Physical and Chemical Kinetics
Final Examination
07-11-2013

Please use the provided paper sheets to write down the solutions of the problems. Write your name and student ID number on a first page and enumerate all subsequent pages. Do not forget to hand in your paperwork after the examination.

Problem 1

Two interacting hydrogen atoms have laboratory velocities with (x, y, z) components of (1×10^3 m/s, 0, 0) and (0, 1×10^3 m/s, 0).

a. Find velocities of the atoms in the center-of-mass frame of reference.

Solution Positions of particle $\mathbf{r}$ and $\mathbf{r}'$ in different frames of references are related as

$$\mathbf{r} = \mathbf{R} + \mathbf{r}',$$

where $\mathbf{R}$ is the position of the second frame of reference relative to the first one. After differentiating we get

$$\mathbf{v} = \mathbf{V} + \mathbf{v}',$$

where V is the velocity of the second frame of reference. By definition, the position of the center-of-mass frame of reference is

$$\mathbf{R_{cm}} = \frac{m_1\mathbf{r_1} + m_2\mathbf{r_2}}{m_1 + m_2}$$

and

$$\mathbf{V} = \frac{m_1\mathbf{v_1} + m_2\mathbf{v_2}}{m_1 + m_2} = \frac{1}{2}(\mathbf{v_1} + \mathbf{v_2})$$

Thus we have

$$\mathbf{v_1'} = \mathbf{v_1} - \mathbf{V} = \frac{1}{2}(\mathbf{v_1} - \mathbf{v_2}) = (0.5 \times 10^3\,\mathrm{m/s}, -0.5 \times 10^3\,\mathrm{m/s}, 0)$$

and

$$\mathbf{v_2'} = \mathbf{v_2} - \mathbf{V} = \frac{1}{2}(\mathbf{v_2} - \mathbf{v_1}) = (-0.5 \times 10^3\,\mathrm{m/s}, 0.5 \times 10^3\,\mathrm{m/s}, 0)$$

b. Find the kinetic energy of relative movement of the hydrogen atoms.

Solution The kinetic energy of the relative movement of the atoms is

$$E_{kin} = \frac{1}{2}\mu\mathbf{v}^2 = \frac{m}{4}(\mathbf{v_2} - \mathbf{v_1})^2 = 1.66 \times 10^{-24}\,\mathrm{g}(1 \times 10^{10} + 1 \times 10^{10})\mathrm{cm}^2/\mathrm{s}^2 = 8.33 \times 10^{-15}\,\mathrm{erg}$$

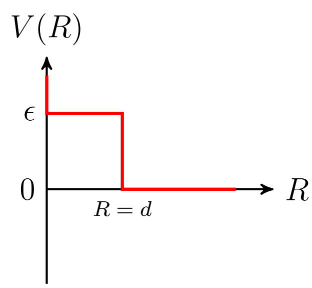
c. Find the total angular momentum of hydrogen atoms relative to the origin of the center-of-mass frame of reference when distance between atoms $r = (1, 1, 0)$cm. .

Solution By definition, the angular momentum is

$$\mathbf{M} = m_1\mathbf{r_1'} \times \mathbf{v_1'} + m_1\mathbf{r_2'} \times \mathbf{v_2'} = \frac{m}{2}(\mathbf{r_2'} - \mathbf{r_1'})(\mathbf{v_2'} - \mathbf{v_1'})$$
$$= 0.5 \times 1.66 \times 10^{-24}\,\mathrm{g} \times \begin{vmatrix} i & j & k \\ 1.0 & 1.0 & 0 \\ -1 & 1 & 0 \end{vmatrix} \times 1.0 \times 10^5\,\mathrm{cm^2/s}$$
$$= 1.66 \times 10^{-19} \times \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \mathrm{g\,cm^2/s}$$

Problem 2

Interaction of particles is described by a repulsive square-well potential with height ϵ at a distance d between particles (see fig.). The relative velocity of the particles before collision is v, impact parameter is b and their relative mass is μ.

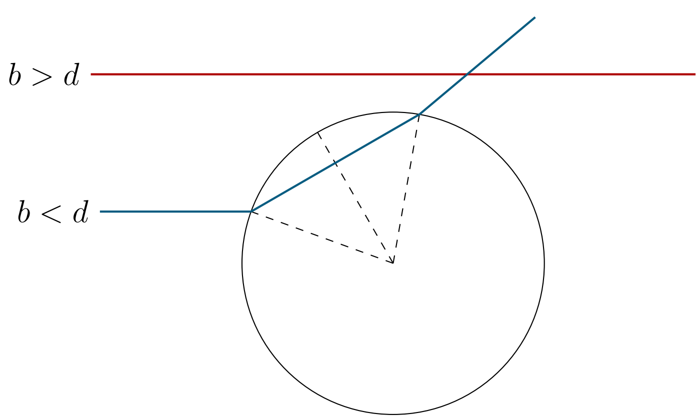


a. What is magnitude of the relative velocity after collision?

Solution The relative kinetic energy for elastic collisions is constant. Therefore, the magnitude of the relative velocity should be also remain constant.

b. Sketch the trajectory of the particle moving in a field with this potential.

Solution Trajectories are shown at the figure.



c. Find the distance of the closest approach between the particles as a function of v, b, μ, ϵ, and d.

Solution At the distance $R = d$ between particles the relative velocity will be stepwise decreased. At the distance of the closest approach we have

$$1 - \frac{b^2}{r_0^2} = \frac{2\epsilon}{\mu v_0^2}$$

and

$$r_0 = \frac{b}{\sqrt{1 - \frac{2\epsilon}{\mu v_0^2}}}$$

Problem 3

Consider nitrogen at temperature $T = 500\,\mathrm{K}$. Molecular weight of nitrogen molecule is $28\,\mathrm{g/mol}$.

a. Find the most probable magnitude of the velocity of nitrogen molecules at this temperature.

Solution The most probable velocity corresponds to the maximum of the distribution function. Thus

$$\frac{\mathrm{d}f}{\mathrm{d}v} = \frac{\mathrm{d}}{\mathrm{d}v} v^2 e^{-mv^2/2kT} = 0 \Rightarrow 2v - \frac{mv^3}{kT} = 0$$

Thus we have $v_m = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}}$. After substituting we get $v_m = \sqrt{\frac{2\times 8.314\times 10^7\,\mathrm{erg/mol\,K}}{28\,\mathrm{g/mol}}} =$

b. What is larger - the most probable velocity or the average velocity? Explain why these velocities are not the same.

Solution Comparing with the value of the average magnitude of velocity $v_{av} = \sqrt{\frac{8kT}{\pi m}}$ we find that $v_{av} > v_m$.

c. Find the sound velocity of nitrogen gas at this temperature.

Solution The sound velocity is given by

$$c = \sqrt{\frac{RT}{M}\gamma}$$

Nitrogen is 2 atomic molecule thus we have $\gamma = 7/5$. After substituting we get

$$c = \sqrt{\frac{8.314 \times 10^7\,\mathrm{erg/mol\,K} \times 500\,\mathrm{K}}{28\,\mathrm{g/mol}} \times \frac{7}{5}} = 4.56 \times 10^4\,\mathrm{cm/s}$$

Problem 4

Formation of the nitrogen oxide proceeds through the Zeldovich mechanism:

$$N_2 + O \xrightarrow{k_1} NO + N$$

$$N + O_2 \xrightarrow{k_2} NO + O$$

a. Assuming that rate coefficient k_2 is much larger than k_1 and concentrations of NO far below equilibrium, derive the expression for the rate of formation of the nitric oxide.

Solution The rate of formation of nitrogen atoms is

$$\frac{d[N]}{dt} = k_1[N_2][O] - k_2[N][O_2]$$

Because $k_2 \gg k_1$ we can use steady state approximation for the concentration of nitrogen atoms,

$$\frac{d[N]}{dt} = 0 \Rightarrow [N] = \frac{k_1[N_2][O]}{k_2[O_2]}$$

After substituting we find

$$\frac{d[NO]}{dt} = k_1[N_2][O] + k_2[N][O_2] = 2k_1[N_2][O]$$

b. Dissociation of oxygen molecules is sufficient fast that it is possible to assume that this reaction in equilibrium with the equilibrium constant K_d. Express the rate of formation of NO through the concentration of oxygen and nitrogen molecules.

Solution In equilibrium concentrations of oxygen atoms and oxygen molecules are related as

$$K_d = \frac{[O]^2}{[O_2]}$$

Expressing the concentration of the oxygen atoms through the concentration of the oxygen molecules we get

$$\frac{d[NO]}{dt} = 2k_1[N_2][O] = 2k_1 K_d^{1/2}[N_2][O_2]^{1/2}$$

c. Find the mole fraction of NO molecules at exit of a combustion chamber. The combustion gases can be treated as air at temperature 2000 K and pressure 10 atm. The residence time of combustion products in the chamber is $\sim$ 1 ms. The rate coefficient $k_1 = 1.8 \times 10^8 e^{-38370/T}$ m^3mol and the equilibrium constant $k_d = 3.97 \times 10^5 T^{-1/2} e^{-31090/T}$mol/$m^3$, where T is in K. The air is composed from 20%O_2 and 80%N_2. Molecular weight of the air is 29 g/mole and contains.

Solution Integrating the expression for the rate of formation of NO molecules we get

$$X([NO]) = \frac{[NO]}{N_t} = \frac{2k_1 K_d^{1/2}[N_2][O_2]^{1/2}}{N_t} = 21.8 \times 10^8 e^{-38370/T} \times$$

$$\left(3.97 \times 10^5 T^{-1/2} e^{-31090/T}\right)^{1/2} \left(\frac{P}{RT}\right)^{1/2} \times 0.8 \times \sqrt{0.2}\tau = 5.8 \times 10^{-4} = 580\,\text{ppm}$$