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TWO-DIMENSIONAL DIFFUSION OF A BINARY MIXTURE OF NEUTRAL GASES

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An expression for the coefficient of two-dimensional diffusion of a binary mixture of neutral gases is obtained within the framework of the kinetic theory.

The notions of an aggregate of particles on the phase interface as of a two-dimensional gaseous system are traditionally used in description of various physicochemical processes [1, 2]. In a number of cases one should consider a binary mixture of particles on the interface [3, 4]. We give the derivation of the coefficient of two-dimensional diffusion for a mixture of two types of uncharged gases within the framework of the kinetic theory following [5].

We use the Boltzmann kinetic equation with account for collisions of particles

$$\frac{\partial f_a}{\partial t} + \mathbf{v}_a \frac{\partial f_a}{\partial \mathbf{r}_a} + \mathbf{F}_a \frac{\partial f_a}{\partial \mathbf{p}_a} = \sum_b I_{ab} (f_a, f_b) , \tag{1}$$

where the subscripts a and b number the types of particles. In the case of elastic collisions of particles, the Boltzmann integral of collisions $I_{ab}(f_a, f_b)$ can be written in the form

$$I (f_a, f_b) = \int d\mathbf{p}_b \, v_{ab} \, d\sigma_{ab} \left\{ f_a^{'} f_b^{'} - f_a f_b \right\} ;$$

here and below the primes refer to the quantities characterizing gas particles after collision, $v_{ab} = |\mathbf{v}_a - \mathbf{v}_b|$, and $d\sigma_{ab}$ is the differential diameter of scattering (an analog of the differential cross section of scattering in a three-dimensional case). We seek the distribution function f_a by the Chapman–Enskog method in the form

$$f_a = f_a^{(0)} + \varepsilon f_a^{(1)} + \varepsilon^2 f_a^{(2)} + \ldots , \tag{2}$$

where the small parameter ε determines frequent collisions of particles, and thus restrict ourselves to the first approximation. The pulse-distribution function of the zeroth approximation $f_a^{(0)}$ obtained with no regard for the left-hand side of Eq. (1) is the two-dimensional Maxwell distribution

$$f_a^{(0)} = \frac{n_a}{2\pi m_a kT} \exp \left[- \frac{(\mathbf{p}_a - m_a \mathbf{v}_0)^2}{2 m_a kT} \right] . \tag{3}$$

For the quantities n_a, $\mathbf{v}_0$, and T to have the meaning of number density of particles, mean mass velocity, and temperature, the equalities

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$$\int f_a d\mathbf{p}_a = n_a\,, \quad \sum_a m_a \int \mathbf{v}_a f_a d\mathbf{p}_a = \rho \mathbf{v}_0\,, \quad \sum_a \frac{1}{2} m_a \int (\mathbf{v}_a - \mathbf{v}_0)^2 f_a d\mathbf{p}_a = nkT$$

must hold. Since they are valid for $f_a = f_a^{(0)}$, similar expressions yield 0 (s = 1, 2, ...) for the following terms of expansion (2):

$$\int d\mathbf{p}_a f_a^{(s)} = 0\,, \tag{4}$$

$$\sum_a m_a \int \mathbf{v}_a f_a^{(s)}\, d\mathbf{p}_a = 0\,, \tag{5}$$

$$\sum_a \frac{1}{2} m_a \int (\mathbf{v}_a - \mathbf{v}_0)^2 f_a^{(s)}\, d\mathbf{p}_a = 0\,. \tag{6}$$

Let $f_a^{(1)} = f_a^{(0)}\varphi_a$. Substituting $f_a^{(1)}$ into the kinetic equation of the first approximation

$$\frac{\partial f_a^{(0)}}{\partial t} + \mathbf{v}_a \frac{\partial f_a^{(0)}}{\partial \mathbf{r}_a} + \mathbf{F}_a \frac{\partial f_a^{(0)}}{\partial \mathbf{p}_a} = \sum_b \left[I_{ab}\,(f_a^{(0)}, f_b^{(1)}) + I_{ab}\,(f_a^{(1)}, f_b^{(0)}) \right],$$

we obtain the equation

$$f_a^{(0)} \left\{ \frac{1}{n_a}\frac{\partial n_a}{\partial t} + \frac{1}{T}\frac{\partial T}{\partial t}\left[\frac{m_a V_a^2}{2kT} - 1\right] + \frac{m_a \mathbf{V}_a}{kT}\frac{\partial \mathbf{v}_0}{\partial t} + \frac{\mathbf{v}_a}{n_a}\frac{\partial n_a}{\partial \mathbf{r}} + \left[\frac{m_a V_a^2}{2kT} - 1\right]\frac{\mathbf{v}_a}{T} \times \right.$$

$$\left. \times \frac{\partial T}{\partial \mathbf{r}} + \frac{m_a \mathbf{V}_a}{kT}\left(\mathbf{v}_a, \frac{\partial}{\partial \mathbf{r}}\right)\mathbf{v}_0 - \frac{\mathbf{V}_a}{kT}\mathbf{F}_a \right\} = \sum_b \int d\mathbf{p}_b\, d\sigma_{ab} v_{ab} f_a^{(0)} f_b^{(0)} \left\{ \varphi_a' + \varphi_b' - \varphi_a - \varphi_b \right\}, \tag{7}$$

where $\mathbf{V}_a = \mathbf{v}_a - \mathbf{v}_0$.

To reduce Eq. (7) to a form more convenient for calculation of the distribution function with account for the first approximation, we use the equations of continuity, motion, and heat transfer in the Euler approximation with no regard for diffusion, viscosity, and heat conduction.

Expressing the time derivatives from the continuity equation

$$\frac{\partial n_a}{\partial t} = -\,\mathrm{div}\,(n_a, \mathbf{v}_0)\,,$$

the equation of gas motion

$$\frac{\partial \mathbf{v}_0}{\partial t} + \left(\mathbf{v}_0, \frac{\partial}{\partial \mathbf{r}}\right)\mathbf{v}_0 = -\frac{1}{\rho}\frac{\partial p}{\partial \mathbf{r}} + \frac{1}{\rho}\sum_a n_a \mathbf{F}_a\,,$$

where $p = nkT$ is the pressure, $\rho = \sum_a n_a m_a$ is the density, and $n = \sum_a n_a$, and the equation of heat transfer

$$\frac{\partial T}{\partial t} + \mathbf{v}_0 \frac{\partial T}{\partial \mathbf{r}} = -\,T\,\mathrm{div}\,\mathbf{v}_0$$

and substituting them into Eq. (7), we obtain

$$f_a^{(0)}\left\{\frac{n}{n_a}\mathbf{V}_a\mathbf{d}_a+\left[\frac{m_aV_a^2}{2kT}-2\right]\mathbf{V}_a\frac{\partial\ln T}{\partial\mathbf{r}}+\frac{m_a}{kT}\left(V_{a,i}V_{a,k}-\frac{1}{2}\delta_{ik}V_a^2\right)\frac{\partial v_{0,i}}{\partial r_k}\right\}=$$

$$=\sum_b\int d\mathbf{p}_b\,d\sigma_{ab}\,v_{ab}\,f_a^{(0)}f_b^{(0)}\left\{\varphi_a'+\varphi_b'-\varphi_a-\varphi_b\right\}, \tag{8}$$

where

$$\mathbf{d}_a=\frac{n_am_a}{\rho p}\left\{\sum_b n_b\mathbf{F}_b-\frac{\rho}{m_a}\mathbf{F}_a\right\}-\frac{n_am_a}{\rho}\frac{\partial\ln p}{\partial\mathbf{r}}+\frac{n_a}{n}\frac{\partial\ln n_aT}{\partial\mathbf{r}}.$$

For a binary mixture of gases

$$\mathbf{d}_1=\frac{n_1n_2}{\rho n}\left\{\frac{m_1\mathbf{F}_2-m_2\mathbf{F}_1}{kT}+(m_2-m_1)\frac{\partial\ln T}{\partial\mathbf{r}}+m_2\frac{\partial\ln n_1}{\partial\mathbf{r}}-m_1\frac{\partial\ln n_2}{\partial\mathbf{r}}\right\}=-\mathbf{d}_2\equiv\mathbf{d}.$$

According to (4)–(6), system (8) must be supplemented by the conditions

$$\int d\mathbf{p}_a\,f_a^{(0)}\varphi_a=0, \tag{9}$$

$$\sum_a m_a\int\mathbf{v}_a\,f_a^{(0)}\varphi_a\,d\mathbf{p}_a=0, \tag{10}$$

$$\sum_a\frac{1}{2}m_a\int(\mathbf{v}_a-\mathbf{v}_0)^2\,f_a^{(0)}\varphi_a\,d\mathbf{p}_a=0. \tag{11}$$

To calculate the coefficient of diffusion, it is sufficient to consider the case where the gradients of temperature and velocity are absent and there are no force fields. Then we seek the function $\varphi_a(\mathbf{V}_a)$ in the form

$$\varphi_a=\sqrt{\frac{m_a}{2kT}}\,C_a\left(\frac{m_aV_a^2}{2kT}\right)n\mathbf{V}_a\mathbf{d}; \tag{12}$$

in this case, conditions (9) and (11) are satisfied automatically. To determine the function C_a, we use its expansion in some orthogonal system of polynomials. In this work, we restrict ourselves to the first term of the expansion in Laguerre polynomials, which is a constant,

$$C_a(x)\approx C_a^{(0)}, \tag{13}$$

and find it. We note that here the additional condition (10) takes the form

$$n_1\sqrt{m_1}\,C_1^{(0)}+n_2\sqrt{m_2}\,C_2^{(0)}=0. \tag{14}$$

To find the coefficient of diffusion, we write the mass density of the flux of particles of one type:

$$\mathbf{J}_a = m_a n_a \langle \mathbf{V}_a \rangle = m_a \int d\mathbf{p}\, f_a^{(0)} \varphi_a \mathbf{V}_a \,. \tag{15}$$

Substituting expressions (3) and (12) into Eq. (15), we obtain for the flux

$$\mathbf{J}_a = -\frac{n^2 m_1 m_2}{\rho} D_{ab} \mathbf{d} \,,$$

where the coefficient of diffusion D_{ab} is

$$D_{ab} = -\frac{\rho n_a}{n m_a m_b} \sqrt{\frac{m_a kT}{2}} \int_0^\infty dx \exp(-x)\, x C_a(x) \,.$$

Substitution of (13) yields

$$D_{ab} = -\frac{\rho n_a}{n m_b} \sqrt{\frac{kT}{2m_a}}\, C_a^{(0)} \,. \tag{16}$$

The equality $D_{ab} = -D_{ba}$ follows from Eqs. (14) and (16).

In order to calculate $C_a^{(0)}$, one should substitute expression (12) into Eq. (8); the latter takes the form

$$f_1^{(0)} \frac{\mathbf{V}_1}{n_1} = \int d\mathbf{V}_2\, d\sigma_{12} v_{12}\, f_1^{(0)} f_2^{(0)} \sqrt{\frac{m_1}{2kT}} \left(\mathbf{V}_1' - \mathbf{V}_1 - \frac{n_1}{n_2} (\mathbf{V}_2' - \mathbf{V}_2) \right) C_1^{(0)} \,. \tag{17}$$

We multiply Eq. (17) by $\mathbf{V}_1$ and integrate it with respect to velocities. On the left-hand side we obtain

$$\int d\mathbf{V}_1\, f_1^{(0)} \frac{V_1^2}{n_1} = \frac{2kT}{m_1} \,; \tag{18}$$

on the right-hand side we have

$$C_1^{(0)} \frac{n_1 n_2 m_1 m_2}{\pi^2 (2kT)^2} \sqrt{\frac{m_1}{2kT}} \frac{\rho}{n_2 m_2} \int d\mathbf{V}_1 d\mathbf{V}_2\, d\sigma_{12} v_{12} \exp\left(-\frac{m_1 V_1^2 + m_2 V_2^2}{2kT} \right) (\mathbf{V}_1, \mathbf{V}_1' - \mathbf{V}_1) \,. \tag{19}$$

With account for the law of conservation of momentum, we obtain from (17)–(19)

$$C_1^{(0)} = \frac{2^{7/2} (kT)^{7/2} \pi^2}{m_1^{5/2} n_1 \rho} \left[\int d\mathbf{V}_1 d\mathbf{V}_2\, d\sigma_{12} v_{12} (\mathbf{V}_1' - \mathbf{V}_1)^2 \exp\left(-\frac{m_1 V_1^2 + m_2 V_2^2}{2kT} \right) \right]^{-1} \,.$$

To calculate the integral, we pass to the system of coordinates of the center of inertia of colliding particles; in this case, the following relations hold:

$$\mathbf{V}_1 - \mathbf{V}_2 = \mathbf{v}_{12} \,; \quad m_1 \mathbf{V}_1 + m_2 \mathbf{V}_2 = \mathbf{P} \,; \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \,;$$

$$\mathbf{V}_1 = \frac{\mu}{m_1} \mathbf{v}_{12} + \frac{\mathbf{P}}{m_1 + m_2} \,; \quad \mathbf{V}_2 = -\frac{\mu}{m_2} \mathbf{v}_{12} + \frac{\mathbf{P}}{m_1 + m_2} \,;$$

$$\mathbf{V}_1' = \frac{\mu}{m_1} v_{12}\mathbf{n} + \frac{\mathbf{P}}{m_1+m_2}\ ; \quad \mathbf{V}_2' = -\frac{\mu}{m_2} v_{12}\mathbf{n} + \frac{\mathbf{P}}{m_1+m_2}\ ;$$

$$m_1V_1^2 + m_2V_2^2 = \mu v_{12}^2 + \frac{P^2}{m_1+m_2}\ ; \quad d\mathbf{V}_1 d\mathbf{V}_2 = \frac{\mu^2}{m_1^2 m_2^2} d\mathbf{v}_{12} d\mathbf{P}\ ; \quad \mathbf{V}_1' - \mathbf{V}_1 = (v_{12}\mathbf{n} - \mathbf{v}_{12}) \frac{\mu}{m_1}\ .$$

Integrating in the new coordinates and bearing in mind that the differential diameter of scattering in the case of impermeable spheres of radii a_1 and a_2 is equal to $d\sigma = (a_1 + a_2)d\varphi$, we obtain

$$C_1^{(0)} = \frac{(kT)^{1/2}\, 2^{1/2}}{6\pi^{3/2}\, n\mu^{1/2}\, (a_1 + a_2)}\ . \tag{20}$$

Substituting expression (20) into (16), for the coefficient of two-dimensional diffusion of a binary mixture we have

$$D_{12} = \frac{1}{3\pi\sqrt{2\pi}} \sqrt{\frac{kT}{\mu}}\, \frac{1}{n}\, \frac{1}{a_1 + a_2}\ . \tag{21}$$

In conclusion, we make some comparative estimates. In [5], the coefficient of diffusion of a binary mixture of gases is presented in a three-dimensional case:

$$\tilde{D}_{12} = \frac{3\sqrt{\pi}}{8\sqrt{2}} \sqrt{\frac{kT}{\mu}}\, \frac{1}{\tilde{n}}\, \frac{1}{(a_1 + a_2)^2}\ ,$$

where the three-dimensional physical quantities corresponding to those present in Eq. (21) and similar to them are denoted by a tilde. Assuming that the two-dimensional density of particles in an arbitrary cross section of a volume chosen at random in the three-dimensional case has the same order as the surface density of particles in the two-dimensional case, i.e., $\tilde{n} \propto l^{-3}$ and $\tilde{n} \propto l^{-2}$, where l is the characteristic distance between the centers of particles, we obtain for the relation of the coefficients of diffusion

$$\frac{D_{12}}{\tilde{D}_{12}} = \frac{8}{9\pi^2}\, \frac{a_1 + a_2}{l}\ . \tag{22}$$

We apply (22) to a binary mixture consisting of atoms of hydrogen and molecules of water; this system is of high priority in considering a number of surface processes. The quantity $(a_1 + a_2)$ is approximately equal to 0.4 nm. If the density of the particles on the surface is high, we can assume that $l \propto (a_1 + a_2)$, and the numerical value of the coefficient of two-dimensional diffusion for these values of the particle density is much lower than its three-dimensional analog: $D_{12}/\tilde{D}_{12} \approx 0$. To lower values of the particle density there corresponds a higher value of l, so that the exceeding of the three-dimensional coefficient of diffusion over the two-dimensional coefficient increases. Thus, we can draw the conclusion that the numerical value of a two-dimensional coefficient of diffusion is always lower (by an order of magnitude or more) than the value of a three-dimensional coefficient of diffusion for the corresponding density of particles. For the mentioned system of atoms of hydrogen and molecules of water with an ultimately high value of the particle density ($l = a_1 + a_2$), we obtain for the coefficient of diffusion $D_{12} \approx 3{\cdot}10^{-8}$ m^2/sec, which is the lower estimate. To lower values of the particle density there will correspond higher values of the coefficient of diffusion.

NOTATION

f_a and f_b, pulse-distribution functions of the particles of types a and b; $\mathbf{r}_a$, radius sector of the particle of type a; $\mathbf{p}_a$, pulse of the particle of type a; $\mathbf{v}_a$, velocity of the particle of type a; $\mathbf{F}_a$, force affecting the particle of type a; m_a and m_b, masses of the particles of types a and b; $I_{ab}(f_a, f_b)$, Boltzmann integral of collisions; ε, small parameter of the frequency of collisions; t, time; $\mathbf{v}_{ab}$, relative velocity of the particles of types a and b; $d\sigma_{ab}$, differential diameter of scattering; $f_a^{(s)}$, sth term in the distribution function of the particles of type a by powers ε; n_a and n_b, number density of the particles of types a and b, respectively; k, Boltzmann constant; T, temperature; $\mathbf{v}_0$, mean mass velocity of the particles; ρ, density of the gas mixture; n, number density of the particles in the gas mixture; p, pressure of the gas mixture; φ_a and φ_b, distribution functions of the particles of types a and b in the first approximation; $\mathbf{V}_a(\mathbf{V}_1)$, velocity of the particle of type a (type 1) relative to the mean mass velocity; $\mathbf{d}_a$, vector of transfer of the particles of type a; δ_{ik} Kronecker symbol (tensor); $C_a(x)$, function characterizing the distribution of the particles of type a in the first approximation; $C_a^{(0)}$, zeroth term of the expansion of the function $C_a(x)$ in Laguerre polynomials; $\mathbf{J}_a$, density of the flux of the particles of type a; $\langle \mathbf{V}_a \rangle$, mean velocity of the particles of type a (relative to the mean mass velocity); D_{ab}, coefficient of diffusion; $\mathbf{P}$, pulse of the center of inertia of colliding particles; μ, reduced mass of the particles; $\mathbf{n}$, unit vector of the direction of the velocity of the particle of type a in the system of coordinates of the center of inertia of colliding particles; a_1 and a_2, radii of the particles of types 1 and 2.

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