

Mutual Diffusion Coefficient in Binary Mixtures and the Lattice Gas Model

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Abstract—A modification of the elementary kinetic theory of a gas mixture in terms of the lattice gas model is proposed. It is assumed that molecules of components of the mixture are spherical and close in size. In calculating the diffusion flux of molecules through a selected plane, instead of the mean thermal velocity of molecules, the mean relative velocity of molecules of components of different types is used. In this case, the flux explicitly depends on the type of component with which a molecule collided last before intersecting the selected plane. The proposed modification allows one to derive an expression for the mutual diffusion coefficient of components of a binary mixture that at low densities of the mixture (as in a rarefied gas phase), is consistent with the expression obtained in the rigorous kinetic theory of gases.

Mass transfer in one aggregation state or another accompanies most chemical and thermophysical processes. In terms of nonequilibrium thermodynamics [1, 2], the phenomenological descriptions of transfer phenomena in the gas, liquid, and solid phases are identical; therefore, it is natural to assume that, at the molecular level, the mathematical description of mass transfer should also be unified. However, in molecular models, kinetic theories developed for each of the phases have to be used. This is because there is currently no unified kinetic theory for all the three phases and the kinetic theories of gas [3–6], liquid, [7–9], and solid [10–12] are based on specific properties of the corresponding phases. For example, in gas, the main role is played by the dispersion of molecular velocities, whereas, in the dense phases (liquid and solid), of prime importance is the spatial nonuniformity of the distribution of molecules. Because of the absence of crystalline order in gas and liquid, the transport of molecules in these phases is faster than that in the solid phase; therefore, gas and liquid exhibit viscous properties, which are absent from a solid (up to its plastic deformation and failure).

This paper was written for the following two reasons. Previous works [13–19] were devoted to the development of a microhydrodynamic approach to describing single-component flows of simple molecules in narrow (nanosized) pores in terms of the simplest molecular model, namely, the lattice gas model [20]. This approach allowed analysis, from a unified standpoint, of flows of molecules at any densities (from those inherent in gases to those characteristic of liquids) in strong adsorption fields and expression of all the dissipative coefficients directly through the atom–atom potentials of interaction of molecules with the

pore walls and between one another (without introduction of any additional empirical parameters of the system). This approach uses the master equations for the dense phases. Naturally, the application of these equations to the gas phase is their extrapolation beyond the domain of definition. Nonetheless, for single-component fluids, good results throughout the density range were obtained, which were consistent with the data of both experiments and molecular dynamics simulations [21–24]. This success was not accidental since the lattice gas model is applicable to all the three phases and has been actively used to calculate their characteristics [7, 10–12, 25–28].

The first reason is that the generalization of this approach to multicomponent gas mixtures [29] led to a well-known contradiction in calculating the mutual diffusion coefficient, expressions for which are derived by describing the mutual diffusion from the standpoint of a purely diffusion process and in terms of the rigorous kinetic theory of gases [3–6, 30]. The contradiction is that the diffusion description leads to the Meyer equation for the mutual diffusion coefficient, which is inconsistent with experimental data. To remove this contradiction, the Stefan–Maxwell hypothesis was made [30], which formulates the rules of selection of types of pairwise collisions that contribute to mutual diffusion. Later, the kinetic theory [3–6] confirmed the validity of this hypothesis. A natural question arises as to how an expression for the mutual diffusion coefficient can be derived in terms of the lattice gas model so that the advantages of the microhydrodynamic approach can be simultaneously retained for a wide range of practical applications (vapor and liquid flows in narrow pores of adsorbents, membranes, catalysts, etc.). It is necessary that the expression for the mutual

diffusion coefficient should be consistent with the kinetic theory of gases and should be applicable to any densities of a mixture (i.e., for any aggregation states).

The second reason is related to a deeper understanding of the generality and difference of the elementary (or phenomenological) and rigorous kinetic theory of gases. It is universally accepted that the elementary theory cannot give the correct result [3–6, 31] since it necessarily leads to the Meyer equation. Nonetheless, the question remains of to what extent the consideration of the molecular velocity distribution determines the essence of the mutual diffusion coefficient, or whether or not it is possible to obtain a correct expression for the mutual diffusion coefficient in terms of the mean thermal velocities of molecules of components of a mixture without using the Boltzmann equation for *nonequilibrium* molecular velocity distribution functions, and, if it is possible, what the conditions for this are. Obviously, the mean velocities of molecules of components that are used in the elementary theory are obtained by averaging over the *equilibrium* molecular velocity distribution function.

For simplicity, let us consider the diffusion transfer of components of a binary mixture of simple spherical molecules of approximately identical shape. This case is described by only one mutual diffusion coefficient; therefore, this case is studied in the largest number of works using molecular models in different phases and is a good example to illustrate the gist of the matter.

DEFINITIONS OF THE MUTUAL DIFFUSION COEFFICIENT

Rarefied gas. In the first-order approximation of the Chapman–Enskog theory of a gas mixture [3–7, 30–32], the diffusion velocity \mathbf{V}_i of component i at constant pressure P and temperature T in the absence of external fields is defined as

$$\mathbf{V}_i = -\sum_j D_{ij} \mathbf{grad}(x_j). \quad (1)$$

In expression (1), D_{ij} are the diffusion coefficients of the multicomponent mixture, which are interrelated as

$$\sum_i x_i D_{ij} = 0, \quad D_{ii} > 0 \quad \text{and} \quad D_{ij} = D_{ji}.$$

Here, $x_i = n_i/n$ (x_i is the mole fraction of component i and n_i is the number density of component i in a unit volume (a characteristic set of particles is used)).

For a binary mixture, $x_1 + x_2$ and $n = n_1 + n_2$; therefore, for such a mixture, there is a single mutual diffusion coefficient $D_{1,2}$ in a frame of reference moving at mean velocity $w = \sum_i n_i v_i / n = w_c + \sum_i x_i \mathbf{V}_i$, where v_i

is the mean velocity of component i and $w_c = \sum_i x_i v_i$

is the mole-average flow velocity.

The mutual diffusion coefficient $D_{1,2}$ can be obtained from the above equations by expressing all the coefficients D_{ij} in terms of D_{12} (in a fixed frame of reference):

$$\begin{aligned} \mathbf{V}_1 - \mathbf{V}_2 &= -(D_{11} \mathbf{grad}(x_1) + D_{12} \mathbf{grad}(x_2)) \\ &\quad + (D_{21} \mathbf{grad}(x_1) + D_{22} \mathbf{grad}(x_2)) \\ &= -(-D_{12} n_2 / n_1 \mathbf{grad}(x_1) + D_{12} \mathbf{grad}(x_2)) \\ &\quad + (D_{12} \mathbf{grad}(x_1) - D_{12} n_1 / n_2 \mathbf{grad}(x_2)) \\ &= D_{12} / (x_1 x_2) \mathbf{grad}(x_1) = -D_{1,2} / (x_1 x_2) \mathbf{grad}(x_1), \end{aligned} \quad (2)$$

where $D_{12} = D_{1,2} > 0$; i.e., the mutual diffusion coefficient depends on the gradients of composition and pressure of the system and also on the contributions of external fields.

In the hard sphere model, mutual diffusion coefficient $D_{1,2}$ is expressed as

$$D_{1,2} = (3\pi/8n\sigma_{12})w_{12}, \quad w_{12} = (kT/2\pi\mu_{12})^{1/2}, \quad (3)$$

where $\sigma_{ij} = \pi d_{ij}^2$, $d_{12} = (d_{11} + d_{22})/2$ is the distance of maximal approach of molecules, d_{ii} is the diameter of a molecule of component i , $\mu_{12} = m_1 m_2 / (m_1 + m_2)$ is the reduced mass of colliding molecules of components 1 and 2, and m_i is the mass of a molecule of component i .

Solid phase. The mutual diffusion coefficient in alloys is experimentally measured at constant pressure and temperature. Two annealed samples of a binary alloy whose molar compositions x_i ($x_1 + x_2 = 1$) in the initial (nonequilibrium) state are different are brought into close contact, and the penetration of atoms through the plane of contact of the samples (plane 0) to either side of the plane is observed. The minimum of the Gibbs potential corresponds to the equalization of the alloy composition on either side of plane 0, which causes mixing of the components. The alloy components differ in mass m_i ; therefore, the difference in diffusion mobility between atoms of different components leads to macroscopic displacements of crystal planes (the Kirkendall effect) [10–12, 33, 34], which are detected by observing displacements of inert markers. The displacements of the markers in the binary alloy indicate displacements of crystallographic layers (planes) as a whole. This is explained by the existence of an uncompensated flow of vacancies, whose sinks take place in the case of climb of dislocations (the Kirkendall effect proper) or formation of pores in crystals (the Frenkel effect) [33]. The collapse of pores because of mechanical instability of the solid or the climb of dislocations sets the planes in macroscopic motion.

At the atomic level, the process develops so that faster light atoms move toward the region with a higher concentration of heavy atoms, whereas heavy atoms move toward the region with a higher concentration of

light atoms in order to compensate a local increase in the total concentration of atoms. The total lattice flow velocity compensates the difference of the diffusion flows of different atoms. An equation of the mutual diffusion coefficient in solid alloys is derived using a scheme of random walk of atoms [10–12, 33, 34]. This scheme is common for all the phases; its equations for gas are presented below. Atoms move by hopping to neighboring vacancies. Within the framework of the Darken theory [10–12], the following expression for the mutual diffusion coefficient $D_{1,2}$ was obtained:

$$D_{1,2} = x_2 D_1 + x_1 D_2, \quad (4)$$

where D_i is the diffusion coefficient of an atom of component i in a fixed frame of reference. In alloys, expressions for the individual diffusion coefficients are represented as $D_i = D_i^* (1 + \partial \ln \gamma_i / \partial \ln x_i)$, where D_i^* and γ_i are the self-diffusion coefficient and the activity coefficient of an atom of component i in an alloy, respectively. Cross diffusion terms in expression (4) are absent to simplify transport models. More rigorous modes take into account the contributions of these terms [11, 12, 34].

Meyer equation and Stefan–Maxwell hypothesis.

To analyze the relationship between the kinetic approaches to the gas and solid phases, let us reproduce the derivation of the Meyer equation for the mutual diffusion coefficient in the gas phase (by describing the diffusion process using the scheme of random walk of atoms) and the Stefan–Maxwell hypothesis.

Let there be a mixture of two gases with mole fractions of molecules of x_1 and x_2 with different molecular masses m_i at constant pressure and temperature ($P, T = \text{const}$). In a nonequilibrium state, the molar composition x_i of the gas differs on either side of a certain selected plane (plane 0). The situation is completely identical to the case of an alloy in a nonequilibrium state. Faster light molecules move toward the region with a higher concentration of heavy molecules, whereas heavy molecules move toward the region with a higher concentration of light molecules in order to compensate a local increase in the total concentration of molecules. In the discussed process of mixing of components of the binary mixture, the difference of the opposite flows of both components creates conditions for the flow of the entire gas; i.e., a convective flow with mean velocity w_0 is formed, which depends on the difference of the diffusion coefficients D_i in a fixed frame of reference. Let N_i be the numbers of molecules of components $i = 1$ and 2; then, the kinetic equations for their transport can be written as

$$\mathbf{J}_i^I = dN_i/dt = w_0 n_i - 0.5 \{ [n_i w_i l_i]_I - [n_i w_i l_i]_{II} \}, \quad (5)$$

where w_i and l_i are the mean thermal velocity and the mean free path of molecules of component i , respectively. The expressions within the square brackets with the subscripts I and II refer to the half-spaces on the left

and the right of plane 0, respectively. Expansion of the right-hand side of the equation in terms of $\text{grad}(n_i)$ in the form $n_i(II) = n_i(I) + l_i \text{grad}(n_i)$ yields

$$\mathbf{J}_i^I = dN_i/dt = w_0 n_i - D_i dn_i/dZ, \quad i = 1, 2. \quad (6)$$

For simplicity, let Z be the coordinate along which molecules move. Below are the expressions for the coefficients D_i that are derived in terms of the elementary kinetic theory using the equilibrium molecular velocity distribution function:

$$D_i = w_i l_i / 2, \quad w_i = (8kT/\pi m_i)^{1/2}. \quad (7)$$

Since $d(N_1 + N_2)/dt = 0$ and $n = n_1 + n_2$, one can write

$$w_0 = [D_1 dn_1/dZ + D_2 dn_2/dZ]/n. \quad (8)$$

Equation (6) with allowance for expression (8) can be transformed to the form

$$\mathbf{J}_i^I = dN_i/dt = -D_{1,2} dn_i/dZ, \quad D_{1,2} = x_2 D_1 + x_1 D_2, \quad (9)$$

where $D_{1,2}$ is the mutual diffusion coefficient of the binary mixture. As a result, Meyer equation (9) is obtained, which is inconsistent with experimental data on a rarefied gas if the quantity l_i is estimated by counting the number of collisions of molecules of component i with molecules of both components $j = 1$ and 2 [30]:

$$l_1 = [2^{1/2} n_1 \sigma_{11} + n_2 \sigma_{12} (1 + m_1/m_2)^{1/2}]^{-1}, \quad (10)$$

$$l_2 = [2^{1/2} n_2 \sigma_{22} + n_1 \sigma_{12} (1 + m_2/m_1)^{1/2}]^{-1}.$$

To avoid the problem of inconsistency of Eqs. (9) and (10) with experimental data, Stefan and Maxwell postulated that, in estimating l_i , account should be taken only of collisions with molecules of the other component $j \neq i$; then, formula (10) can be represented in the form [30]

$$l_1^{\text{SM}} = [n_2 \sigma_{12} (1 + m_1/m_2)^{1/2}]^{-1}, \quad (11)$$

$$l_2^{\text{SM}} = [n_1 \sigma_{12} (1 + m_2/m_1)^{1/2}]^{-1}.$$

As a result, formula (9) implies the known Stefan–Maxwell formula

$$D_{1,2}^{\text{SM}} = w_{12} / (n \sigma_{12}), \quad w_{12} = (2kT/\pi \mu_{12})^{1/2}, \quad (12)$$

which agrees well with experimental data, and the rigorous kinetic theory [3–7] substantiated this procedure for selecting types of collisions.

Thus, although the particle transport mechanisms in an ideal gas and a solid alloy differ, the mutual diffusion coefficients in formulas (4) and (9) in a moving frame of reference are identically expressed through the diffusion coefficients D_i of individual components in a fixed frame of reference. Note also that the Kirkendall effect was repeatedly used in the theory of gas flows in wide channels to describe wall effects [35]. Hence, it follows that the difference between formulas (4) and (9) is determined by the procedure for constructing the

expression for $D_{1,2}$ rather than by the difference in molecular migration mechanism between different phases.

Analysis of definitions. Formal constructions of irreversible thermodynamics [1, 2] lead to the same structure of molecular transfer equations (they are diffusion equations) in the gas, liquid, and solid phases, although the mechanisms of elementary processes of migration of components differ. In the gas phase, everything is determined by pairwise collisions. In the solid phase, displacements of molecules occur by a vacancy mechanism and, for hopping of an atom in an alloy, the atom should acquire, by a fluctuation mechanism, the energy required to surmount the activation barrier. In the latter case, the hopping involves (indirectly or directly) all the neighboring atoms that affect the local oscillation frequencies and the activation energy of the migrating atom. In the liquid phase, the influence of neighboring molecules is also significant.

Diffusion equations are generalizations of experimental data in terms of Fick's law. Their molecular interpretation is based on the consideration of the scheme of random walk of molecules over relatively long time intervals. Such walk simulates the free motion of molecules in gas between collisions or models the elementary hopping of atoms in the liquid and solid phases. Such processes are described by analyzing the opposite flows of particles, which give rise to a resultant diffusion flow. The thermodynamics of irreversible processes [1, 2] gives an ordinary structure of equations describing the flows of molecules at $P, T = \text{const}$:

$$\mathbf{J}_i = -D_{ii}\text{grad}(n_i) - D_{ij}\text{grad}(n_j), \quad i = 1 \text{ and } 2. \quad (1a)$$

If the diffusion velocities of components are expressed in terms of the diffusion fluxes as $\mathbf{V}_i = \mathbf{J}_i/n_i$, then their difference can be written as

$$\begin{aligned} \mathbf{V}_1 - \mathbf{V}_2 &= -(D_{11} - D_{12})/n_1\text{grad}(n_1) \\ &\quad - (D_{22} - D_{21})/n_2\text{grad}(n_2) \\ &= -(x_2D_{11} + x_1D_{22} - D_{12})/(x_1x_2)\text{grad}(x_1). \end{aligned} \quad (2a)$$

This equation differs from Eq. (2) by the presence of cross terms. Equations (2) and (2a) coincide at $D_{ii} = 0$. In this case, the flow velocity is written from Eq. (8) as $w_0 = (D_{11} - D_{22})\text{grad}(x_1)$ and is also zero, which signifies the absence of convective flow of the mixture.

On the other hand, if $D_{12} = D_{1,2}$ and Meyer–Darken equations (4) and (9) are valid, then the difference of the diffusion velocities of both components is zero, which indicates the flow of the mixture as a whole. This takes place in the convective flow with respect to a fixed frame of reference, whereas Eq. (2) was introduced for the diffusion velocities of components in a frame of reference moving with the convective flow. Thus, the validity of the Meyer–Darken equations means the absence of mutual diffusion from the standpoint of the kinetic theory of gases. In other words, the definitions

of the rigorous kinetic theory of gases and the purely diffusion interpretation of the mutual diffusion coefficient according to the scheme of random walk of components of a mixture are mutually exclusive.

The Stefan–Maxwell hypothesis suggests that the elementary kinetic theory should take into account in more detail the type of colliding molecules. But formula (12) cannot be automatically extended to the dense phases. Therefore, let us discuss a modification of the elementary kinetic theory that follows from the specificity of the theory of the dense phases and the requirement of the Stefan–Maxwell hypothesis.

MODIFICATION OF THE RANDOM WALK SCHEME

To determine how the drawbacks of the Meyer formula can be eliminated, let us discuss the scheme for constructing this equation from the standpoint of the theory of condensed media. The existing kinetic theory of gases cannot be directly generalized to the dense phases; therefore, the lattice gas model is used, which is applicable to any media [20]. The purpose of this consideration is to generalize the scheme of hopping in the lattice gas model to a rarefied gas and to construct an expression for the mutual diffusion coefficient in terms of hopping of molecules.

Lattice gas model [20, 26–28, 36]. The volume V of the system is divided into cells, where the volume of each is on the order of the volume of particle, $v_0 = \lambda^3$ (where λ is the linear size of a cell), in order to rule out the double occupation of a cell by different molecules. Then, $V = Nv_0$, where N is the number of cells in the system (a fully occupied structure). Let z be the number of nearest cells of the lattice structure. At each cell, there can be only a single particle: either a molecule of component i (if the center of mass of the molecule is within the cell) or a vacancy v . The subscript i refers to the type of a component of the mixture, and s is the number of differently occupied states of a cell of the system; i.e., the number of components is $s - 1$. The fact that a molecule is within a cell does not mean that its center of mass is fixed; the molecule has translational, rotational, and vibrational degrees of freedom [37]. Such a description of the system is standard in analyzing any interphase equilibrium processes (adsorption, absorption, vapor–liquid equilibrium, etc.) [20, 25]. In this case, the properties of the system are considered as functions of the thermostat parameters. The relationship between the states of the system and the thermostat is expressed by isotherms following from the condition that the chemical potentials of molecules in the system and the thermostat are equal. The same point of view turns out to be fruitful in studying a single-phase system of arbitrary density [38].

The concentration of molecules of component i is usually considered to be equal to the number of these molecules N_i in a unit volume: $n_i = N_i/V$. In the lattice

gas model, the concentration of a component of a fluid is characterized by the ratio $\theta_i = N_i/N$ of the number of particles in a certain volume to the maximum possible number of closely packed particles in the same volume; i.e., $\theta_i = n_i v_0$. The full occupation of the volume is

defined as $\theta = \sum_{i=1}^{s-1} \theta_i$. The relationship between the total

concentration n of molecules and the occupancy θ is expressed by the formula $n = \theta/v_0$.

Isotherms determine the relationship between the pressures $\{p\}$ in the thermostat ($\{p\} \equiv p_1, \dots, p_{s-1}$ is the total set of all partial pressures p_i of components of the mixture, $1 \leq i \leq s-1$) and the partial occupancies $\{\theta_i\}$ of the volume of the system. The isotherms have the form [14–17, 20]

$$a_i p_i = \theta_i \Lambda_i / \theta v, \quad (13)$$

where the function Λ_i characterizes the intermolecular interactions. The specific form of this function was presented earlier [20] in considering dense mixtures. If the intermolecular interactions are ignored, $\Lambda_i = 1$ (an ideal system).

The quantity $a_i = \beta F_i / F_{i0}$, where F_i and F_{i0} are the statistical sums of a molecule of component i in a cell and the thermostat, respectively, and $\beta = (kT)^{-1}$. In the thermostat, as a rule, the gas is assumed to be ideal.

The equation of state of an ideal system in the lattice gas model has the form [26, 27, 39]

$$\beta P v_0 = -\ln(1 - \theta), \quad (14)$$

which differs from a conventional virial expansion [3–7]. However, at low densities, from Eq. (14), the equation of state of an ideal gas follows in the form $\beta P v_0 = \theta$ or $\beta P = n$.

Conditions of the theory of condensed phases.

There are two features that distinguish between the kinetic theories of gas and solid.

The first feature is the following. The kinetic theory of dense systems does not consider collisions between molecules but operates with the probabilities of transition of molecules from one point in space to another. These transition probabilities are expressed through the states of the thermostat and a selected group of molecules. They depend on the lateral interactions between all the components of the system.

To calculate the mutual diffusion coefficients, it becomes necessary to explicitly take into account collisions between molecules of different types. Taking this into account is readily combined with constructing the molecular transition probabilities if type j of component with which a molecule i collided last within region I (or II) before intersecting the selected plane (plane 0). The conventional elementary kinetic theory implicitly considers collisions of all molecules after intersecting plane 0, i.e., molecules in the other region, region II (or I) (in the rigorous kinetic theory of gas, this aspect

is not discussed, although the collision integral contains the characteristics of molecules both before and after collision, but all of them are related to a certain elementary gas volume without referring to the position of plane 0).

The second feature is the following. From the standpoint of the equilibrium distribution of molecules, an ideal gas is a rarefied system in which, on the average, all the particles are at an approximately equal distance ρ . Otherwise, any deviation from the uniform distribution of molecules should lead to density fluctuations only because of the difference in molecular mass between components of the mixture. However, the latter are impossible without the effect of intermolecular interactions, which are ruled out by the definition of an ideal gas.

In the kinetic theory, there are two main molecular linear sizes: the size σ of a molecule (which is uniquely related to the cell size in the lattice gas model as $\lambda \approx 2^{1/6} \sigma$: the λ scale) and the mean free path l_i of a molecule (the l scale). In addition, there is a third characteristic linear quantity: the mean distance ρ between molecules of the gas phase (the ρ scale), which is defined as $\rho = v_0^{1/3}$ (v_0 is the volume per molecule of the mixture); in the lattice gas model, $\rho = \lambda/(\theta)^{1/3}$.

The quantity ρ is used [32] in the kinetic theories to define the dimensionless density parameter as the ratio $(\lambda/\rho)^3$, in terms of which one can construct expansions. But this quantity alone plays no functional role. In the proposed modification of the lattice gas model, the fact of the existence of the mean distance ρ between molecules allows one to interpret ρ as an analogue of lattice constant, which depends on the density θ of the mixture. In the dense phases, $l = \rho = \lambda$. This enables one to introduce a unified method for describing the system in transition from the dense phase to the rarefied gas, for which $\lambda \ll \rho \ll l_i$. The first sign \ll should be understood rather conditionally since, for the rarefied gas at $\theta = 10^{-3}$ – 10^{-4} , the difference is about an order of magnitude: $\rho = (10-22)\lambda$. At the same time, the differences between ρ and l_i reach two orders of magnitude: $l_i = 1/(2^{1/2} \pi n d_{ii}^2) = \rho^3/(2^{1/2} \pi d_{ii}^2) \approx (30-140)\rho$.

Consequences of the lattice gas model. In the dense phases, the number of feasible molecular transition probabilities is relatively small and depends on the number of bonds between neighboring cells of the lattice structure to which a particle can hop if there is a vacancy. The lateral interactions are taken into account completely. With an increase in the mean distance between molecules, the number of probabilities of molecular transitions between different points in space abruptly increases and the consideration of the lateral interactions is complicated. To simplify the description of these probabilities, let us use the lattice gas model constructed on the lattice with a constant on the ρ scale. Then, the contributions of the lateral interactions on the

l scale are replaced by the contributions on the ρ scale. This significantly simplifies the calculation since, if these contributions are small on the ρ scale, then they are all the more negligible on the l scale.

In the lattice gas model, there is a strong proof of self-consistency of describing the dynamics of molecular processes and the equilibrium state of a mixture at any densities and temperatures [20]. The use of the ρ scale allows one to retain this important property of the lattice gas model, and on the l scale, one can describe the dynamic processes occurring on the ρ scale (ρ an equilibrium characteristic since it appears in the equation of state). Thus, one can retain all the advantages of the lattice gas model and take into account the effect of the lateral interactions on the dynamics of elementary processes.

Combining the two features discussed, one can see that, for a molecule of component f to move from cell f in region I toward cell g in region II, this molecule should preliminarily collide with a molecule of component j at cell ξ within region I. To describe such motion, instead of the mean velocity w_i of a molecule of component i (expression (7)), which is conventionally used in the elementary kinetic theory, it is necessary to use the mean relative velocity of a molecule of component i after its collision with a molecule of component j . This velocity of a molecule of component i is written as $w_{i(j)} = (kT/2\pi\mu_{ij})^{1/2}$.

Another consequence of the lattice gas model is that the distance (measured in units of the ρ scale) between regions I and II, over which density gradients for both components are considered, is the same for all components (this condition was used in deriving Eq. (4) [10–12, 34]). Therefore, in constructing a diffusion equation for an ideal gas, the condition $l_i = l = \text{const}$ should be met. This condition directly implies that, for a mixture, unlike formula (11), l is expressed just as for a single-component system: $l \sim (n\langle\sigma\rangle)^{-1}$, where $\langle\sigma\rangle$ is the mean section of colliding molecules in the mixture, although the l value, as in Eq. (10), can depend through $\langle\sigma\rangle$ on the molar composition of the mixture.

Consideration of collisions. Let us construct equations of the type of the Meyer equation with allowance for the noted refinements for the case of comparable sizes of molecules of components of a gas mixture. The flow of molecules of component i that intersects plane 0 consists of two contributions. These molecules move at relative velocities $w_{i(j)}$ after collision with molecules of components $j = 1$ (the first contribution) and $j = 2$ (the second contribution). Correspondingly, it is necessary to take into account the mole fraction x_j of each component j with which molecules of component i collide. For this reason, instead of the mean velocity w_i , Eqs. (5) and (6) should involve the sum $w_{i(1)}x_1 + w_{i(2)}x_2$. Expression (5) for the flux of the first component is rewritten as

$$\mathbf{J}_1^t = dN_1/dt = w_0n_1 - 0.5\{[n_1(w_{1(1)}x_1 + w_{1(2)}x_2)]_I - [n_1(w_{1(1)}x_1 + w_{1(2)}x_2)]_II\}. \quad (5a)$$

As above, the expressions within the square brackets with the subscripts I and II refer to the half-spaces on the left and the right of plane 0, respectively. Expansion of the right-hand side of the last equation in terms of $\text{grad}(n_1)$ gives (for clarity, the quantity l_i is retained, which will be concretized below)

$$\mathbf{J}_1^t = w_0n_1 - 0.5l_1[(2w_{1(1)}x_1 + w_{1(2)}x_2)dn_1/dz + w_{1(2)}x_1dn_2/dz]. \quad (15)$$

Or, taking into account that $\text{grad}(x_2) = -\text{grad}(x_1)$, one can write the expression in the general form for both components ($j \neq i$):

$$\mathbf{J}_i^t = w_0n_i - 0.5l_i[2w_{i(i)}x_i + w_{i(j)}(1 - 2x_i)]dn_i/dz, \quad (16) \\ i = 1 \text{ and } 2.$$

As above, hence, it follows that

$$w_0 = \{l_1[2w_{1(1)}x_1 + w_{1(2)}(1 - 2x_1)]dn_1/dz + l_2[2w_{2(2)}x_2 + w_{2(1)}(1 - 2x_2)]dn_2/dz\}/(2n). \quad (17)$$

Then, instead of formula (9), a new expression for the mutual diffusion coefficients is obtained:

$$D_{1,2} = \{l_1w_{1(2)}x_2 + l_2w_{2(1)}x_1 + 2x_1x_2[l_1(w_{1(1)} - w_{1(2)}) + l_2(w_{2(2)} - w_{2(1)})]\}/2. \quad (18)$$

In formula (18), let us *replace* l_i by l and, by analogy with expression (7), introduce $D_{i(j)} = w_{i(j)}l/2$ —the diffusion coefficients of molecules of component i that are involved in transport after the last collision with a molecule of component j . As a result, the final expression is obtained:

$$D_{1,2} = x_2(x_2 - x_1)D_{1(2)} + x_1(x_1 - x_2)D_{2(1)} + 2x_1x_2(D_{1(1)} + D_{2(2)}) = D_{1(2)}(x_1 - x_2)^2 + 2x_1x_2(D_{1(1)} + D_{2(2)}). \quad (19)$$

The second equality takes into account that, since $w_{1(2)} = w_{2(1)}$, the condition $D_{1(2)} = D_{2(1)}$ is met (however, in the dense phases, the last equality may be invalid).

ANALYSIS OF THE NEW EQUATION

In the limiting cases of low mole fractions of the first or second component, the contribution of the second term in expression (19) is minimal and this expression appears as expression (12), $D_{1,2} = D_{1,2}^{\text{SM}}$, within the framework of the Meyer scheme. Note that it is fundamentally impossible to reduce Eq. (9) to formula (12). Even at a low concentration of one of the components, the mutual diffusion coefficient is expressed through the velocity w_j rather than the relative velocity $w_{i(j)}$ (the velocity w_i ignores the mass of the second component).

Comparison of the expressions for $D_{1,2}$ and $D_{1,2}^{\text{SM}}$ at low mole fractions x_i allows one to formally define the rule of *replacement* of the partial mean free paths l_i by l . The replacement is performed by the formula $l = l_1x_2 + l_2x_1$ if, instead of formulas (10), their lattice analogues $l_i = 1/(n\langle\sigma_i\rangle)$ are used. These analogues include the mean sections of collisions of molecule i with molecules of other components of the mixture, which are defined as $\langle\sigma_i\rangle = \sigma_{i1}x_1 + \sigma_{i2}x_2$.

However, in the general case, formula (19) differs from expression (12) for $D_{1,2}^{\text{SM}}$. Equation (19) involves a quadratic dependence on the molar composition of a mixture, which is symmetric about $x_1 = x_2 = 0.5$. For an equimolar composition, the coefficient $D_{1,2}$ is minimal since the tendency for mixing of components is minimal. The maximal deviation of $D_{1,2}(x_1 = 0.5)$ from $D_{1,2}^{\text{SM}}$ depends on the ratio between the masses and the sizes of components.

For the case of comparable sizes of components ($\sigma_{11} \approx \sigma_{22} \approx \sigma_{12}$), $\langle\sigma\rangle = \sigma_{12}$ according to formula (12); then, at any molar composition of the mixture,

$$l = 1/(n\sigma_{12}). \quad (20)$$

In this case, the difference between formulas (19) and (12) depends only on the mass ratio $m_{21} = m_2/m_1$. The use of formula (20) leads to the maximal deviation (as $m_{21} \rightarrow \infty$) of $D_{1,2}$ (expression (19)) from $D_{1,2}^{\text{SM}}$ (expression (12)), which is equal to $(1 - 1/2^{1/2}) < 0.3$, i.e., smaller than 30%. Obviously, the condition $m_{21} \gg 1$ is in poor agreement with the assumptions $\sigma_{11} \approx \sigma_{22} \approx \sigma_{12}$. For mixtures with comparable sizes and masses of molecules of components, e.g., for a He–Ar mixture (at $m_{21} = 10$ and $\sigma_{\text{HeHe}} = 0.26$, $\sigma_{\text{ArAr}} = 0.34$ nm [7]), the maximal deviation between formulas (19) and (12) is ~11%; for an H₂–Ar mixture (at $m_{21} = 20$ and $\sigma_{\text{H}_2\text{H}_2} = 0.29$ nm), the maximal deviation is ~16%; and, for an Ar–Kr mixture (at $m_{21} = 2.1$ and $\sigma_{\text{KrKr}} = 0.36$ nm), the maximal deviation is only 1.2%.

These deviations are on the same order as the maximal discrepancy between formula (12) and experimental data; e.g., for a He–Ar mixture, the discrepancy is ~10% [3]. As a rule, in the experimental data, with an increase in the fraction of the heavy component, the mutual diffusion coefficient increases (by 8–13%) [3–5, 7]. A more accurate analysis in the second approximation of the rigorous kinetic theory can explain such an increase only within 4% [5], which is no more than half as much as the experimentally observed increase. Note that formula (19) describes the experimental dependence of the mutual diffusion coefficient on the mole fraction with an accuracy up to 10%.

Finally, as above, let us consider the difference $\mathbf{V}_1 - \mathbf{V}_2$ of the diffusion velocities. Taking into account the collisions of molecules leads to an expression for the

flux of molecules that is similar to formula (1a). However, according to formula (15), the coefficients D_{ij} depend on the molar composition: $D_{ii} = 2D_{i(i)}x_i + D_{i(j)}x_j$ and $D_{ij} = D_{i(i)}x_i$. As a result, one can obtain

$$\begin{aligned} \mathbf{V}_1 - \mathbf{V}_2 &= -(D_{11} - D_{12})/n_1 \text{grad}(n_1) \\ &- (D_{22} - D_{21})/n_2 \text{grad}(n_2) = -[D_{1(2)}(x_1 - x_2)^2 \\ &+ 2x_1x_2(D_{1(1)} + D_{2(2)})]/(x_1x_2) \text{grad}(x_1) \\ &= -D_{1,2}/(x_1x_2) \text{grad}(x_1). \end{aligned} \quad (2b)$$

Thus, the modified scheme of random walk leads to full agreement with the rigorous kinetic theory, which determines the relationship between the difference of the diffusion velocities of components and the mutual diffusion coefficient.

Let us also discuss the behavior of the convective flow velocity in the new modification of the lattice gas model: $w_0 = 2K \text{grad}(x_1)$, where $K = (D_{1(1)} - D_{1(2)})x_1 - (D_{2(2)} - D_{2(1)})x_2$. The form of the proportionality factor K suggests that the convective flow velocity w_0 is determined by all the types of collisions of molecules throughout the range of compositions of the mixture. At a low fraction of one of the components, e.g., component 2, $K = D_{1(1)} - D_{1(2)}$ and the flow depends on the difference of the contributions made by collisions of molecules of component 1 with molecules of components 1 and 2. For an equimolar composition, $K = (D_{1(1)} - D_{2(2)})/2$ and the convective flow is determined only by collisions between molecules of the same component, which corresponds to the maximal deviation from $D_{1,2}^{\text{SM}}$. Nonetheless, this deviation is small (approximately up to 15%) since the contributions of collisions between molecules of the same component significantly compensate one another.

Formula (19) shows that the correct expression for the molecular transport can be obtained without using the Boltzmann equation (only through the mean thermal velocity of molecules) at low mole fractions of one of the components of a binary mixture. The case $m_{21} \gg 1$ at $x_2 \sim 1$ corresponds to a Lorentzian mixture (a light admixture among heavy particles), which has been well studied in the rigorous kinetic theory of gases [3–5]. For such a mixture, the new approach correctly describes the temperature dependence and the effect of the mass. Numerical differences (1/2 and 1/3) between formulas (19) (or (12)) and the exact theory [3–5] for a Lorentzian mixture are because the dispersion of velocities is taken into account, but this systematic difference plays no role in analyzing the experimental temperature and concentration data (and is reduced to a shift of the reference point for these data). Similarly, the new approach gives a correct result for the case $m_{21} \rightarrow 0$ at $x_2 \sim 0$, which corresponds to an anti-Lorentzian mixture (a heavy admixture among light particles).

Thus, the consideration of the transport of molecules in an ideal gas from the standpoint of condensed

phases causes noticeable modification of the expression for the mutual diffusion coefficient. The presented procedure for deriving the mutual diffusion coefficient using relations (9)–(11) is purely formal and has no physical meaning because formulas (11) diverge as x_1 or x_2 tends to zero. Unlike formulas (11), the new approach within the framework of the elementary kinetic theory does not operate with nonphysical quantities and gives $D_{1,2}$ that are close to a constant value (see expression (12)) at any composition of the mixture, which is in satisfactory agreement with experimental data.

CONCLUSIONS

The analysis of the definitions demonstrated that one and the same term, *mutual diffusion coefficient*, is used for gases and alloys in different senses under different conditions (in the absence and the presence of a convective flow). The rigorous kinetic theory substantiates the Stefan–Maxwell hypothesis in the first-order hydrodynamic approximation, in which direct differentiation with respect to the change in the properties of a mixture over distances l is not performed and the selection of “necessary” collisions is ensured by the fact that the collision integral for identical components of the mixture is zero. The Meyer–Darken scheme explicitly considers the concentration gradients of both components in two different local volumes that are at a distance l from each other and are separated by plane 0. In principle, the Meyer–Darken scheme is applicable to all the phases in which there is a convective flow caused by the difference of the diffusion flows of components; this has found use in the theory of solid alloys.

The constructed modified elementary theory for gas is actually intermediate between the rigorous kinetic theory and the purely diffusion approach. The constructed theory simultaneously uses the notion of convective flow caused by diffusion and takes into account molecular collisions, which give rise to flows of walking molecules. By and large, diffusion becomes a non-single-particle process of walk of molecules in a gas or solid thermostat. As a result, the flows of molecules in gas become nonlinear in concentrations, which determines the concentration dependence of the phenomenological coefficients of the thermodynamics of irreversible processes. The nonlinearity of collisions determines a qualitative change in the character of the mutual diffusion coefficient through the presence of the relative velocities $w_{i(j)}$ of molecules in $D_{i(j)}$ in comparison with w_i in the coefficients D_i , which corresponds to the definition of $D_{1,2}$ for the gas phase. The modification of the lattice gas model ensured consistency with the rigorous kinetic theory at low mole fractions of any of the components and provided the correct determination of the mutual diffusion coefficient at any compositions of a mixture. The quantitative deviations from the rigorous theory for molecules of components that are

quite close in size to one another are less than 15% and are comparable to deviations of experimental data and to deviations obtained using the Stefan–Maxwell formula (~10%).

The constructed modification of the elementary kinetic theory can be generalized to dense gas and liquid mixtures, which enables one to use microhydrodynamic equations [29] for describing the flows of mixtures at any densities.

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NOTATION

- a_i —ratio of the statistical sums of a molecule of component i in the system and the thermostat;
- D_{ij} —diffusion coefficient of a multicomponent mixture;
- $D_{i(j)}$ —diffusion coefficient of molecules of component i that are involved in transport after the last collision with a molecule of component j ;
- $D_{1,2}$ —mutual diffusion coefficient of a binary mixture;
- d_{ii} —diameter of a molecule of component i ;
- F_i, F_{i0} —statistical sums of a molecule of component i in a cell and a thermostat;
- k —Boltzmann constant;
- \mathbf{J}_i —diffusion flux of molecules of component i ;
- \mathbf{J}_i^t —total flux of molecules of component i ;
- l_i —mean free path of a molecule of component i ;
- m_i —mass of a molecule of component i ;
- N —number of cells in the system;
- N_i —number of molecules of component i ;
- h —total number density of all the components of a mixture;
- n_i —number density of component i in a unit volume ($n = n_1 + n_2$);
- P —pressure;
- p_i —partial pressure of component i in the thermostat;
- s —occupancy of a cell;
- T —temperature;
- V —volume of the system;
- \mathbf{V}_i —diffusion velocity of component i ;
- v —vacancy;
- v_0 —volume of a cell;
- w_i —mean thermal velocity of molecules of component i in the gas phase;

$w_{i(j)}$ —mean relative velocity of a molecule of component i after collision with a molecule of component j ;
 w_0 —convective flow velocity;
 x_i —mole fraction of component i ;
 Z —coordinate along which the flow of molecules moves;
 z —number of nearest cells;
 $\beta = 1/kT$ —inverse thermal energy;
 θ —full occupation of a volume;
 θ_i —concentration of component i of a fluid;
 λ —linear size of a cell;
 μ_{ij} —reduced mass of colliding molecules of components i and j ;
 ρ —mean distance between molecules;
 σ —diameter of the hard sphere of a molecule;
 σ_{ij} —distance of maximal approach of molecules of components i and j .

SUBSCRIPTS AND SUPERSSCRIPTS

i, j —components of a mixture;
 SM—Stefan–Maxwell hypothesis;
 1, 2—components of a binary mixture.

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