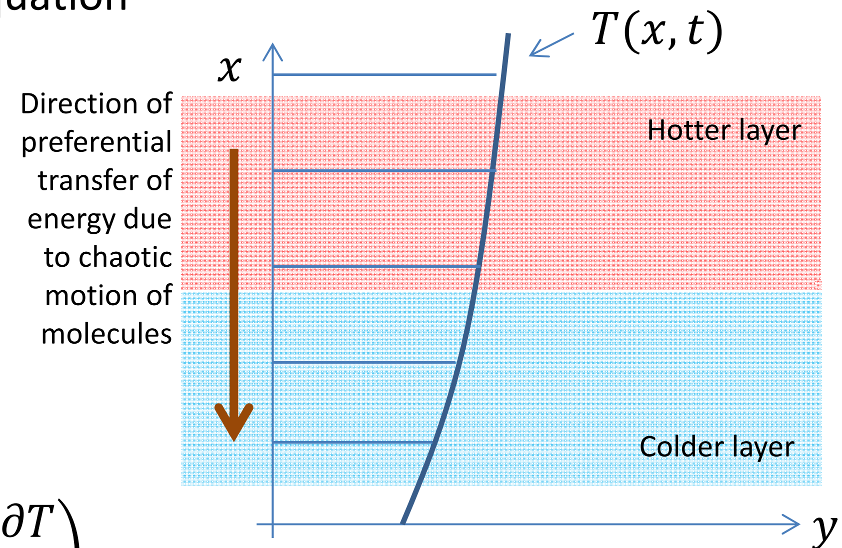
(1.7.12) $$\kappa = \frac{C\lambda}{6} mn \frac{3}{2}\frac{k_B}{m} = \mu c_V \sim \sqrt{T}$$

is called the **thermal conductivity (coefficient)**. The transfer equation takes the form

$$\frac{\partial}{\partial t}(\rho c_V T) = -\frac{\partial q_x}{\partial x}$$

(1.7.13) or

$$\frac{\partial}{\partial t}(\rho c_V T) = \frac{\partial}{\partial x}\left(\kappa \frac{\partial T}{\partial x}\right).$$



1.7. Diffusion, viscous drag, and heat conduction

and is called the **heat conduction equation**.

The heat flux density τ_{xy} has unit of J/s/m^2 = W/s . The linear relationship between the heat flux density and gradient of temperature, Eq. (1.7.11) is known as **Fourier's law of heat conduction**. It was first established experimentally. We showed that this experimental law in gases is explained by the chaotic motion of molecules.

Eq. (1.7.12) establishes two important facts that are in agreement with experiments:

1. Thermal conductivity of gases does not depend on number density
2. Thermal conductivity is proportional to viscosity i.e. varies with temperature as the viscosity does. Experiments show that the **Prandl number**

(1.7.14)
$$Pr = \frac{c_p \mu}{\kappa},$$

where c_p is the specific heat at constant pressure ($c_p = (5/2)R$ for a monatomic gas), in a "reasonable" range of T is independent of temperature and its value for many gases is about 2/3. Then κ varies with temperature as μ in Eq. (1.7.9), i.e. $\kappa = \kappa_0 (T/T_0)^\omega$.

Our elementary theory fails to predict the accurate value of *Pr*. The "accurate" kinetic theory shows that for any monatomic gas $Pr = 2/3$, and thus

(1.7.15)
$$\kappa = \frac{3}{2} c_p \mu.$$

In particular, for hard sphere molecules (use Eq. (1.7.10)),

(1.7.16)
$$\kappa = \frac{75\sqrt{\pi}}{64} \frac{k_B}{\sigma_T} \sqrt{\frac{k_B}{m} T}.$$

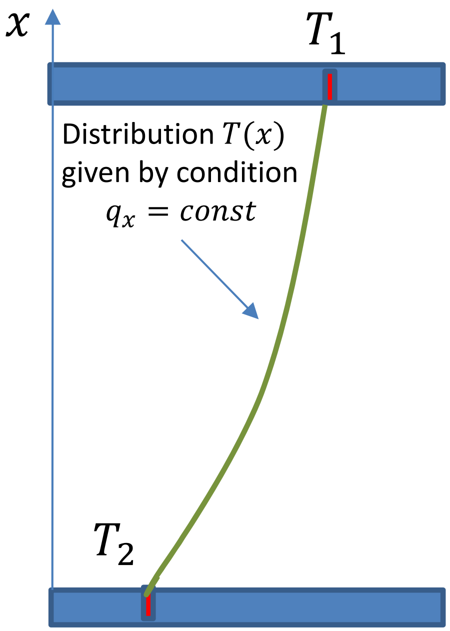
1.7. Diffusion, viscous drag, and heat conduction

The "standard" test problem for heat conduction is the steady-state *heat conduction in a gas between two parallel planes at fixed temperatures* T_1 and T_2.

This problem allows one to illustrate the principal difference between transfer processes in continuum and free molecular flow regime.

In free molecular flow, the temperature is constant because the flow is formed by two homogeneous streams of molecules that do not interact with each other: Stream of molecules moving from bottom to top and equilibrated with the bottom wall at temperature T_2 and stream of molecules moving from the top to the bottom and equilibrated with the top wall at T_1. Without collisions, energy between these two streams is not equilibrated.

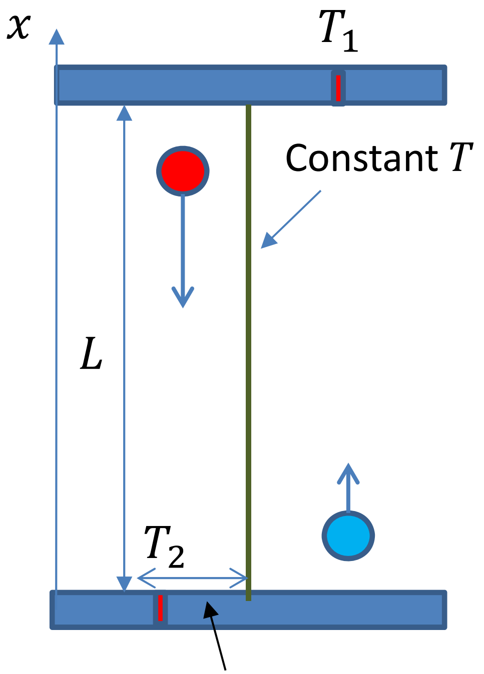
$Kn = \lambda / L \ll 1$



In heat conduction problem, the gas density n is not a constant, since for the mechanical equilibrium (no bulk velocity and macroscopic flow) pressure should be constant across domain, i.e. $n(x)$ is given by the condition

$$p = n(x) k_B T(x) = const.$$

$Kn = \lambda / L \gg 1$



Temperature jump: Difference between surface temperature and gas temperature

1.8. Appendix: Probability and Bernoulli trial

- Random outcome and event. Sure and impossible events
- Union and intersection of events. Compliment, and mutually exclusive events
- Statistical definition of probability of a random event
- Calculation of probabilities
- Dependent and independent random events. Conditional probability
- Bernoulli trial

1.8. Appendix: Probability and Bernoulli trial

Let's assume that we consider some stochastic system, process, or phenomenon that can be repeated many times in identical conditions.

- The **elementary event** or **outcome** A_i is the random output of any individual observation or measurement.
- The **event** A is an arbitrary set of possible outcomes.
- The **sure event** Ω is the event that includes all possible outcomes.
- The **impossible event** $\emptyset$ is an event that has no chance to occurring. It includes neither of the outcomes.

Example: Playing die

Stochastic process (experiment): Rolling the die and registering the number of dots N on the top face.

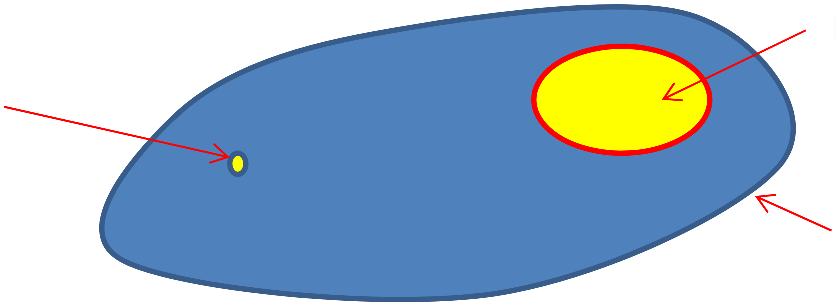
Outcome: The number of dots N on the top face after individual rolling of the die.

Possible outcomes:
$A_1 = \{N = 1\}, A_2 = \{N = 2\}, \ldots, A_6 = \{N = 6\}$

Examples of events:
$A = \{ N = 1 \text{ or } N = 5 \}$
$B = \{ N = 1 \text{ and } N > 4 \} = \{N = 1 \text{ or } N = 5 \text{ or } N = 6\}$
$\Omega = \{N = 1 \text{ or } N = 2 \text{ or } \ldots \text{ or } N = 5 \text{ or } N = 6 \}$
$\emptyset = \{N < 1 \text{ or } N > 6\}$

1.8. Appendix: Probability and Bernoulli trial

- Every elementary event is an **element** (point) of Ω.
- Every event is a **subset** of points of Ω.
- It is illustrative to use **Venn diagrams** to demonstrate the relationship between the sure event, elementary events, and various other events.

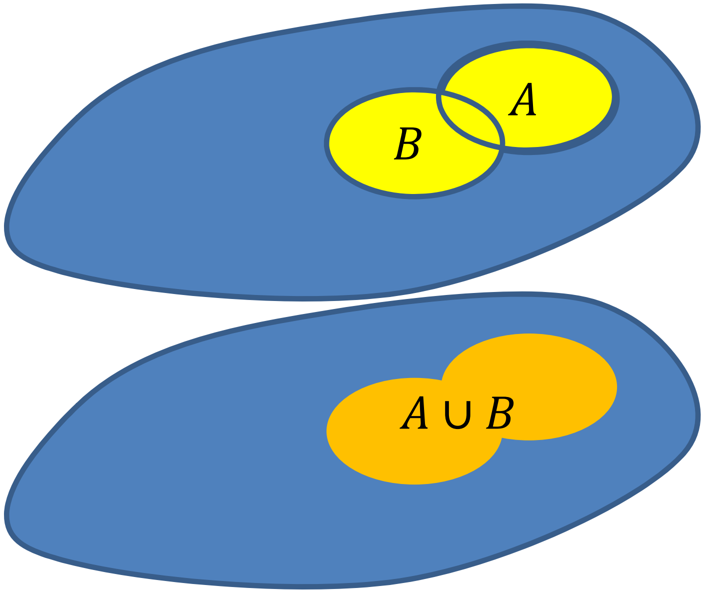


Elementary event, outcome, point A_i

Event A = subset, subarea

Sure event Ω, full set, full area

- A **union** $A \cup B$ of two events A and B is the event which happens if A **or** B happen.



Example: Playing die

$A = \{N = 1 \text{ or } N = 2\}$

$B = \{N = 2 \text{ or } N = 6\}$

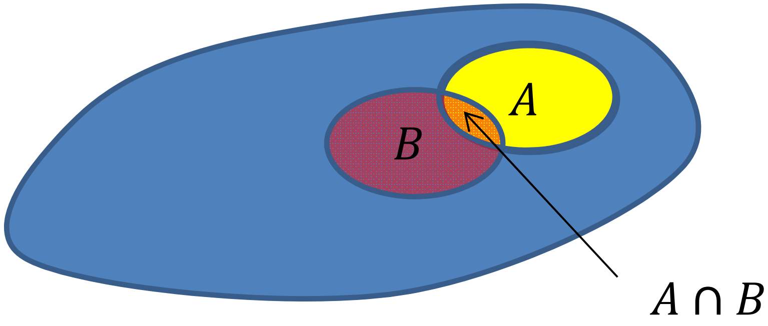
$C = \{N = 5\}$

$A \cup B = \{N = 1 \text{ or } N = 2 \text{ or } N = 6\}$

$A \cup C = \{N = 1 \text{ or } N = 2 \text{ or } N = 5\}$

1.8. Appendix: Probability and Bernoulli trial

- An **intersection** $A \cap B$ of two events A and B is the event which happens if A **and** B happen simultaneously.



Example: Playing die

$A = \{N = 1 \text{ or } N = 2\}$

$B = \{N = 2 \text{ or } N = 6\}$

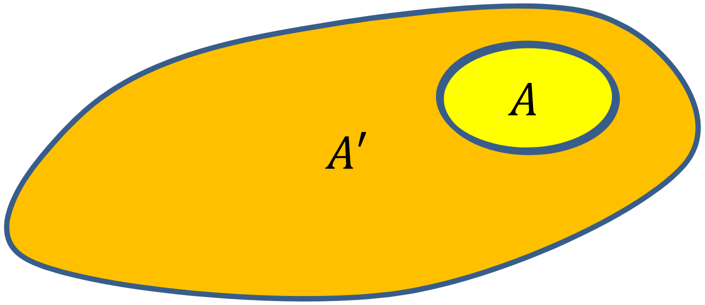
$C = \{N = 5\}$

$A \cap B = \{ N = 2 \}$

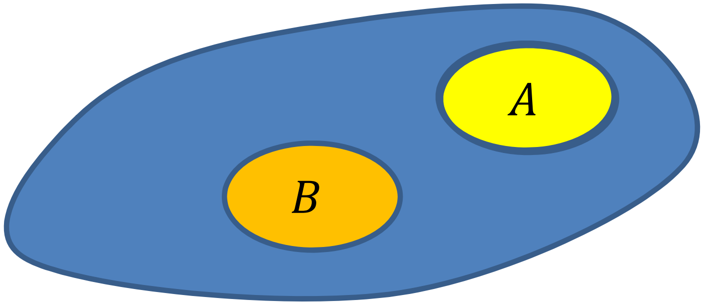
$A \cap C = \emptyset$

$A' = \{N = 3 \text{ or } N = 4 \text{ or } N = 6 \text{ or } N = 6\}$

- Event A' is called **compliment** to event A if $A \cup A' = \Omega$ and $A \cap A' = \emptyset$.
- Events A and B are called **mutually exclusive** if $A \cap B = \emptyset$.



A' is compliment to A

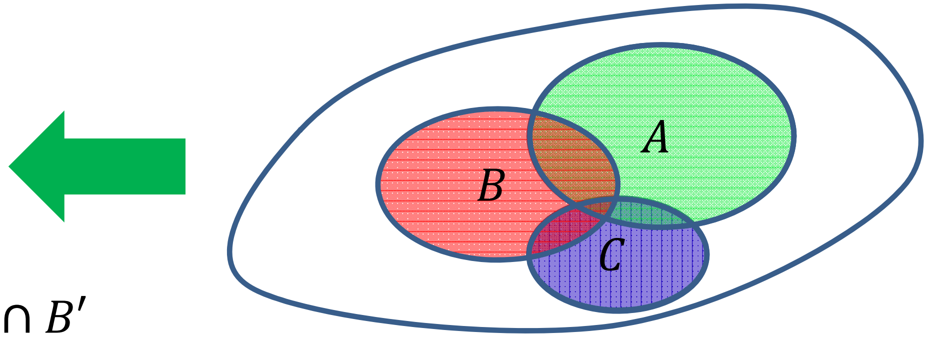


A and B are mutually exclusive

1.8. Appendix: Probability and Bernoulli trial

Simple rules for random events

- $(A')' = A$
- $A \cup B = B \cup A, A \cap B = B \cap A$
- $A \cup (B \cup C) = (A \cup B) \cup C$
- $A \cap (B \cup C) = (A \cap B) \cup (A \cap C)$
- $(A \cup B)' = A' \cup B', (A \cap B)' = A' \cap B'$
- $A \cup A = A, A \cap A = A$
- $A \cup \Omega = \Omega, A \cap \Omega = A$
- $A \cup \emptyset = A, A \cap \emptyset = \emptyset$



All these rules can be easily proved with Venn diagrams.

Probability of a random event

Probability of a random event A is a numerical measure of our degree of confidence that the event A happen during a single outcome (experiment, measurement) of the considered stochastic system (process, phenomenon).

There are at least four different definitions of probability. We will use only an intuitively clear, **statistical definition** of probability.

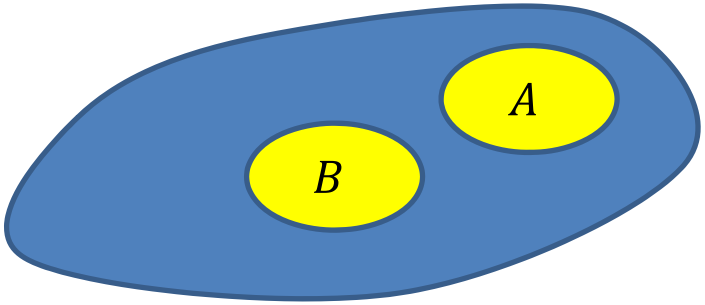
1.8. Appendix: Probability and Bernoulli trial

Let's assume that we repeat our observation (experiment) N times ($N \gg 1$) independently from each other, but in identical conditions and random event A happened $N(A)$ times among N.

Probability $P(A)$ of event A is the *relative frequency* of this event among others, calculated in the limit $N \to \infty$:

$$\boxed{P(A) = \lim_{N\to\infty} \frac{N(A)}{N}} \qquad (1.8.1)$$

Simple properties of probability drawn from the fact that $N(A) \le N$ for any random event:



- $0 \le P(A) \le 1$.
- $P(\emptyset) = 0$, because $N(\emptyset) = 0$.
- $P(\Omega) = 1$, because $N(\Omega) = N$.
- If $A \subset B$, then $P(A) \le P(B)$, because $N(A) \le N(B)$.
- If A and B are mutually exclusive events ($A \cap B = \emptyset$), the probability of a union is equal to the sum of probabilities (**summation rule**):

  $$\boxed{P(A \cup B) = P(A) + P(B)} \qquad (1.8.2)$$

  because for mutually excusive events $N(A \cup B) = N(A) + N(B)$.
- Since $A \cup A' = \Omega$, $A \cap A' = \emptyset$, then $P(\Omega) = P(A) + P(A')$ and $P(A') = 1 - P(A)$.

1.8. Appendix: Probability and Bernoulli trial

Independent events and conditional probability

The **conditional probability** $P(A|B)$ is the probability of event A calculated under the condition that event B occurs. This probability accounts for the fact that occurrence of event B changes probability of event A:

$$P(A|B) = \lim_{N\to\infty} \frac{N(A\cap B)}{N(B)} = \lim_{N\to\infty} \frac{N(A\cap B)/N}{N(B)/N} = \frac{P(A\cap B)}{P(B)} \qquad (1.8.3)$$

or

$$P(A\cap B) = P(A|B)P(B) = P(B|A)P(A) \qquad (1.8.4)$$

It is reasonably to call two random events A and B **independent** if the happening of one of these event does not affect the probability of occurrence of another, i.e. if $P(A|B) = P(A)$ and $P(B|A) = P(B)$.

In order to draw Eq. (1.8.3), B has to occur, i.e. $P(B) \neq 0$.

Then for independent events A and B we have the **multiplication rule**:

$$\boxed{P(A\cap B) = P(A)P(B) \quad \Longleftrightarrow \quad A \text{ and } B \text{ are independent}} \qquad (1.8.5)$$

The main purpose of the probability theory is to formulate rules that allow us to calculate probabilities of complex events based on known probabilities of simple events.

1.8. Appendix: Probability and Bernoulli trial

Example: Non-independent events

A box contains 10 screws, three of which are defective. Two screws are drawn at random. Find the probability that neither of the two screws is defective.

Solution: We consider the events:

- A: First drawn screw nondefective
- B: Second drawn screw nondefective

Two possible scenario:

1. The second screw is drawn **with replacement**: We put the first screw back to the box and then draw the second one. A and B are independent.
2. The second screw is drawn **without replacement**: We draw the second from 9 screws in the box. A and B are dependent.

Clearly, $P(A) = \frac{7}{10}$ because 7 of the 10 screws are nondefective and we sample at random, so that each screw has the same probability $(\frac{1}{10})$ of being picked. If we sample with replacement, the situation before the second drawing is the same as at the beginning, and $P(B) = \frac{7}{10}$. The events are independent, and the answer is

$$P(A \cap B) = P(A)P(B) = 0.7 \cdot 0.7 = 0.49 = 49\%.$$

If we sample without replacement, then $P(A) = \frac{7}{10}$, as before. If A has occurred, then there are 9 screws left in the box, 3 of which are defective. Thus $P(B|A) = \frac{6}{9} = \frac{2}{3}$, and Eq. (5.2.3) yields the answer

$$P(A \cap B) = \frac{7}{10} \cdot \frac{2}{3} = 47\%.$$

1.8. Appendix: Probability and Bernoulli trial

The previous example falls into general category of problems known as Bernoulli trial that can be solved with or without replacement. We will consider the Bernoulli trial with replacement.

Bernoulli trial with replacement

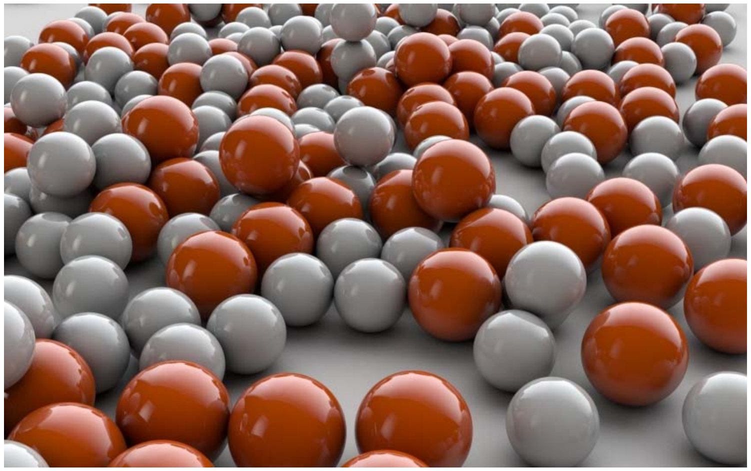
A **Bernoulli trial** (or **binomial trial**) is a random experiment or test with exactly two possible outcomes, "success" and "failure", in which the known probability of success is the same every time the experiment is conducted.

Two elementary events (outcomes): A_1, A_2. The sure event $\Omega = \{A_1, A_2\}$

Two known probabilities of every outcome: $p = P(A_1)$, $q = P(A_2) = 1 - p$.

Example 1: Rolling die. $A_1 = \{N = 6\}$, $A_2 = \{1 \leq N \leq 5\}$, $p = 1/6$, $q = 5/6$.

Example 2: A pile of L grey and *M* red balls. We pick up at random one ball from the pile, determine its color and *return* the ball to the pile.



$A_1 = \text{Ball is gray}, P(A_1) = p = L/(L+M)$.

$A_2 = \text{Ball is red}, P(A_2) = q = M/(L+M) = 1 - p$.

This is the **Bernoulli trial with replacement**, since every test is performed in the *same conditions* (We determine color and *return* ball to the pile).

1.8. Appendix: Probability and Bernoulli trial

Assume that we performed the test n times. The major question in the Bernoulli trial is: What is the probability $P(k)$ of choosing k ($0 \leq k \leq n$) grey balls after n test?
First let's consider an example when $n = 3$ and calculate $P(1)$.
In three sequential tests we can chose 1 grey ball as follows

Event	Test 1	Test 2	Test 3	Probability (all tests in a sequence are independent)
Event $A1$	Grey	Red	Red	$P(A1) = pqq = p^k\,(1-p)^{n-k}$
Event $A2$	Red	Grey	Red	$P(A2) = qpq = p^k\,(1-p)^{n-k}$
Event $A3$	Red	Red	Grey	$P(A3) = qqp = p^k\,(1-p)^{n-k}$

Since events $A1$, $A2$, and $A3$ are mutually excusive, one can use the summation rule:

$$P(1) = P(A1 \cup A2 \cup A3) = P(A1) + P(A2) + P(A3) = 3p_1^1(1-p_1)^2$$

In the general case (arbitrary n and k) one can obtain:

$$\boxed{P(k) = \binom{n}{k} p^k\,(1-p)^{n-k}} \qquad (1.8.6)$$

where the integer value denoted as $\binom{n}{k}$ is called the **binomial coefficient** and is equal to the number of different events with k grey balls drawn in n tests

$$\binom{n}{k} = \frac{n!}{k!\,(n-k)!}$$

In our example ($n = 3$ and $k = 1$), $\binom{3}{1} = \frac{3!}{1!(3-1)!} = \frac{3\cdot2\cdot1}{1\cdot2\cdot1} = 3$.