Chapter 2
Molecular models

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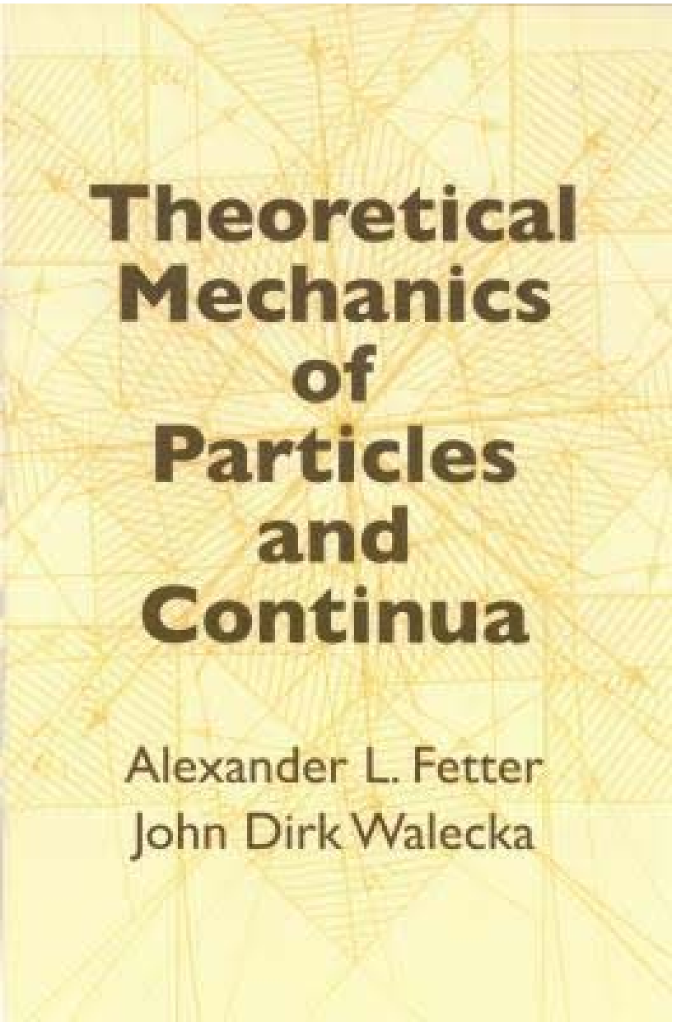
Additional reading:

Sections 1.4, 1.5



Theoretical
Mechanics
of
Particles
and
Continua

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2.1. Degrees of freedom. Molecular models. Simple gas

- Degrees of freedom and energy of molecules
- Molecular model
- Simple gas

1.1. Degrees of freedom. Molecular models. Simple gas

Degrees of freedom of molecules

In mechanics, **the number of degrees of freedom** is the number of independent motions that are allowed to a body or the number of independent parameters that are necessary to describe the position of a body.

An atom considered as point mass has 3 **translational degrees of freedom** (three coordinates are necessary to described its position).

A rigid body has 6 degrees of freedom, 3 coordinates of the center of mass and 3 angles that describe orientation of a body with respect to axis of coordinate system.

N-atomic molecule (molecule composed of N atoms) has $3N$ degrees of freedom, since every atom can move with respect to others. It is convenient to consider the overall motion of individual atoms in the molecule as a composition or "superposition" of three types of motion

- **Translational motion** of the center of mass of molecules (N_{tr} =3 translational degrees of freedom).
- **Rotational motion** of molecule as a whole around the center of mass (N_{rot} =2 or 3 **rotational degrees of freedom**).
- Relative or **vibrational motion** of atoms with respect to each other with

$$N_{vibr} = 3N - 3 - N_{rot}$$

vibrational or **internal degrees of freedom**.

Both rotational and vibrational degrees of freedom are often called the **internal degrees of freedom**.

1.1. Degrees of freedom. Molecular models. Simple gas

Monatomic molecule (atom): $N = 1$, $N_{tr} = 3$, $N_{rot} = 0$, $N_{vibr} = 0$.
Diatomic molecule: $N = 2$, $N_{tr} = 3$, $N_{rot} = 2$, $N_{vibr} = 1$.
Triatomic molecule: $N = 3$, $N_{tr} = 3$, $N_{rot} = 3$, $N_{vibr} = 3$.

Then the total energy of N-atomic molecule of mass m can be written as

(2.1.1)
$$E = E_{tr} + E_{rot} + E_{vibr},$$

where $E_{tr} = m\mathbf{v}_c^2/2$ is the **translational energy**, E_{rot} is the **energy of rotational degrees of freedom**, and E_{vibr} is the **energy of vibrational degrees of freedom**.

The importance of the representation of motion of atoms in a molecule in the form of superposition of translational, rotational, and vibrational motions is based on the fact that E_{tr}, E_{rot}, and E_{vibr} can play different role in collisions. For example, at standard conditions, the vibrational degrees of freedom of N_2 and O_2 are not excited (i.e., E_{vibr} does not change during collisions). Then one can neglect E_{vibr} in Eq. (2.1.1) and assume that a molecule has 5 degrees of freedom. This approach is routinely used in thermodynamics of diatomic gases.

Energy exchange between vibrational and over degrees of freedom can be described only based on quantum mechanics (vibrational energy is quantized). The translational and often rotational degrees of freedom can be satisfactory described by classical mechanics.

A collision is called **elastic** if total translational energy of colliding molecules before and after the collision does not change, i.e. if there is no energy exchange between translational and other degrees of freedom and

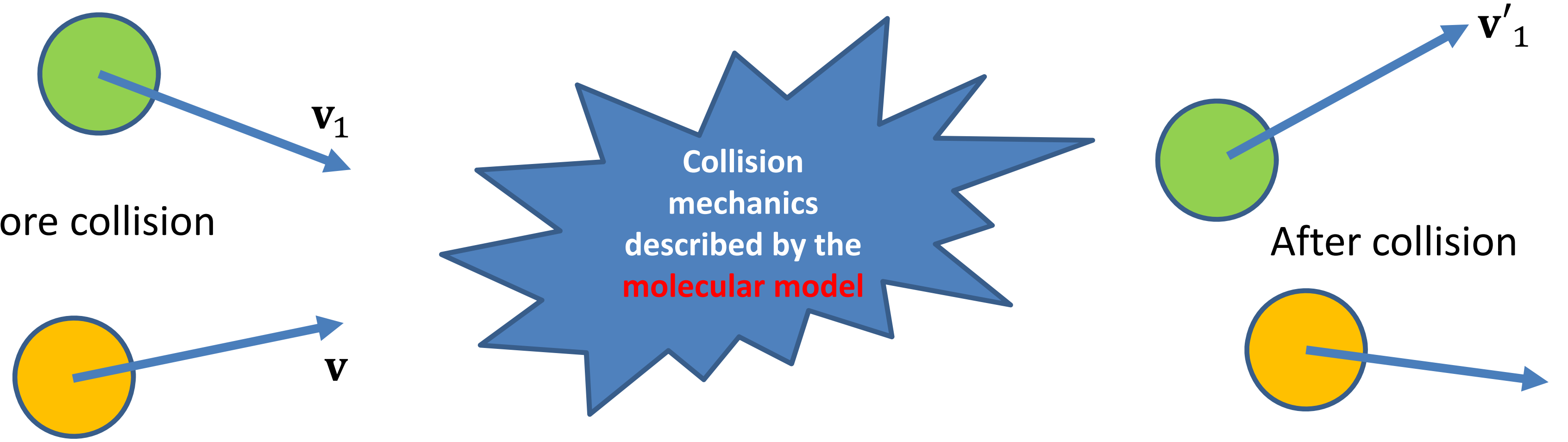
$$E_{tr1} + E_{tr2} = E'_{tr1} + E'_{tr2}.$$

We use prime to denote parameters of molecules after a collision

2.1. Degrees of freedom. Molecular models. Simple gas

Molecular model

The kinetic theory describes process in gases that happen on the length and time scale that are much larger than the length and time scales of individual collision. From this point of view, any collision is considered as an instant change of molecular velocities and internal variables from the state before the collision to the state after the collision



Molecular model is a model that describes internal structure of individual molecules and their interactions with each other and allows one to predict velocities and internal state variables (e.g., E_{rot} and E_{vibr}) of molecules after a binary collision as functions of their velocities and internal state variables before the collision as well as parameters specifying relative position of molecules during collision. A molecular model allows one to establish the following relationships

$$\mathbf{v}' = \mathbf{v}'(\mathbf{v}, \mathbf{v}_1, \dots), \qquad \mathbf{v'}_1 = \mathbf{v'}_1(\mathbf{v}, \mathbf{v}_1, \dots).$$

2.1. Degrees of freedom. Molecular models. Simple gas

In order to establish such relationships, we need to consider in detail the process of individual binary collision based on a known law of interaction between molecules.

“Simple” gas

In our course, we will consider only molecular models of a **“simple” gas**, i.e. a gas where all molecules are identical, and every molecule is considered as a point mass m without internal structure, which does not chance its physical properties under any conditions (no chemical reactions, ionization, etc.).

In this model, every molecule has only three translation degree of freedom and all binary collisions are elastic. Interaction forces between molecules then must be

- **Potential** or **conservative** (i.e. they have potential energy; if this is not the case then energy conservation law cannot be satisfied) and
- **Central** (i.e. directed along the line connecting the centers of interacting molecules; if this is not the case then the angular momentum conservation law cannot be satisfied).

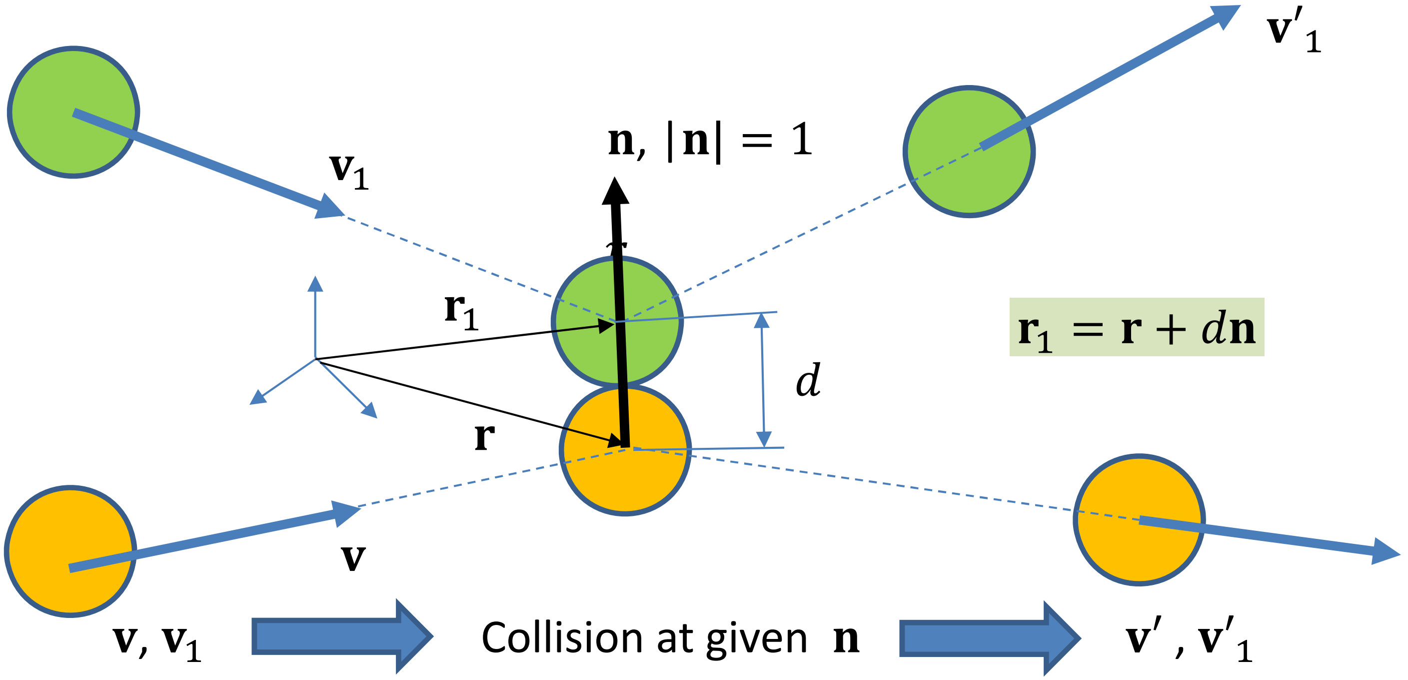
Such model accurately describes properties of **monatomic gases** composed of individual atoms (noble gases, atomic vapors of various substances), but it can be also used for quantitative (and, sometimes quantitative) studies of gases composed of polyatomic molecules.

2.2. Model of hard sphere (HS) molecules

- Model of hard sphere (HS) molecules
- Conservation law during a collision of hard spheres
- Relationship between velocities before and after collision

2.2. Model of Hard Sphere (HS) molecules

The **model of hard sphere (HS) molecules** is the molecular model, when individual molecules are considered as non-deformable, non-rotating spheres of diameter d. Binary collision of HS molecules is assumed to be an instant change of velocities of colliding molecules when molecules “touch” each other, i.e. when distance between centers of spheres is equal to d.



$\mathbf{v}, \mathbf{v}_1$ ⇒ Collision at given $\mathbf{n}$ ⇒ $\mathbf{v}', \mathbf{v}'_1$

The state of molecules before the collision is characterized by velocities $\mathbf{v}$ and $\mathbf{v}_1$, and relative position is characterized by the *unit vector* $\mathbf{n}$. Our major goal is to calculate velocities after the collision $\mathbf{v}'$ and $\mathbf{v}'_1$ as functions of $\mathbf{v}$ and $\mathbf{v}_1$, and $\mathbf{n}$.

We will show that unique values of $\mathbf{v}$ and $\mathbf{v}_1$ can be derived from the conservation laws *assuming instant collision between non-deformable spheres*.

2.2. Model of Hard Sphere (HS) molecules

Conservation laws during a collision of hard spheres

In closed mechanical systems, linear momentum, angular momentum, and total energy conserve. Let's write the equations of conservation of these quantities for two states right before and after the collision, when positions of molecules are given by $\mathbf{r}$ and $\mathbf{r}_1$:

(2.2.1) $$m\mathbf{v} + m\mathbf{v}_1 = m\mathbf{v}' + m\mathbf{v}'_1,$$

(2.2.2) $$\mathbf{r} \times (m\mathbf{v}) + \mathbf{r}_1 \times (m\mathbf{v}_1) = \mathbf{r} \times (m\mathbf{v}') + \mathbf{r}_1 \times (m\mathbf{v}'_1),$$

(2.2.3) $$\frac{m\mathbf{v}^2}{2} + \frac{m\mathbf{v}_1^2}{2} = \frac{m\mathbf{v}'^2}{2} + \frac{m\mathbf{v}_1'^2}{2}.$$

HS model describes only elastic collisions

In order to simplify these equations let's introduce the center of mass velocity $\mathbf{v}_c$, relative velocity $\mathbf{c}_r$, and represent $\mathbf{r}_1$ as $\mathbf{r}_1 = \mathbf{r} + d\mathbf{n}$:

(2.2.4) $$\mathbf{v}_c = \frac{m\mathbf{v} + m\mathbf{v}_1}{m + m} = \frac{\mathbf{v} + \mathbf{v}_1}{2}, \qquad \mathbf{c}_r = \mathbf{v}_1 - \mathbf{v},$$

(2.2.5) $$\mathbf{v} = \mathbf{v}_c - \frac{\mathbf{c}_r}{2}, \qquad \mathbf{v}_1 = \mathbf{v}_c + \frac{\mathbf{c}_r}{2}.$$

Then Eq. (2.2.1) reduces to

(2.2.6) $$\mathbf{v}'_c = \mathbf{v}_c,$$

This is the consequence of the linear momentum conservation law

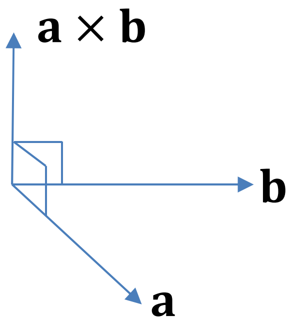
i.e. the center-of-mass velocity does not change during the collision. Eq. (2.2.2) reduces to

$$\mathbf{r} \times \left(\mathbf{v}_c - \frac{\mathbf{c}_r}{2}\right) + (\mathbf{r} + d\mathbf{n}) \times \left(\mathbf{v}_c + \frac{\mathbf{c}_r}{2}\right) = \mathbf{r} \times \left(\mathbf{v}'_c - \frac{\mathbf{c}'_r}{2}\right) + (\mathbf{r} + d\mathbf{n}) \times \left(\mathbf{v}'_c + \frac{\mathbf{c}'_r}{2}\right).$$

2.2. Model of Hard Sphere (HS) molecules

In the last equation, most of terms cancel each other, so it reduces to

(2.2.7)
$$\mathbf{n} \times \mathbf{c}_r = \mathbf{n} \times \mathbf{c}'_r.$$



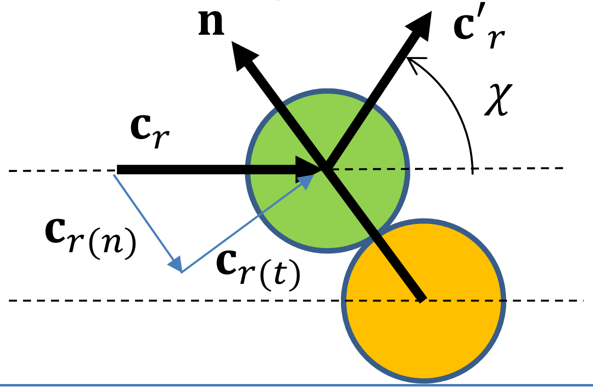
Note that cross product $\mathbf{a} \times \mathbf{b}$ is a vector orthogonal to the plane of vectors $\mathbf{a}$ and $\mathbf{b}$. Then vectors $\mathbf{n}$, $\mathbf{c}_r$, and $\mathbf{c}_r$ lye in the same plane. This plane is called the **collisions plane**. This is the first consequence of the angular momentum conservation law. Eq. (2.2.3) reduces to

$$\left(\mathbf{v}_c - \frac{\mathbf{c}_r}{2}\right)^2 + \left(\mathbf{v}_c + \frac{\mathbf{c}_r}{2}\right)^2 = \left(\mathbf{v}_c{}' - \frac{\mathbf{c}'_r}{2}\right)^2 + \left(\mathbf{v}'_c + \frac{\mathbf{c}'_r}{2}\right)^2$$

or

(2.2.8)
$$\mathbf{c}_r'^2 = \mathbf{c}_r^2,$$

i.e. the absolute value of relative velocity does not change during the collision. This is the consequence of the energy conservation law. *Thus, the only result of the collision is the deflection of the relative velocity vector on angle χ in the collision plane.* The angle χ is called the **deflection angle**.



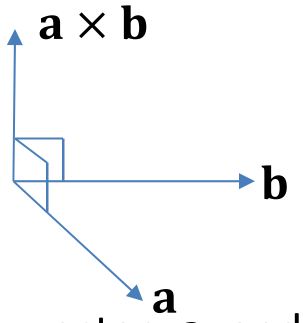
In order to find χ, let's introduce normal (along center-to-center direction $\mathbf{n}$) and tangential components of vector $\mathbf{c}_r$,

$$\mathbf{c}_{r(n)} = (\mathbf{c}_r \cdot \mathbf{n})\mathbf{n},$$
$$\mathbf{c}_{r(t)} = \mathbf{c}_r - \mathbf{c}_{r(n)},$$

and apply Eq. (2.2.7):

2.2. Model of Hard Sphere (HS) molecules

$$\mathbf{n} \times \left(\mathbf{c}_{r(n)} + \mathbf{c}_{r(t)}\right) = \mathbf{n} \times \left(\mathbf{c}'_{r(n)} + \mathbf{c}'_{r(t)}\right)$$



or

$$\mathbf{n} \times \mathbf{c}_{r(t)} = \mathbf{n} \times \mathbf{c}'_{r(t)}.$$

Now we can multiply the last equation by $\mathbf{n}$:

$$\left(\mathbf{n} \times \mathbf{c}_{r(t)}\right) \times \mathbf{n} = \left(\mathbf{n} \times \mathbf{c}'_{r(t)}\right) \times \mathbf{n}.$$

Using the definition of the cross product, one can prove that for arbitrary vector $\mathbf{a}$ and orthogonal unit vector $\mathbf{n}$ the following equation holds: $(\mathbf{n} \times \mathbf{a}) \times \mathbf{n} = \mathbf{a}$. Thus, the last equation reduces to

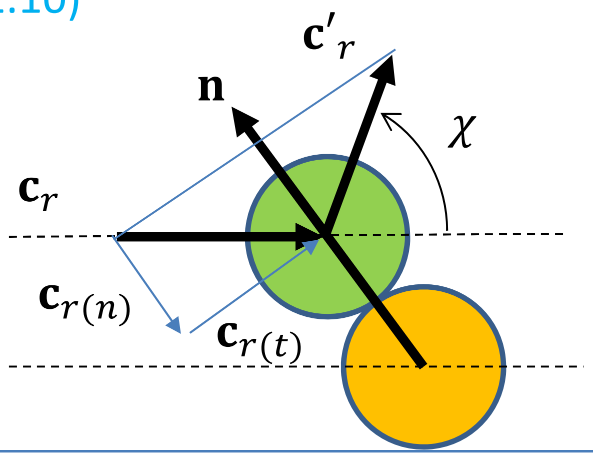
(2.2.9)

$$\mathbf{c}'_{r(t)} = \mathbf{c}_{r(t)}.$$

This is the second consequence of Eq. (2.2.2): The tangential component of the relative velocity does not change during the collision. Then Eq. (2.2.8) and (2.2.9) show that the only result of collisions of HS is the change of the direction of the normal component of the relative velocity:

(2.2.10)

$$\mathbf{c}'_{r(n)} = -\mathbf{c}_{r(n)}.$$



Then combining Eqs. (2.2.9) and (2.2.10) one can obtain

$$\mathbf{c}'_r = \mathbf{c}_{r(t)} - \mathbf{c}_{r(n)},$$

$$\mathbf{c}'_r = \mathbf{c}_r - 2(\mathbf{c}_r \cdot \mathbf{n})\mathbf{n}.$$

(2.2.11)

Eq. (2.2.11) completely describes mechanics of collision of HS molecules.

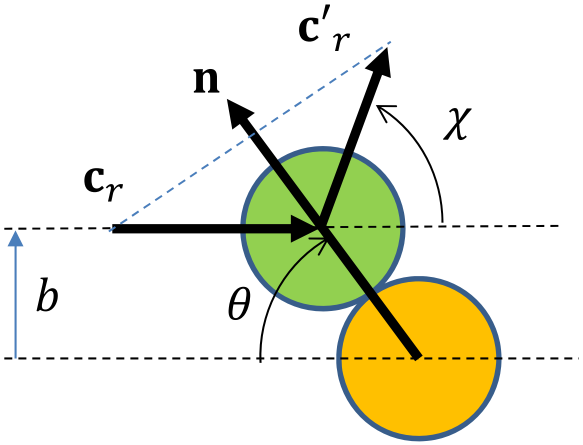
2.2. Model of Hard Sphere (HS) molecules

Relationship between velocities before and after collision

Now we can combine Eqs. (2.2.5), (2.2.6), and (2.2.11) in order to obtain $\mathbf{v}$ and $\mathbf{v}_1$:

(2.2.12)

$$\mathbf{v}' = \mathbf{v} + [(\mathbf{v}_1 - \mathbf{v}) \cdot \mathbf{n}]\mathbf{n},$$
$$\mathbf{v}'_1 = \mathbf{v}_1 - [(\mathbf{v}_1 - \mathbf{v}) \cdot \mathbf{n}]\mathbf{n}.$$



Relative position of molecules during the collision can be defined by the **collision parameter** b (see figure). Then

$$\sin\theta = \frac{b}{d}, \qquad (2.2.13)$$

$$\chi = \pi - 2\theta = \pi - 2\,\mathrm{asin}\left(\frac{b}{d}\right). \qquad (2.2.14)$$

In the HS model, the internal structure of molecules is neglected, so that this model is applicable primarily for collisions of monatomic molecules (noble gases, dissociated oxygen and nitrogen, metal vapors, etc.). Although this model crudely approximates the real process of interaction between molecules, it is historically the first and currently one of the most popular models in the kinetic theory. It is capable of qualitatively description of collisional process in multiple applications of RGD.

The predictions based on the HS model can be often brought in quantitative agreement with more complicated models and experiments by the appropriate choice of HS diameter d.

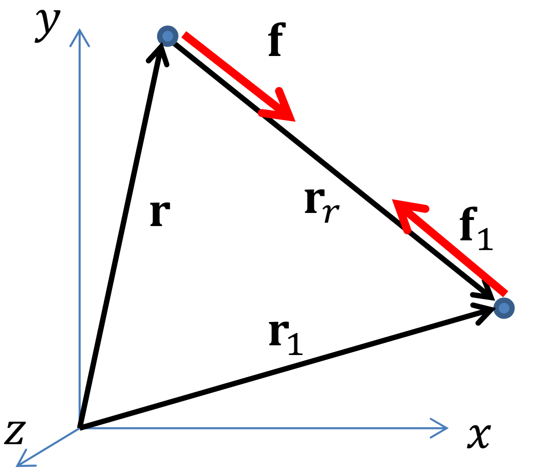
2.3. Interatomic potentials

- Interatomic potentials of monatomic gases
- Lennard-Jones potential
- Repulsive potential
- Morse potential
- Calculation of forces

2.3. Interatomic potentials

Interatomic potentials of monatomic gases

$$r_r = |\mathbf{r}_r| = |\mathbf{r}_1 - \mathbf{r}|$$



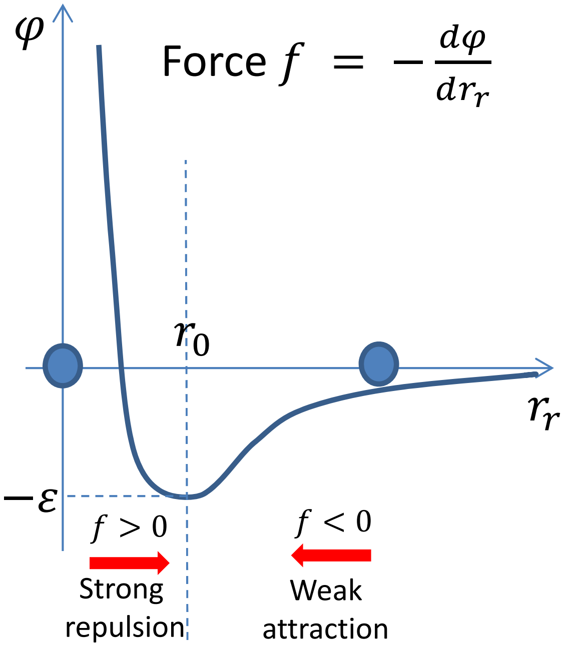
In the case of a monatomic gas, when every molecule is a point mass that has only translational energy, it is naturally to assume that the forces between molecules are **conservative**, i.e. preserve total mechanical energy, and **central**, i.e. directed along a line connecting interacting particles.

Then, it is shown in mechanics that interaction forces can be completely defined by the **potential energy** (often called **interatomic potential**) φ *that depends only on distance between molecules* r_r, $\varphi = \varphi(r_r)$, and interaction forces are equal to

$$\mathbf{f} = -\nabla_{\mathbf{r}}\varphi = -\frac{\partial\varphi}{\partial\mathbf{r}} = -\left(\frac{\partial\varphi}{\partial x}\mathbf{i}+\frac{\partial\varphi}{\partial y}\mathbf{j}+\frac{\partial\varphi}{\partial z}\mathbf{k}\right),$$

We will systematically use this notation for vectors of **gradients**

$$\mathbf{f}_1 = -\nabla_{\mathbf{r}_1}\varphi = -\frac{\partial\varphi}{\partial\mathbf{r}_1} = -\left(\frac{\partial\varphi}{\partial x_1}\mathbf{i}+\frac{\partial\varphi}{\partial y_1}\mathbf{j}+\frac{\partial\varphi}{\partial z_1}\mathbf{k}\right).$$



Physical experiments in molecular physics and quantum mechanical calculations show that typical dependence of φ on r_r looks like shown in the picture. Distance between particles r_0 when $f = 0$ is the **equilibrium distance** and $\varepsilon = -\varphi(r_0)$ is the **depth of the potential well**.

2.3. Interatomic potentials

Actual dependences of φ on r_r are complicated or unknown. So for practical purposes, $\varphi(r_r)$ is approximated by a some simple function. Such approximations are called **model potentials**.

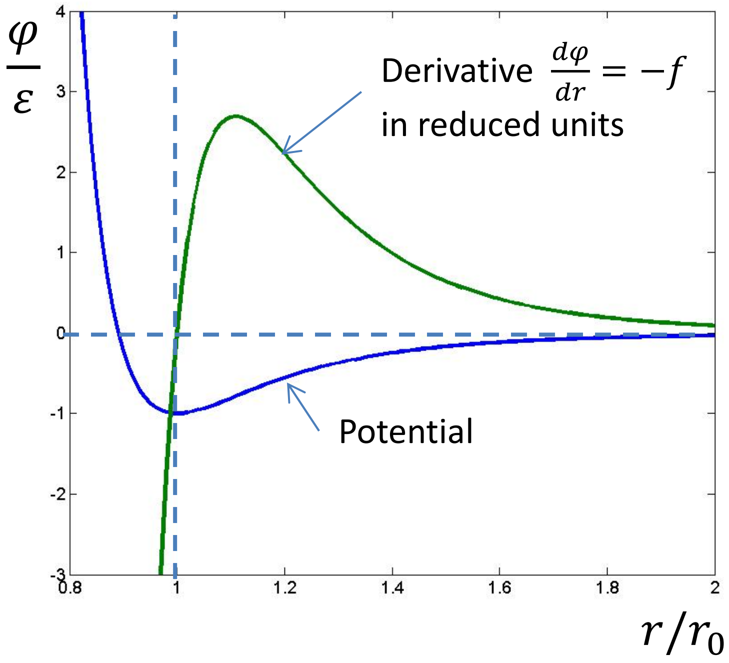
Lennard-Jones potential

The model potential in the form of a difference of two power functions

$$\varphi(r) = \frac{A}{r^m} - \frac{B}{r^n}, \tag{2.3.1}$$

where A, B, m, and n are given constants, is called the **(generalized) Lennard-Jones potential**. The first term describes repulsion at $r < r_0$, and the second term describes attraction at $r > r_0$.

It is shown in quantum mechanics that the van der Waals attraction is described by the potential that varies as $\sim 1/r^6$, so usually $n = 6$. Adequate description of the repulsive force requires $m = 11 - 15$, so the average value $m = 12$ is often used. For the particular choice of $m = 12$ and $n = 6$, Eq. (2.3.1) can be re-written as



$$\varphi(r) = \varepsilon\left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6}\right] \tag{2.3.2}$$

or

$$\sigma = r_0/\sqrt[6]{2}$$

$$\varphi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{2.3.3}$$

and called **(12-6) Lennard-Jones potential** or simply **Lennard-Jones potential**. In Eqs. (2.3.2) and (2.3.3), ε is the depth of the potential well and r_0 is the equilibrium distance.

2.3. Interatomic potentials

In the reduced units, φ/ε and r/r_0, the Lennard-Jones potential is unique and we cannot control the width of the potential well.

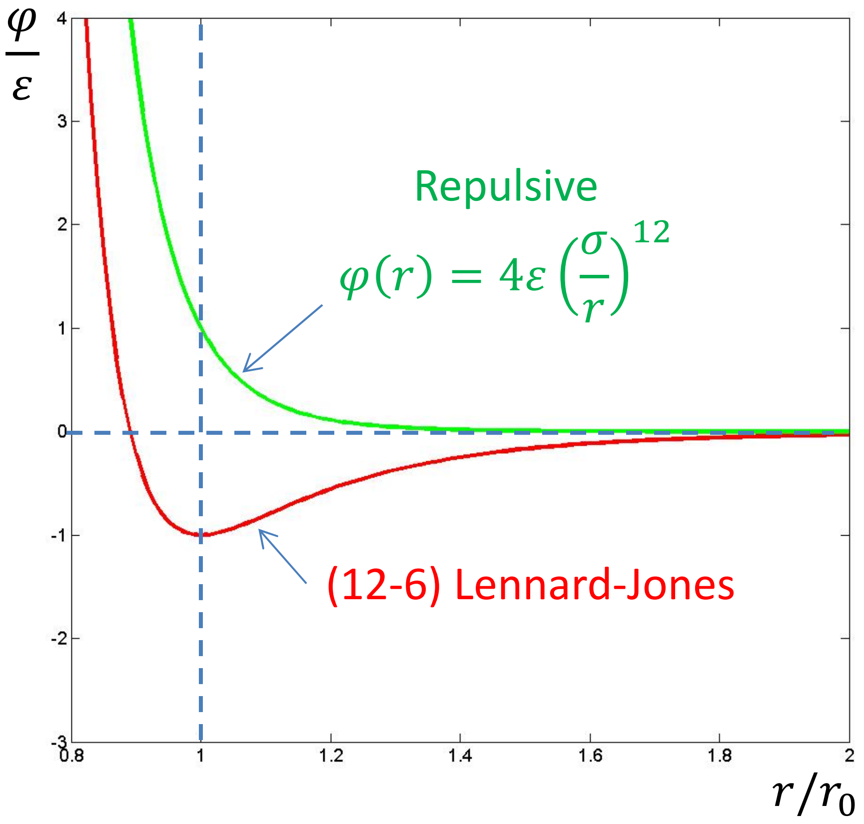
Repulsive potential

In gas flows without phase changes (e.g., condensation), the repulsive forces play the primary role, while the effect of attraction is often marginal. Then one can simplify the molecular model given by the Eq. (2.3.1) by neglecting the attraction term and using purely the **repulsive potential**

(2.3.4) $$\varphi(r) = \frac{A}{r^s},$$

where constants A and s can be chosen to match a given gas property, usually viscosity, at a given temperature.

The molecular models based on the repulsive potentials are the most popular models for modelling of monatomic gas flows.



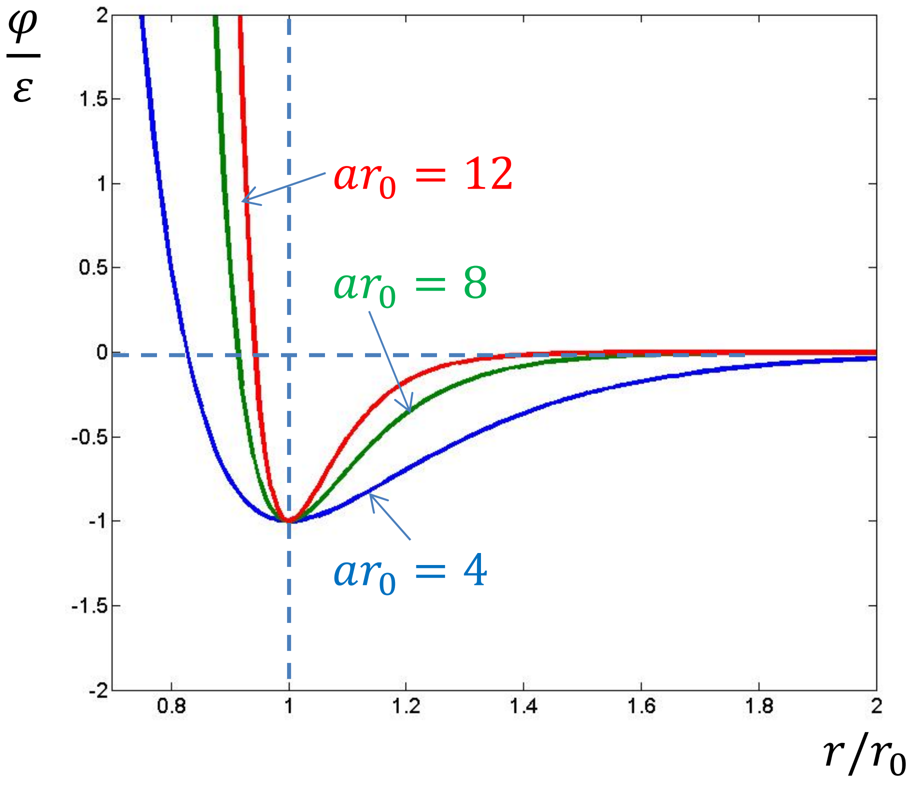
2.3. Interatomic potentials

Morse potential

The model potential in the form

(2.3.5) $$\varphi(r) = \varepsilon\left(e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}\right),$$

where ε, r_0, and a are given constants, is called the **Morse potential**. In Eq. (2.3.5), ε is the depth of the potential well, r_0 is the equilibrium distance, and a is an additional parameter that determines the bond "rigidity" close to the equilibrium position.



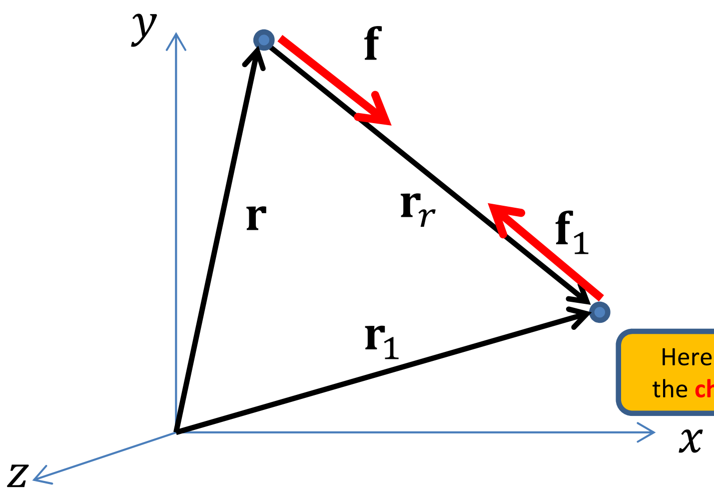
The Morse potential has three adjustable parameters that can be used to match three material properties known from experiments.

Parameter a can use used, in particular, in order to vary the width of the potential well: With increasing a, the width of the potential well decreases, as illustrated in the figure, and potential becomes more “stiff” around the equilibrium distance.

In the reduced units, φ/ε and r/r_0, the Morse potential is defined by the only one parameter ar_0.

2.3. Interatomic potentials

Calculation of forces



$$\mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k},$$

$$\mathbf{r}_1 = x_1\mathbf{i} + y_1\mathbf{j} + z_1\mathbf{k},$$

$$\mathbf{r}_r = \mathbf{r}_1 - \mathbf{r} = x_r\mathbf{i} + y_r\mathbf{j} + z_r\mathbf{k},$$

$$r_r = |\boldsymbol{r}_r| = \sqrt{(x_1 - x)^2 + (y_1 - y)^2 + (z_1 - z)^2},$$

$$\varphi(r_r) = \varphi(x_r, y_r, z_r) = \varphi(x, y, z, x_1, y_1, z_1).$$

Here we use the **chain rule**

$$\frac{\partial\varphi}{\partial x} = \frac{d\varphi}{dr_r}\frac{\partial r_r}{\partial x} = -\frac{d\varphi}{dr_r}\frac{x_1 - x}{r_r} \qquad \frac{\partial\varphi}{\partial x_1} = \frac{d\varphi}{dr_r}\frac{\partial r_r}{\partial x_1} = \frac{d\varphi}{dr_r}\frac{x_1 - x}{r_r} \qquad \frac{\partial\varphi}{\partial x_r} = \frac{d\varphi}{dr_r}\frac{\partial r_r}{\partial x_r} = \frac{d\varphi}{dr_r}\frac{x_r}{r_r} = \frac{\partial\varphi}{\partial x_1}$$

In mechanics, the potential force exerted on a point mass is equal to the negative gradient of the potential energy with respect to coordinates of this particle:

$$\mathbf{f} = -\frac{\partial\varphi}{\partial\mathbf{r}} = -\left(\frac{\partial\varphi}{\partial x}\mathbf{i} + \frac{\partial\varphi}{\partial y}\mathbf{j} + \frac{\partial\varphi}{\partial z}\mathbf{k}\right) = \frac{d\varphi}{dr_r}\frac{\mathbf{r}_r}{r_r}, \tag{2.3.6}$$

$\mathbf{r}_r/r_r$ is the unit vector directed from molecule 1 to molecule 2

$$\mathbf{f}_1 = -\frac{\partial\varphi}{\partial\mathbf{r}_1} = -\left(\frac{\partial\varphi}{\partial x_1}\mathbf{i} + \frac{\partial\varphi}{\partial y_1}\mathbf{j} + \frac{\partial\varphi}{\partial z_1}\mathbf{k}\right) = -\frac{d\varphi}{dr_r}\frac{\mathbf{r}_r}{r_r}, \tag{2.3.7}$$

$$\mathbf{f}_1 = -\mathbf{f} = -\frac{d\varphi}{dr_r}\frac{\mathbf{r}_r}{r_r}. \tag{2.3.8}$$

i.e. third Newton's law is automatically satisfied.

2.4. Mechanics of a binary collision

- Equations of motion of molecules during a binary collision
- Conservation laws during a binary collision
- Equations of relative motion
- Conservation of angular momentum and collision plane
- Conservation of total energy
- Equation of motion in polar coordinates on the collision plane
- Deflection angle
- Relationship between velocities before and after collision

2.4. Mechanics of a binary collision

Equations of motion of molecules during a binary collision

The goal of this section is to find post-collisional velocities after a binary collision of two molecules (point masses m), if interaction is described by the interatomic potential $\varphi(r)$. For this purpose, let's introduce an inertial framework with Cartesian coordinates $Oxyz$. In this framework, state of two interaction molecules at time t is defined by the position vectors $\mathbf{r}$, $\mathbf{r}_1$ and velocity vectors $\mathbf{v}$, $\mathbf{v}_1$. Variation of $\mathbf{r}$, $\mathbf{r}_1$,$\mathbf{v}$, and $\mathbf{v}_1$ along particle trajectories is described the **equations of motion** that include kinematic relationships between position and velocity vectors,

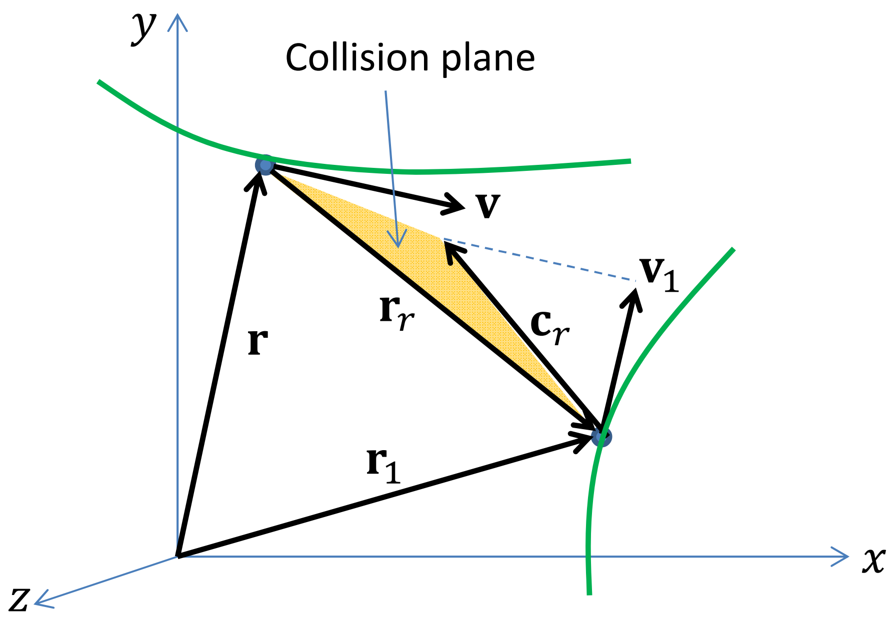
(2.4.1) $$\frac{d\mathbf{r}}{dt} = \mathbf{v}, \qquad \frac{d\mathbf{r}_1}{dt} = \mathbf{v}_1$$

and equations of Newton's second law of motion

(2.4.2) $$m\frac{d\mathbf{v}}{dt} = \mathbf{f}, \qquad m\frac{d\mathbf{v}_1}{dt} = \mathbf{f}_1,$$

where $\mathbf{f}$ and $\mathbf{f}_1$ are the interaction forces exerted on molecules 1 and 2. These forces are defined by the interatomic potential $\varphi(r) = \varphi(|\mathbf{r}_1 - \mathbf{r}|)$, e.g.

$$\mathbf{f} = -\frac{\partial \varphi}{\partial \mathbf{r}} = -\left(\frac{\partial \varphi}{\partial x}\mathbf{i} + \frac{\partial \varphi}{\partial y}\mathbf{j} + \frac{\partial \varphi}{\partial z}\mathbf{k}\right).$$



This system includes 12 scalar equations (3 coordinate and 3 velocity component of individual molecule x 2). We will show that this system of 12 equations can be reduced to a single equation using the conservation laws!

2.4. Mechanics of a binary collision

Conservation laws during a binary collision

Let's introduce the **total linear momentum** $\mathbf{P}$, **angular momentum** $\mathbf{L}$, and **mechanical energy** H

$$\mathbf{P} = m\mathbf{v} + m\mathbf{v}_1,$$

$$\mathbf{L} = \mathbf{r} \times (m\mathbf{v}) + \mathbf{r}_1 \times (m\mathbf{v}_1),$$

$$H = \frac{m\mathbf{v}^2}{2} + \frac{m\mathbf{v}_1^2}{2} + \varphi(|\mathbf{r}_1 - \mathbf{r}|),$$

Hereinafter

$$\dot{a} = \frac{da}{dt}$$

and show that these quantities are conserved during the binary collision:

$$\dot{\mathbf{P}} = m\dot{\mathbf{v}} + m\dot{\mathbf{v}}_1 = \mathbf{f} + \mathbf{f}_1 = 0.$$

$$\dot{\mathbf{L}} = \dot{\mathbf{r}} \times (m\mathbf{v}) + \mathbf{r} \times (m\dot{\mathbf{v}}) + \dot{\mathbf{r}}_1 \times (m\mathbf{v}_1) + \mathbf{r}_1 \times (m\dot{\mathbf{v}}_1) = \mathbf{r} \times \mathbf{f} + \mathbf{r}_1 \times \mathbf{f}_1 = (\mathbf{r}_1 - \mathbf{r}) \times \mathbf{f}_1 = 0.$$

$$\dot{H} = m\mathbf{v} \cdot \dot{\mathbf{v}} + m\mathbf{v}_1 \cdot \dot{\mathbf{v}}_1 + \frac{\partial \varphi}{\partial \mathbf{r}} \cdot \dot{\mathbf{r}} + \frac{\partial \varphi}{\partial \mathbf{r}_1} \cdot \dot{\mathbf{r}}_1 = m\mathbf{v} \cdot \dot{\mathbf{v}} + m\mathbf{v}_1 \cdot \dot{\mathbf{v}}_1 - \mathbf{f} \cdot \mathbf{v} - \mathbf{f}_1 \cdot \mathbf{v}_1 = 0.$$

Here $\dot{\varphi}$ is calculated with the **chain rule** ($\varphi(t) = (x(t), y(t), z(t), x_1(t), y_1(t), z_1(t))$):

$$\dot{\varphi} = \frac{\partial \varphi}{\partial x}\frac{dx}{dt} + \frac{\partial \varphi}{\partial y}\frac{dy}{dt} + \frac{\partial \varphi}{\partial z}\frac{dz}{dt} + \frac{\partial \varphi}{\partial x_1}\frac{dx_1}{dt} + \frac{\partial \varphi}{\partial y_1}\frac{dy_1}{dt} + \frac{\partial \varphi}{\partial z_1}\frac{dz_1}{dt} = \frac{\partial \varphi}{\partial \mathbf{r}} \cdot \dot{\mathbf{r}} + \frac{\partial \varphi}{\partial \mathbf{r}_1} \cdot \dot{\mathbf{r}}_1.$$

Thus, during a binary collision of molecules of monatomic gas the following conservation laws are valid

(2.4.3) $$\mathbf{P} = m\mathbf{v} + m\mathbf{v}_1 = const,$$ **Linear momentum c. l.**

(2.4.4) $$\mathbf{L} = \mathbf{r} \times (m\mathbf{v}) + \mathbf{r}_1 \times (m\mathbf{v}_1) = const,$$ **Angular momentum c. l.**

(2.4.5) $$H = \frac{m\mathbf{v}^2}{2} + \frac{m\mathbf{v}_1^2}{2} + \varphi(|\mathbf{r}_1 - \mathbf{r}|) = const.$$ **Mechanical energy c. l.**

2.4. Mechanics of a binary collision

Equations of relative motion

In order to simplify Eqs. (2.4.1)-(2.4.2), let's first use the linear momentum conservation law. Let's introduce the center-of-mass velocity position $\mathbf{r}_c$ and velocity $\mathbf{v}_c$ vectors, as well relative position $\mathbf{r}_r$ and velocity $\mathbf{c}_r$ vectors,

$$\mathbf{r}_c = \frac{m\mathbf{r} + m\mathbf{r}_1}{m + m} = \frac{\mathbf{r} + \mathbf{r}_1}{2}, \qquad \mathbf{r}_r = \mathbf{r}_1 - \mathbf{r}, \qquad \mathbf{v}_c = \frac{m\mathbf{v} + m\mathbf{v}_1}{m + m} = \frac{\mathbf{v} + \mathbf{v}_1}{2}, \qquad \mathbf{c}_r = \mathbf{v}_1 - \mathbf{v}. \tag{2.4.6}$$

Then we can write the sum and difference of Eqs (2.4.1) and (2.4.2)

$$\frac{d}{dt}\frac{\mathbf{r} + \mathbf{r}_1}{2} = \frac{\mathbf{v} + \mathbf{v}_1}{2}, \qquad \frac{d(\mathbf{r}_1 - \mathbf{r})}{dt} = \mathbf{v}_1 - \mathbf{v},$$

$$m\frac{d}{dt}\frac{\mathbf{v} + \mathbf{v}_1}{2} = \frac{\mathbf{f} + \mathbf{f}_1}{2} = 0, \qquad m\frac{d(\mathbf{v}_1 - \mathbf{v})}{dt} = \mathbf{f}_1 - \mathbf{f}.$$

Linear momentum c. l.

Left pair of equations reduces to equations

$$\frac{d\mathbf{r}_c}{dt} = \mathbf{v}_c, \qquad m\frac{d\mathbf{v}_c}{dt} = 0 \tag{2.4.7}$$

that describe the motion of the center of mass and imply that the center of mass moves with constant velocity $\mathbf{v}_c$. This is the consequence of the linear momentum conservation law, since Eq. (2.4.4) reduces to $\mathbf{P} = 2m\mathbf{v}_c = const$. The right pair of equations reduces to equations

$$\frac{d\mathbf{r}_r}{dt} = \mathbf{c}_r, \qquad \frac{m}{2}\frac{d\mathbf{c}_r}{dt} = -\frac{d\varphi}{dr_r}\frac{\mathbf{r}_r}{r_r} \tag{2.4.8}$$

Here we use Eq. (2.3.8)

that describe relative motion of molecules and can be solved independently of Eqs. (2.4.7). Thus, 12 Eqs. (2.4.1)-(2.4.2) reduce the system of 6 equations of relative motion.

2.4. Mechanics of a binary collision

Conservation of angular momentum and collision plane

Now let's use the angular momentum conservation law and re-write it in terms of center-of-mass and relative motion parameters. The simplest approach to do it is to first find positons and velocity vectors of individual molecules in terms of $\mathbf{r}_c$, $\mathbf{v}_c$, $\mathbf{r}_r$, and $\mathbf{c}_r$:

(2.4.9) $$\mathbf{r} = \mathbf{r}_c - \frac{\mathbf{r}_r}{2}, \qquad \mathbf{v} = \mathbf{v}_c - \frac{\mathbf{c}_r}{2}, \qquad \mathbf{r}_1 = \mathbf{r}_c + \frac{\mathbf{r}_r}{2}, \qquad \mathbf{v}_1 = \mathbf{v}_c + \frac{\mathbf{c}_r}{2}.$$

Then

$$\mathbf{L} = m\left(\mathbf{r}_c - \frac{\mathbf{r}_r}{2}\right) \times \left(\mathbf{v}_c - \frac{\mathbf{c}_r}{2}\right) + m\left(\mathbf{r}_c + \frac{\mathbf{r}_r}{2}\right) \times \left(\mathbf{v}_c + \frac{\mathbf{c}_r}{2}\right)$$

can be reduced to (consider as exercise)

(2.4.10) $$\mathbf{L} = 2m\mathbf{r}_c \times \mathbf{v}_c + \frac{m}{2}\mathbf{r}_r \times \mathbf{c}_r = \mathbf{L}_c + \mathbf{L}_r = const$$

The first term is the **angular momentum of the center of mass** $\mathbf{L}_c$. It is conserved, since the center of mass moves with constant velocity as $\mathbf{r}_c(t) = \mathbf{r}_c(0) + \mathbf{v}_c t$:

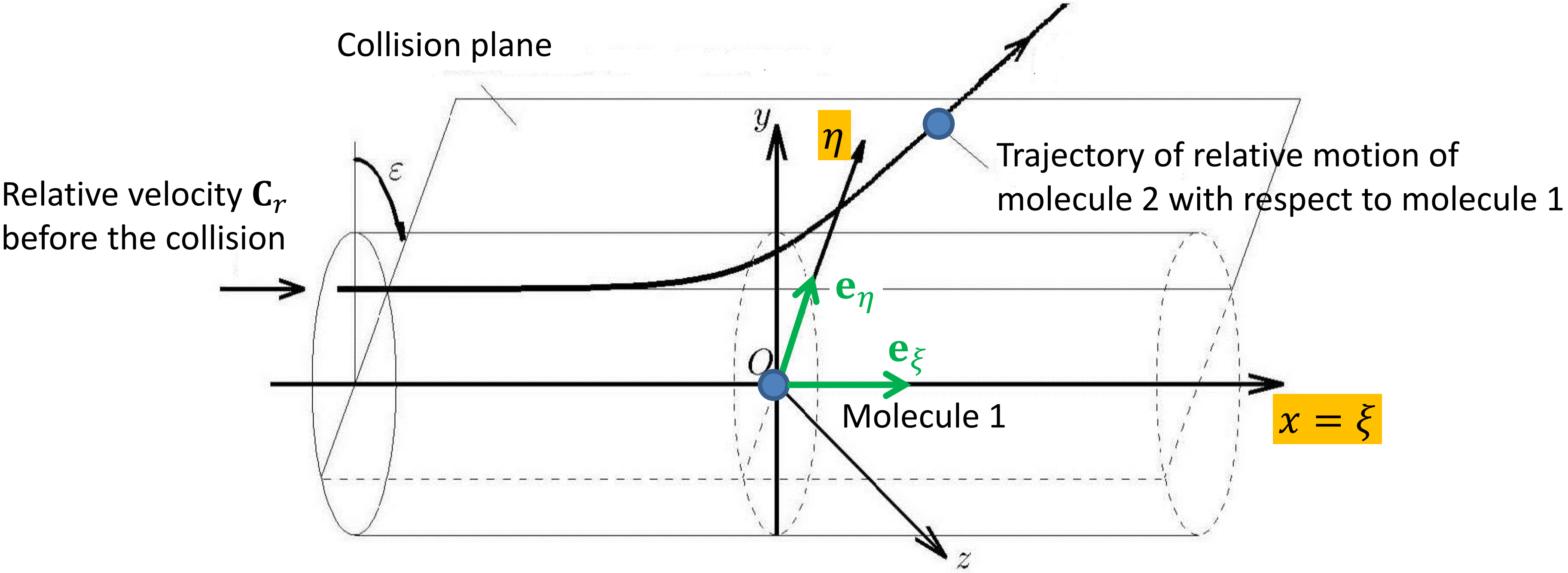
(2.4.11) $$\mathbf{L}_c = 2m\mathbf{r}_c \times \mathbf{v}_c = 2m(\mathbf{r}_c(0) + \mathbf{v}_c t) \times \mathbf{v}_c = 2m\mathbf{r}_c(0) \times \mathbf{v}_c = const.$$

Then during the binary collision the **angular momentum of relative motion** $\mathbf{L}_r$ is also conserved:

(2.4.12) $$\mathbf{L}_r = \frac{m}{2}\mathbf{r}_r \times \mathbf{c}_r = const.$$

But we know that $\mathbf{r}_r \times \mathbf{c}_r$ is a vector normal to the plane of vectors $\mathbf{r}_r$ and $\mathbf{c}_r$, and since$\mathbf{r}_r \times \mathbf{c}_r = const$, *during collision* $\mathbf{r}_r$ *and* $\mathbf{c}_r$ *always lye in the same plane* that is called the **collision plane**. This is the consequence of the angular momentum conservation law.

2.4. Mechanics of a binary collision



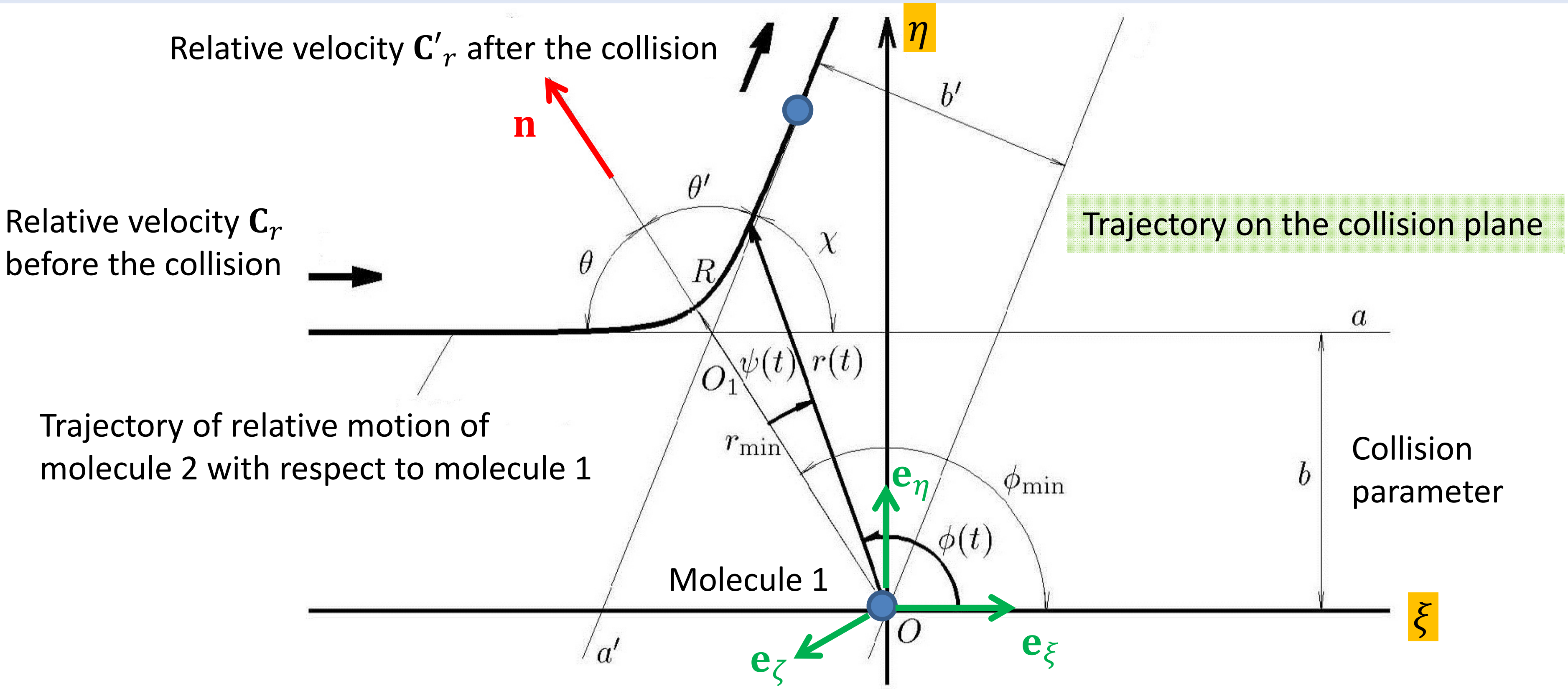
It means that the trajectory of the relative motion of particles is a planar curve that lies in the collision plane. Let's introduce a specific Cartesian coordinates that moves together with molecule 1, where the center O coincides with molecule 1 and axis Ox is directed along the relative velocity of molecule 2 with respect to molecule 1 before the collision:

$$\mathbf{C}_r = \lim_{t \to -\infty} \mathbf{c}_r \,, \qquad C_r = |\mathbf{C}_r|.$$

When the position of the collision plane is characterized by the constant **azimuthal angle** ε and there will be only 4 equations with respect to components of $\mathbf{r}_r$ and $\mathbf{c}_r$ on the collision plane:

$$\mathbf{r}_r = \xi \mathbf{e}_\xi + \eta \mathbf{e}_\eta, \qquad \mathbf{c}_r = c_\xi \mathbf{e}_\xi + c_\eta \mathbf{e}_\eta.$$

2.4. Mechanics of a binary collision


Relative velocity $\mathbf{C}'_r$ after the collision

Relative velocity $\mathbf{C}_r$ before the collision

Trajectory on the collision plane

Trajectory of relative motion of molecule 2 with respect to molecule 1

Collision parameter

Molecule 1

On the collision plane, relation position of the molecules before the collision can be characterized by the **collision parameter** b. Then $\mathbf{L}_r$ can be found in terms of $C_r = |\mathbf{C}_r|$ and b:

$$\mathbf{L}_r = \frac{m}{2} \lim_{t\to-\infty} \mathbf{r}_r \times \mathbf{c}_r = \frac{m}{2} \lim_{t\to-\infty} |\mathbf{c}_r||\mathbf{r}_r| \sin(\widehat{\mathbf{r}_r, \mathbf{c}_r})\, \mathbf{e}_\zeta = -\frac{m}{2} C_r b \mathbf{e}_\zeta,$$

(2.4.13)
$$L_r = |\mathbf{L}_r| = \frac{m}{2} C_r b.$$

$\mathbf{e}_\zeta$ is the unit vector normal to the collision plane and forming right-hand triplet $(\mathbf{e}_\xi, \mathbf{e}_\eta, \mathbf{e}_\zeta)$.

2.4. Mechanics of a binary collision

Conservation of energy

Now let's use the mechanical energy conservation law and re-write it in terms of center-of-mass and relative motion parameters. Then

$$H = \frac{m}{2}\left(\mathbf{v}_c - \frac{\mathbf{c}_r}{2}\right)^2 + \frac{m}{2}\left(\mathbf{v}_c + \frac{\mathbf{c}_r}{2}\right)^2 + \varphi(|\mathbf{r}_r|),$$

can be reduced to (consider as exercise)

(2.4.14) $$H = \frac{2m\mathbf{v}_c^2}{2} + \frac{m/2\mathbf{c}_r^2}{2} + \varphi(|\mathbf{r}_r|) = H_c + H_r = const.$$

The first term, the **kinetic energy of the center of mass** H_c, is conserved:

$$H_c = \frac{2m\mathbf{v}_c^2}{2} = const.$$

Then during the binary collision the **mechanical energy of relative motion** H_r is also conserved:

(2.4.15) $$H_r = \frac{m/2\mathbf{c}_r^2}{2} + \varphi(|\mathbf{r}_r|) = const.$$

If we apply the last equation to the state of molecules before ($t \to -\infty$) and after ($t \to \infty$) the collision, we obtain ($\varphi(|\mathbf{r}_r|) \to 0$ in both cases)

(2.4.16) $$H_r = \frac{m/2C_r^2}{2} = \frac{m/2C_r'^2}{2} \quad \Longrightarrow \quad C_r' = C_r \ ,$$

i.e., **the absolute value of relative velocity before and after the collision is the same**. This is the major consequence of the energy conservation law.

2.4. Mechanics of a binary collision

Equation of motion on the collision plane in polar coordinates

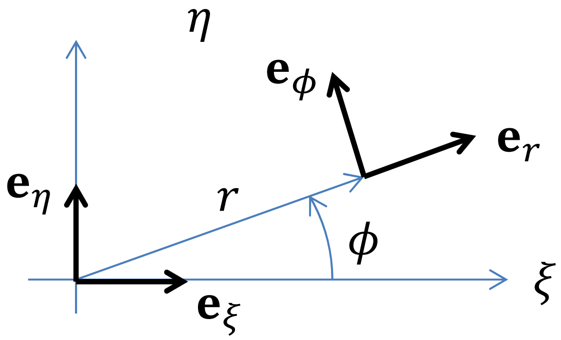
Now let's introduce the polar coordinates (r, ϕ) on the collision plane. Then

$$\mathbf{e}_r = \cos\phi\,\mathbf{e}_\xi + \sin\phi\,\mathbf{e}_\eta,$$

$$\mathbf{e}_\phi = -\sin\phi\,\mathbf{e}_\xi + \cos\phi\,\mathbf{e}_\eta,$$

$$\mathbf{r}_r = \xi\mathbf{e}_\xi + \eta\mathbf{e}_\eta = r\mathbf{e}_r,$$

$$\mathbf{c}_r = \dot{\mathbf{r}}_r = \dot{r}\mathbf{e}_r + r\dot{\mathbf{e}}_r = \dot{r}\mathbf{e}_r + r\dot{\phi}\mathbf{e}_\phi.$$



$$r = \sqrt{\xi^2 + \eta^2}$$

$$\phi = \operatorname{atan}\frac{\eta}{\xi}$$

In order to get differential equations with respect to r and ϕ let's use Eqs. (2.4.12) and (2.4.14)

$$\mathbf{L}_r = \frac{m}{2}[\mathbf{r}_r \times \mathbf{c}_r] = \frac{m}{2}\left[(r\mathbf{e}_r) \times (\dot{r}\mathbf{e}_r + r\dot{\phi}\mathbf{e}_\phi)\right] = \frac{mr^2\dot{\phi}}{2}\mathbf{e}_r \times \mathbf{e}_\phi,$$

(2.4.17) $$L_r = |\mathbf{L}_r| = -\frac{mr^2\dot{\phi}}{2},$$

$$H_r = \frac{m/2\mathbf{c}_r^2}{2} + \varphi(|\mathbf{r}_r|) = \frac{m/2}{2}\left(\dot{r}\mathbf{e}_r + r\dot{\phi}\mathbf{e}_\phi\right)^2 + \varphi(r),$$

(2.4.18) $$H_r = \frac{m/2}{2}\left(\dot{r}^2 + \left(r\dot{\phi}\right)^2\right) + \varphi(r).$$

Note that in Eqs. (2.4.16) and (2.4.17) L_r and H_r are know constants, since they can be calculated with Eqs. (2.4.13) and (2.4.16) by using only relative velocity C_r and collision parameter b that are supposed to be known. Then we can consider Eqs. (2.4.16) and (2.4.17) as

2.4. Mechanics of a binary collision

differential equations with respect to r and ϕ :

(2.4.19)
$$\dot{r}^2 = \frac{4(H_r - \varphi(r))}{m} - \frac{4L_r^2}{(mr)^2}, \qquad \dot{\phi} = -\frac{2L_r}{mr^2}.$$

In order to find an equation for $\dot{r}$ we need to choose a sign at the square root. Simple analysis show that the trajectory on the collision plane (see slide 25) is symmetric with respect to the angle ϕ_{min} that corresponds to approaching of molecules at the minimum distance r_{min} (so $\theta = \theta'$ in slide 25). At $r = r_{min}$, $\dot{r} = 0$, so r_{min} (but not ϕ_{min}) can be found from the equation

(2.4.20)
$$\frac{4(H_r - \varphi(r_{min}))}{m} = \frac{4L_r^2}{(mr_{min})^2}.$$

Then we can replace Eqs. (2.4.18) with

(2.4.21)
$$\dot{r} = \pm 2\sqrt{\frac{H_r - \varphi(r)}{m} - \frac{L_r^2}{(mr)^2}}, \qquad \dot{\phi} = -\frac{2L_r}{mr^2},$$

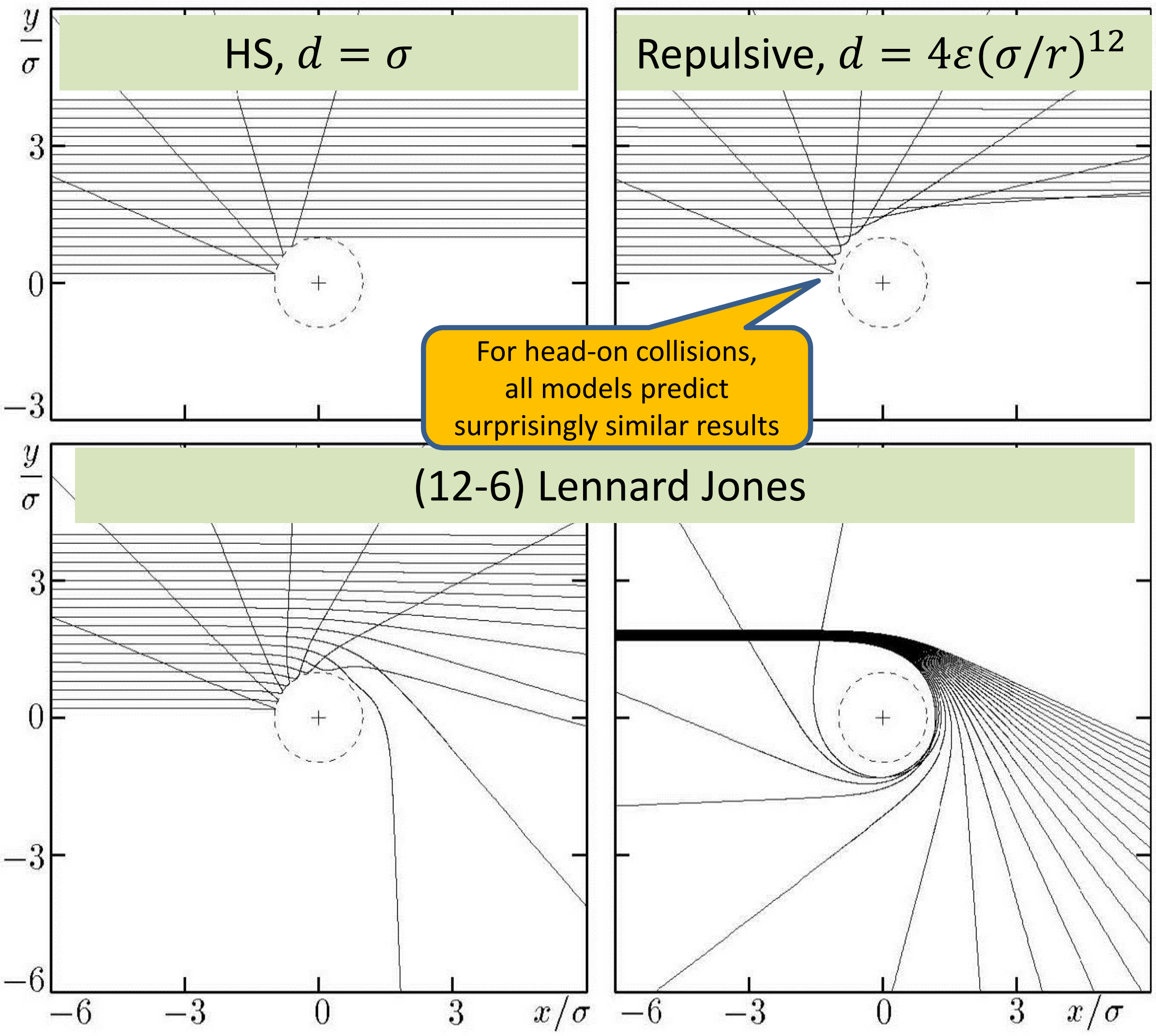
where different signs at the square roots corresponds to different branches of the trajectory. Let's consider only the branch where molecules approach each other and $\dot{r} = 0$. If we introduce $\psi = \phi_{min} - \phi$, then we can exclude time t from the consideration and replace Eq. (2.4.21) with the only equation that defines $\psi = \psi(r)$:

(2.4.22)
$$\frac{d\psi}{dr} = \frac{L_r}{mr^2\sqrt{\frac{H_r - \varphi(r)}{m} - \frac{L_r^2}{(mr)^2}}}.$$

This equation predicts trajectory on the collision plane for given H_r and L_r, i.e. for given C_r and b, see Eqs. (2.4.13) and (2.4.16)

2.4. Mechanics of a binary collision

We can find trajectories of molecules on the collision plane during a binary collision by numerical integration of differential equation (2.4.22). Some results are shown in the figure.



HS, $d = \sigma$

Repulsive, $d = 4\varepsilon(\sigma/r)^{12}$

(12-6) Lennard Jones

For head-on collisions, all models predict surprisingly similar results

These trajectories are obtained for Ar at $C_r = 300$ m/s.

"Wrapping" of trajectories around the central molecules in a range of b occurs due to weak attraction forces accounted for in the Lennard-Jones potential. Due to symmetry of trajectory, formation of a close orbit (that corresponds to a stable dimer - diatomic molecule) in binary collision is practically impossible.

If the attractive force decreases faster than $1/r^2$, then, at small H_r, there will be a value of b at which particle can be trapped and form a dimer (see details in Johnson, "Introduction to Atomic and Molecular Collisions").

A closed orbit can be efficiently formed if the excess of kinetic energy is taken away by a third particle participating in a collision. This is how (through rare triple collisions) dimers can form from atoms during condensation of monatomic gases.

2.4. Mechanics of a binary collision

Deflection angle

The R.H.S. of differential equation (2.4.22) does not depend on ψ, so the equation can be integrated from the point where $\psi = 0$ and $r = r_{min}$:

$$\psi(r) = \int_{r_{min}}^{r} \frac{L_r dr}{mr^2 \sqrt{\frac{H_r - \varphi(r)}{m} - \frac{L_r^2}{(mr)^2}}}.$$

Angle θ in slide 25 corresponds to $r \to \infty$ (state of the molecules after collision):

(2.4.23)
$$\theta(b, C_r) = \int_{r_{min}}^{\infty} \frac{L_r dr}{mr^2 \sqrt{\frac{H_r - \varphi(r)}{m} - \frac{L_r^2}{(mr)^2}}}.$$

Finally, the deflection angle χ, the angle between relative velocity vectors before and after the collision), is equal to

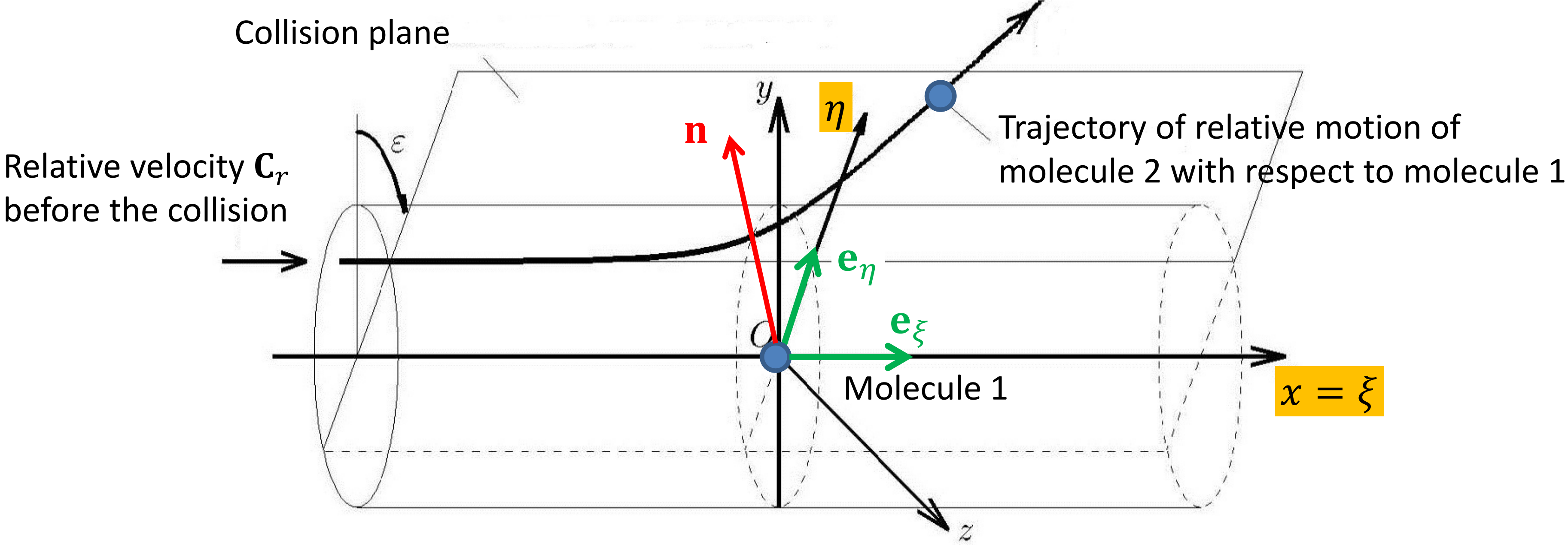
Compare with Eq. (2.2.14) for the HS model

(2.4.24)
$$\chi(b, C_r) = \pi - 2\theta(b, C_r) = \pi - 2 \int_{r_{min}}^{\infty} \frac{L_r dr}{mr^2 \sqrt{\frac{H_r - \varphi(r)}{m} - \frac{L_r^2}{(mr)^2}}}.$$

Here L_r H_r, and r_{min} are defined by b and C_r according to Eqs. (2.4.13), (2.4.16), and (2.4.20). Contrary to the HS model, χ depends on the relative velocity of molecules before the collision.

2.4. Mechanics of a binary collision

Relationship between velocities before and after collision



Collision plane

Relative velocity $\mathbf{C}_r$ before the collision

Trajectory of relative motion of molecule 2 with respect to molecule 1

Let's introduce a unit vector $\mathbf{n}$ directed along the line corresponding to the minimum distance between molecules (see also slide 25). Components of this vector depends on ε, b and C_r:

(2.4.25) $$\mathbf{n}(\varepsilon, b, C_r) = -\cos\theta(b, C_r)\,\mathbf{e}_x + \sin\theta(b, C_r)\left[\cos\varepsilon\,\mathbf{e}_y + \sin\varepsilon\,\mathbf{e}_z\right].$$

Then equations for $\mathbf{v}'$ and $\mathbf{v}'_1$ can be obtained precisely in the same form as for the HS model:

(2.4.26) $$\begin{gathered}\mathbf{v}' = \mathbf{v} + [(\mathbf{v}_1 - \mathbf{v})\cdot\mathbf{n}]\mathbf{n},\\ \mathbf{v}'_1 = \mathbf{v}_1 - [(\mathbf{v}_1 - \mathbf{v})\cdot\mathbf{n}]\mathbf{n}.\end{gathered}$$

The major difference between Eq. (2.4.26) and (2.2.12) is in $\mathbf{n}$: For arbitrary interatomic potential $\theta(b, C_r)$ is given by Eq. (2.4.23), while for the HS model it is defined by Eq. (2.2.13).

2.4. Mechanics of a binary collision

In order to use Eq. (2.4.26) for practical calculations we need to know how to define components of vector $\mathbf{n}$ in the global coordinate system, i.e. in the same coordinate system, where we know components of the velocity vectors $\mathbf{v}$ and $\mathbf{v}_1$. It can be easily done, e.g., if at some time during collision we know position vectors of molecules $\mathbf{r}$ and $\mathbf{r}_1$. Then Eq. (2.4.25) can be re-written as

(2.4.27) $$\mathbf{n}(\varepsilon, b, C_r) = -\cos\theta(b, C_r)\,\mathbf{e}_\xi + \sin\theta(b, C_r)\mathbf{e}_\eta\,,$$

where, according to definition of $\mathbf{e}_\xi$ and collision plane, $\mathbf{e}_\xi$ and $\mathbf{e}_\eta$ can be calculated as follows:

(2.4.28) $$\mathbf{e}_\xi = \frac{\mathbf{v}_1 - \mathbf{v}}{|\mathbf{v}_1 - \mathbf{v}|}, \qquad \mathbf{e}_\zeta = -\frac{(\mathbf{r}_1 - \mathbf{r}) \times (\mathbf{v}_1 - \mathbf{v})}{|(\mathbf{r}_1 - \mathbf{r}) \times (\mathbf{v}_1 - \mathbf{v})|}, \qquad \mathbf{e}_\eta = \mathbf{e}_\xi \times \mathbf{e}_\zeta.$$

Here $\mathbf{e}_\zeta$ is a unit vector normal to the collision plane.

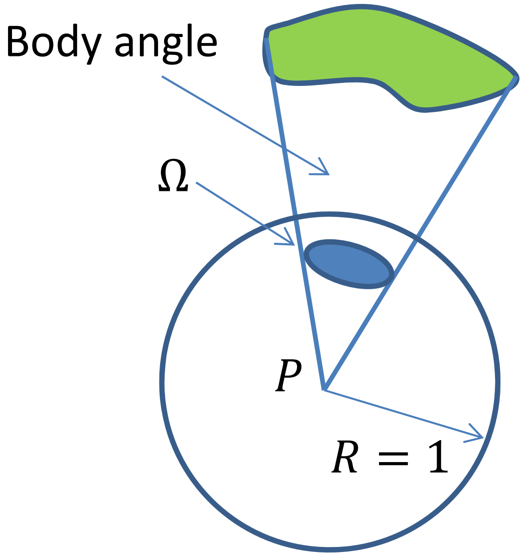
2.5. Collision cross sections

- Prerequisite: Solid angle
- Cutoff of interatomic potentials
- Total collision cross-section
- Differential collision cross section
- Cross sections of HS molecules
- Scattering

2.5. Collision cross sections

Prerequisite: Solid angle

Solid angle in 3D space is a volume bounded by a cone with the vertex in some point P.
Solid angles are measured by the area Ω that is cut by the cone on the surface of a sphere of unit radius with the center in point P. Correspondingly, the value of Ω for any body angle varies from 0 to 4π. It is measured in **steradians**.

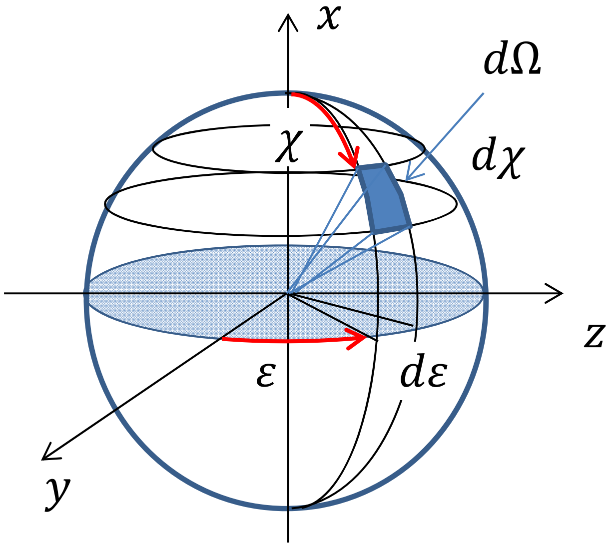


In order to measure various solid angles with the same vertex P, it is convenient to use **spherical angles**: **longitudinal angle** ε and **co-latitude** χ :

$$0 \le \varepsilon \le 2\pi$$
$$0 \le \chi \le \pi$$

A unit vector (**direction**) $\mathbf{a}$ that corresponds to given ε and χ has the following components:

$$\mathbf{a}(\varepsilon, \chi) = \cos\chi\,\mathbf{i} + \sin\chi\,[\cos\varepsilon\,\mathbf{j} + \sin\varepsilon\,\mathbf{k}].$$



If we fix some ε and χ and give increments $d\varepsilon$ and $d\chi$ to these angles, then we obtain a cone (solid angle) of size

$$d\Omega = \sin\chi\, d\chi d\varepsilon. \qquad (2.5.1)$$

2.5. Collision cross sections

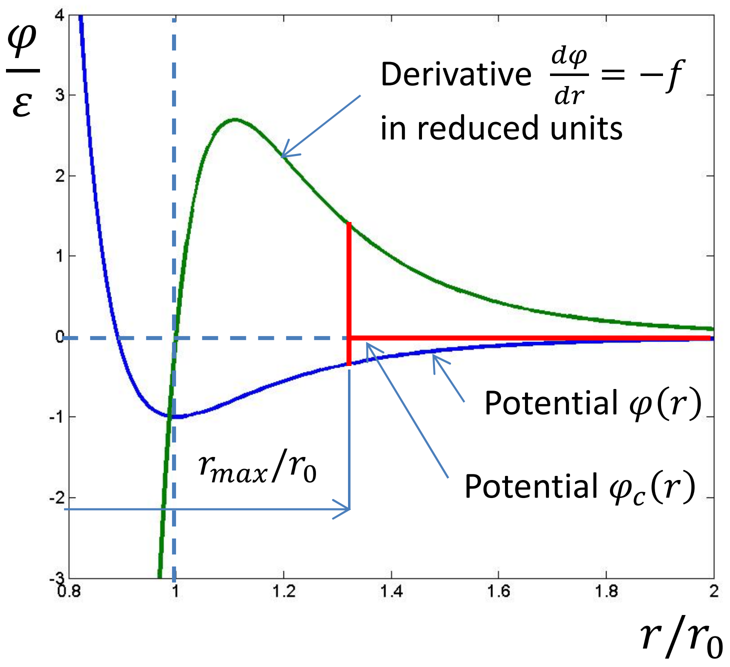
Cutoff of interatomic potential

Interatomic potentials $\varphi(r)$ introduced in Section 2.3 only asymptotically approach zero when $r \to \infty$. It means that the interaction force f between molecules exists at any finite distance, although if r is large, then the magnitude of the force is so small that there is no practical reason to take it into account.

The use of interatomic potentials with non-zero force at any finite distance contradicts the kinetic theory of dilute gases, which states that only binary collisions are important, since then at any time a molecule interacts simultaneously with all other molecules.

In order to get rid of this difficulty, **cutoff interatomic potentials** are used in practical calculations: It is assumed that $\varphi_c(r)$ is zero if $r > r_{max}$ where r_{max} is the **cutoff distance**, i.e. maximum distance between molecules, where forces are non-zero. Then Eq. (2.4.24) for the deflection angle takes the form

$$\chi = \pi - 2 \int_{r_{min}}^{r_{max}} \frac{L_r dr}{m r^2 \sqrt{\dfrac{H_r - \varphi(r)}{m} - \dfrac{L_r^2}{(mr)^2}}}. \qquad (2.5.3)$$



$$\varphi_c(r) = \begin{cases} \varphi(r) & r \le r_{max} \\ 0 & r > r_{max} \end{cases} \qquad (2.5.2)$$

1. Such cutoff implies a jump in the force at $r = r_{max}$. In practical calculations, **smooth** cutoff is also applied, when $\varphi_c(r)$ varies smoothly from $\varphi(r)$ to 0 in a range $r_1 \le r \le r_{max}$.
2. Usually $r_{max} \sim (3-4) r_0$.
3. There is reason to assume that r_{max} is not a constant, but depends on C_r (see section 2.6).

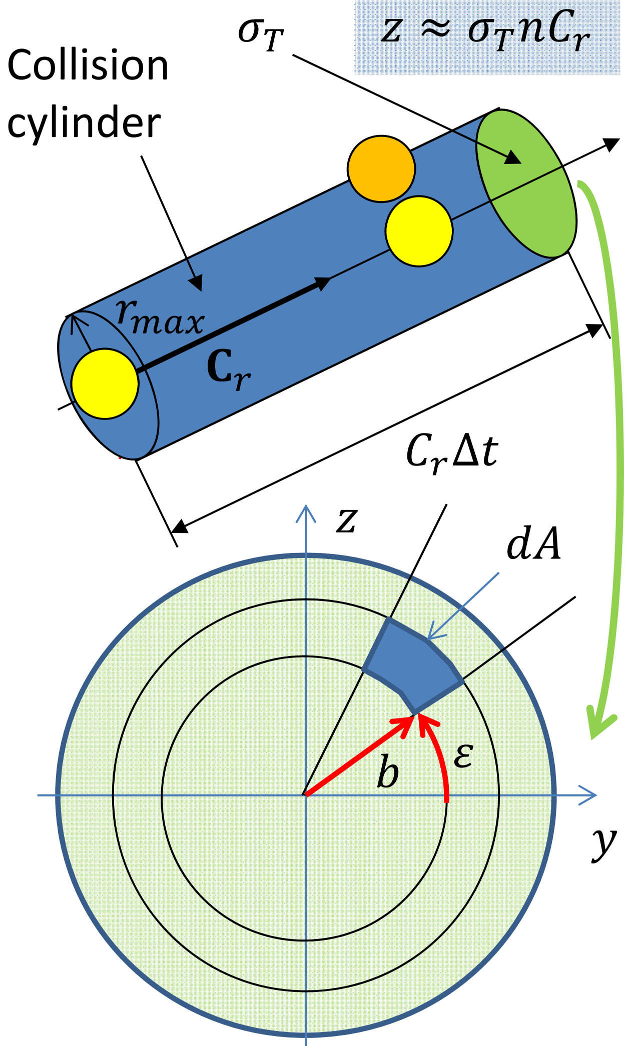
2.5. Collision cross sections

Total collision cross section

Let's assume that we use only a cutoff interatomic potential with the cutoff distance r_{max} (for the HS model, $r_{max} = d$). In calculations of the collision frequency z in Section 1.4 we found that z depends on the total collision cross section of HS molecules. If we want to extend this consideration and count collisions for molecules interacting via a cutoff potential, then we need to assume that the collision cylinder has diameter $r_{max} = r_{max}(C_r)$. The cross-sectional area of the collision cylinder is called the **total collision cross section** σ_T

(2.5.4) $$\sigma_T(C_r) = \pi r_{max}^2.$$

$$z \approx \sigma_T n C_r$$



Let's assume that we cannot define accurately b and ε that specify relative position of molecules before their collision on the cross section of the collision cylinder. On the contrary, let's assume that the position is random and position of molecule 2 with respect to molecule 1 on the cross section is distributed with equal probability. Then probability dP to have a collision with

(2.5.5) $$b < \hat{b} \le b + db, \qquad \varepsilon < \hat{\varepsilon} \le \varepsilon + d\varepsilon$$

is equal to

$$dP = \frac{dN}{N} = \frac{dA}{\sigma_T} = \frac{b\,db\,d\varepsilon}{\sigma_T} \qquad (2.5.6)$$

2.5. Collision cross sections

Differential collision cross section

If C_r is fixed, then the deflection angle is a function of b according to Eq. (2.5.3):

(2.5.7)
$$\chi(b, C_r) = \pi - 2 \int_{r_{min}}^{r_{max}} \frac{L_r dr}{mr^2 \sqrt{\frac{H_r - \varphi(r)}{m} - \frac{L_r^2}{(mr)^2}}}.$$

It means that if before a collision relative position of molecules satisfies Eq. (2.5.5), then after the collision the direction of relative velocity $\mathbf{C}'_r$ satisfies the equations

$$\chi < \hat{\chi} \leq \chi + d\chi, \qquad \varepsilon < \hat{\varepsilon} \leq \varepsilon + d\varepsilon,$$

where

(2.5.8)
$$d\chi = \frac{d\chi}{db} db$$

or, direction of relative velocity $\mathbf{C}'_r$ is within the body angle $d\Omega = \sin\chi\, d\chi d\varepsilon$. The coefficient of proportionality between area $dA = bdbd\varepsilon$, which corresponds to the relative position of molecules on the cross section of collision cylinder **before the collision** and body angle $\Omega = \sin\chi\, d\chi d\varepsilon$, where the relative velocity of molecules **after the collision** $\mathbf{C}'_r$ is directed within, is called the **differential collision cross section** $\sigma(\chi, C_r)$:

(2.5.9)
$$dA = \sigma(\chi, C_r) d\Omega.$$

If one combines Eqs. (2.5.6) and (2.5.9), then probability to find $\mathbf{C}'_r$ directed within $d\Omega$ is

(2.5.10)
$$dP = \frac{\sigma(\chi, C_r)}{\sigma_T(C_r)} d\Omega.$$

2.5. Collision cross sections

Thus, the ratio σ/σ_T defines probability of deflection (scattering) into an infinitely small body angle $d\Omega$ at given value of C_r.

Let's find an equation for $\sigma(\chi, C_r)$. Eq. (2.5.9) reduces to

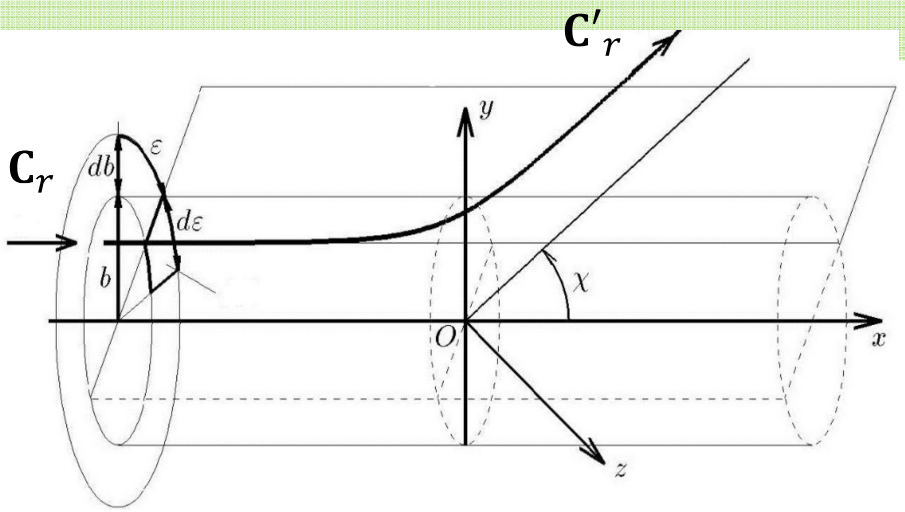
$$b\,db\,d\varepsilon = b\left|\frac{db}{d\chi}\right| d\chi\, d\varepsilon = \sigma(\chi, C_r)\sin\chi\, d\chi\, d\varepsilon.$$

Here

$$\frac{db}{d\chi} = \left(\frac{d\chi}{db}\right)^{-1} \qquad (2.5.11)$$

and derivative $d\chi/db$ can be calculated by differentiating Eq. (2.5.7). Then

$$\sigma(\chi, C_r) = \frac{b(\chi, C_r)}{\sin\chi}\left|\frac{db(\chi, C_r)}{d\chi}\right|. \qquad (2.5.12)$$



Here we use the calculus rule for derivatives of inverse functions: If functions $b(\chi)$ and $\chi(b)$ are **mutually inverse**, i.e. $b\big(\chi(b)\big) = b$, then derivative of $b(\chi)$ can be calculated using derivative of $\chi(b)$ in the form given by Eq. (2.5.11).

Eq. (2.5.12) allows one to find σ vs. χ and C_r for any given interatomic potential. The relationship between the total and differential cross sections is established by the equation

$$\int_{4\pi} \sigma(\chi, C_r)\,d\Omega = \int_0^{2\pi}\int_0^{\pi} \sigma(\chi, C_r)\sin\chi\, d\chi\, d\varepsilon = \int_0^{2\pi}\int_0^{r_{max}(C_r)} b\,db\,d\varepsilon = \pi r_{max}^2(C_r) = \sigma_T(C_r). \qquad (2.5.13)$$

This equation also is in agreement with Eq. (2.5.10): Probability of deflection into the full body angle of 4π must be equal to 1.

2.5. Collision cross sections

Cross sections of HS molecules

Eq. (2.5.12) can be applied even for HS molecules of diameter d. In this case the relationship between χ and b is given by Eq. (2.2.14) or

$$b = d\cos\frac{\chi}{2} \qquad \Longrightarrow \qquad \frac{db}{d\chi} = -\frac{d}{2}\sin\frac{\chi}{2}.$$

Then

(2.5.14)
$$\sigma = \frac{d^2}{4} = const, \qquad \sigma_T = \int\limits_{4\pi} \sigma d\Omega = \frac{d^2}{4} 4\pi = \pi d^2.$$

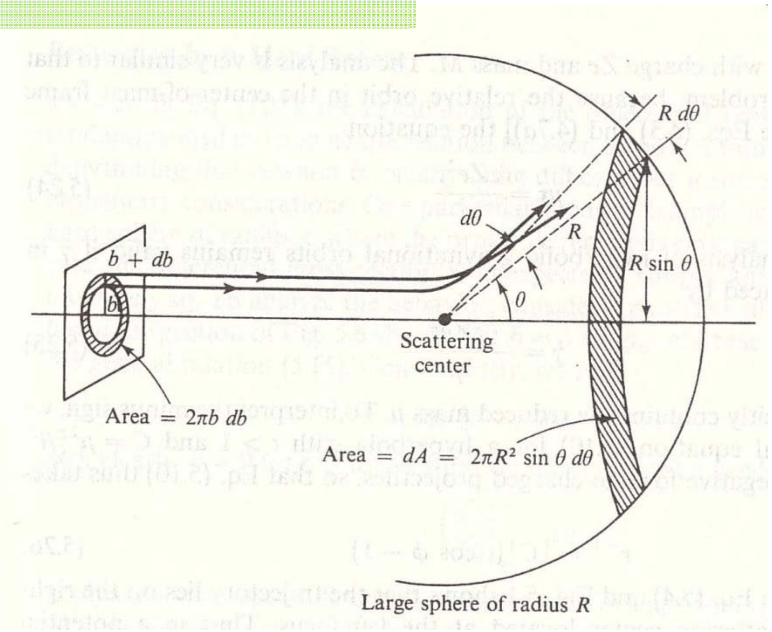
Scattering

The problem of calculation of trajectories of relative motion of one molecule with respect another considered in Sections 2.4 and 2.5 is an example of the general problem in physics and mechanics known as a **problem of elastic particle scattering on the force center**.

It can be also used to predict gravitational or Coulomb scattering of particles of various physical nature in the central fields of gravity or electrostatic force.

In particular, solution of this problem was used by English physicist Rutherford to explain experiments on scattering of alpha particles moving through a thin gold film. These experiments led to the development of the planetary Rutherford model of the atom and eventually to the Bohr model.

See https://en.wikipedia.org/wiki/Rutherford_scattering.



Fetter and Walecka, "Theoretical Mechanics of Particles and Continua"

2.6. Variable Hard Sphere (VHS) model

- Cross sections for the repulsive potential
- Variable Hard Sphere (VHS) model
- Parameterization of the VHS model based on the viscosity data

2.6. Variable Hard Sphere (VHS) model

Our goal is to study how the cross sections depend on the relative velocity of molecules. This question can be relatively easily answered if interaction between molecules is described by repulsive interatomic potential in the form of Eq. (2.3.4).

Cross sections for the repulsive potential

Let's write the full system of equations that allows one to find the differential cross section:

$$H_r = \frac{mC_r^2}{4}, \qquad L_r = -\frac{m}{2} C_r b, \qquad \frac{4\left(H_r - \varphi(r_{min})\right)}{m} = \frac{4L_r^2}{(mr_{min})^2},$$

$$\chi(b, C_r) = \pi - 2 \int_{r_{min}}^{\infty} \frac{L_r dr}{mr^2 \sqrt{\frac{H_r - \varphi(r)}{m} - \frac{L_r^2}{(mr)^2}}}.$$

$$\text{If} \quad \varphi(r) = \frac{A}{r^s}$$

then this system reduces to

(2.6.1) $$C_r^2 - \frac{4A}{mr_{min}^s} = \frac{(C_r b)^2}{r_{min}^2}, \qquad \chi = \pi - 2 \int_{r_{min}}^{\infty} \frac{C_r b dr}{r^2 \sqrt{C_r^2 - \frac{4A}{mr^s} - \frac{(C_r b)^2}{r^2}}}.$$

Now let's introduce reduced units

$$\bar{r} = \frac{r}{b}, \qquad \bar{r}_{min} = \frac{r_{min}}{b}, \qquad \Lambda = C_r b^{s/2},$$

2.6. Variable hard sphere (VHS) model

and re-write Eq. (2.6.11) in the reduced units as follows:

$$\Lambda^2 - \frac{4A}{m\bar{r}_{min}^s} = \frac{\Lambda^2}{\bar{r}_{min}^2}, \qquad \chi = \pi - 2\int_{\bar{r}_{min}}^{\infty} \frac{\Lambda d\bar{r}}{\bar{r}^2\sqrt{\Lambda^2 - \frac{4A}{m\bar{r}^s} - \frac{\Lambda^2}{\bar{r}^2}}}.$$

One can see that χ is defined not by individual values of C_r and b, but only $\Lambda = C_r b^{s/2}$:

$$\chi(b, C_r) = \mathrm{X}(\Lambda) = \mathrm{X}\left(C_r b^{s/2}\right).$$

For the repulsive potential, χ monotonously decreases with increasing b (see plots in slide 29). So we can introduce a function $\mathrm{X}^{-1}(\chi)$ that is inverse to $\mathrm{X}(\Lambda)$:

$$C_r b^{s/2} = \Lambda = \mathrm{X}^{-1}(\chi) \qquad \Longrightarrow \qquad b = C_r^{-\frac{2}{s}}\Theta(\chi), \qquad \Theta(\chi) = \left[\mathrm{X}^{-1}(\chi)\right]^{\frac{2}{s}}.$$

The last equation allows us to find derivative $db/d\chi$ and cross section using Eq. (2.5.12):

$$\sigma(\chi, C_r) = \frac{b}{\sin\chi}\left|\frac{db(\chi, C_r)}{d\chi}\right| = \frac{1}{C_r^{4/s}}\frac{\Theta(\chi)|\Theta'(\chi)|}{\sin\chi}. \tag{2.6.2}$$

The total cross section is equal to (see Eq. (2.5.13))

$$\sigma_T(C_r) = \int_0^{2\pi}\int_{\chi_{min}}^{\pi} \sigma \sin\chi \, d\chi d\varepsilon = \frac{S}{C_r^{4/s}}, S = 2\pi\int_{\chi_{min}}^{\pi} \Theta(\chi)|\Theta'(\chi)|d\chi = \pi\left[\Theta^2(\chi_{min}) - \Theta^2(\pi)\right]. \tag{2.6.3}$$

In the last equation, it is assumed that a cutoff potential is used and $\chi_{min} > 0$. In the case of the repulsive potential without a cutoff, $\Theta(\chi_{min}) \rightarrow \infty$ when $\chi_{min} \rightarrow 0$, and σ_T diverges.

Thus, both differential and total cross sections decrease with increasing C_r (why?).

2.6. Variable hard sphere (VHS) model

The particular case of the repulsive potential when $s = 4$ and $C_r \sigma(\chi, C_r)$ does not depend on C_r is called the **model of Maxwell molecules**.

Variable Hard Sphere (VHS) model

In the model of the repulsive potential, the effect of C_r on σ is easy to account for, while angular dependence of σ on χ is given by the complicated term $\Theta(\chi)|\Theta'(\chi)|/\sin\chi$ in Eq. (2.6.2). The experience of kinetic calculations shows that it is important to take into account the dependence of σ on C_r in order to obtain agreement with physical experiments in terms of the dependence of viscosity and thermal conductivity on temperature, while peculiarities of angular scattering has marginal effects in multiple applications.

Then one can combine the dependence of σ on C_r given by Eq. (2.6.3) with the independency of σ on χ characteristic for the HS model and adopt the differential cross section in the form

(2.6.4)
$$\sigma(C_r) = \frac{const}{C_r^{\varpi}} = \sigma_{Ref} \left(\frac{C_{r,Ref}}{C_r} \right)^{\varpi},$$

where $\varpi = 4/s$ and σ_{Ref} is the differential cross section at reference velocity $C_{r,Ref}$. According to Eq. (2.4.14) for HS molecules one can write

(2.6.5)
$$\sigma_{Ref} = \frac{d_{Ref}^2}{4} \qquad \sigma(C_r) = \frac{d^2\,(C_r)}{4}, \qquad d(C_r) = d_{Ref} \left(\frac{C_{r,Ref}}{C_r} \right)^{\frac{\varpi}{2}}.$$

The molecular model where the differential cross section is given by Eq. (2.6.4) or (2.6.5) is called the **Variable Hard Sphere (VHS) model**. It can be viewed as a Hard Sphere model where molecules at binary collisions have a variable diameter that depends on their relative velocity.

2.6. Variable hard sphere (VHS) model

The total cross section is then equal to

(2.6.6) $$\sigma_T(C_r) = \pi d^2\,(C_r) = \sigma_{T,Ref}\left(\frac{C_{r,Ref}}{C_r}\right)^{\varpi}, \qquad \sigma_{T,Ref} = \pi d_{Ref}^2.$$

The VHS model was suggested by G.A. Bird, an "inventor" of the DMSC method, and currently this is the most popular molecular model for DSMC simulations of various flows.

Parameterization of the VHS model based on the viscosity data

The VHS model has two adjustable parameters d_{Ref} at given $C_{r,Ref}$ and ϖ. Both parameters are usually chosen to match known dependence of the viscosity on temperature in a temperature range under consideration. In particular, exponent ϖ can be related to the viscosity exponent ω in the experimental power law of viscosity on temperature (see Eq. (1.7.9)):

(2.6.7) $$\mu(T) = \mu_{Ref}\left(\frac{T}{T_{Ref}}\right)^{\omega}.$$

We established a simple estimate for the viscosity (see Eq. (1.7.7)):

(2.6.8) $$\mu = \frac{C\lambda}{6}mn \sim \frac{\sqrt{T}}{\sigma_T}.$$

Let's make a reasonable assumption: σ_T in Eq. (2.6.8) can be estimated as a function of temperature according to Eq. (2.6.6) if C_r is the thermal velocity, i.e. $C_r \sim \sqrt{T}$. Then

2.6. Variable hard sphere (VHS) model

(2.6.9)

$$\mu = \sim \frac{\sqrt{T}}{\sigma_T(C_r)} \sim \sqrt{T}(C_r)^{\varpi} \sim \sqrt{T}\left(\sqrt{T}\right)^{\varpi} = T^{\frac{\varpi+1}{2}}.$$

Then by comparing Eq. (2.6.7) and (2.6.9):

(2.6.10)

$$\omega = \frac{\varpi + 1}{2} \quad \text{or} \quad \varpi = 2\omega - 1.$$

Since $1/2 \le \omega \le 1$, ϖ varies in the range $0 \le \varpi \le 1$. Since $\varpi = 4/s$, this range of ϖ corresponds to the range of s in Eq. (2.6.1) from 4 to ∞.

The case $\varpi = 0$ ($\omega = 0, s \to \infty$) corresponds to the model of HS molecules.

The case $\varpi = 1$ ($\omega = 1, s = 4$) corresponds to the model of **pseudo-Maxwell molecules**, i.e. molecules that have VHS cross section, but $C_r\sigma(\chi, C_r)$ does not depend on C_r. The models of Maxwell and pseudo-Maxwell molecules are different by the angular dependences of the differential cross sections on the deflection angle χ.

"Accurate" theory also results in Eq. (2.6.10). The theory also establishes the following relationships between μ_{Ref}, T_{Ref} in Eq. (2.6.7) and $\sigma_{T,Ref}$, $C_{r,Ref}$ in Eq. (2.6.6):

(2.6.11)

$$C_{r,Ref} = \frac{\sqrt{4RT_{Ref}}}{[\Gamma(5/2 - \omega)]^{\frac{1}{2\omega-1}}},$$

2.6. Variable hard sphere (VHS) model

(2.6.12)
$$\mu_{Ref} = \frac{15m\sqrt{\pi R T_{Ref}}}{2(5-2\omega)(7-2\omega)\sigma_{T,Ref}},$$

where $\Gamma(x)$ is the **gamma function**:

(2.6.13)
$$\Gamma(x) = \int_0^{\infty} \xi^{x-1} e^{-\xi} d\xi \, .$$

See details in Bird, "Molecular gas Dynamics and the Direct Simulations of Gas Flows."

The process of parametrization of a VHS model for a particular gas species, which viscosity as a function of temperature is given in a tabulated form, then includes the following steps:

1. Choose the temperature range for the problem under consideration and T_{Ref}.
2. Fit the tabulated data on viscosity vs. temperature to the power law given by Eq. (2.6.7) and find μ_{Ref} and ω using, e.g., the **least-square method**.
3. Find $\sigma_{T,Ref}$ from Eq. (2.6.12).
4. Find $C_{r,Ref}$ from Eq. (2.6.11).

Values of ω and d_{Ref} for multiple gas species are given in Bird, "Molecular gas Dynamics and the Direct Simulations of Gas Flows."