Full Articles

Mutual diffusion coefficient in binary mixtures in different aggregation states

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An equation for the mutual diffusion coefficient for the components of a binary mixture occurring in various aggregation states has been derived. Situations of this type arise in narrow pores in which the adsorbate density sharply changes across the pore cross-section. The equation was derived with the assumption that molecules of the mixture components have a spherical shape and are similar in size. The constructed equations are based on the lattice-gas model applicable to any aggregation state. The migration of particles is described in terms of the transition state theory. At low mixture densities corresponding to an ideal gas phase, the equations are based on expressions of the rigorous kinetic theory of gases. The theory takes into account the change in the mechanism of particle migration in different phases: from pair collisions for the gas to the overcoming of the activation barrier by thermofluctuation for dense phases.

Key words: transport of molecules, narrow pores, self-diffusion coefficients, mutual diffusion coefficients, viscosity coefficients.

Mass transfer between mixtures of atoms and molecules plays an important role for chemical reactions in any aggregation state. From the standpoint of nonequilibrium thermodynamics,[1,2] its formal description is the same for all phases. On passing to molecular models, one should use the kinetic theories developed particularly for each phase. This is due to the lack of a unified kinetic theory applicable to any of the three phases. Naturally, the kinetic theories of gases,[3—6] liquids,[7—9] and solids[10—12] are based on different properties of the phases. In the gas, the crucial role belongs to the spread of molecular velocities of molecules, while in dense phases (liquids or solids), this is the spatial inhomogeneity of the distribution of molecules. The lack of order in gases or liquids, unike crystalline solids, is favorable for faster transport of molecules compared to solids, which gives rise to the viscosity properties of these media, which are missing from the solid phase.

The problem of the mutual diffusion coefficient in mixtures is significant for considering the transport pro-

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cesses in narrow pores (with widths of up to 10—15 nm). A specific feature of narrow-pore systems is that the walls of most porous materials attract the adsorbate molecules. The situation where pure adsorbates or their mixtures occur in the central part of the pore in the rarefied state or on the pore walls in the liquid-like state is encountered most often.[13—17] As a result, an adsorbate film flow is formed along the pore wall, and thus, sharp density and flow rate gradients appear. The formation of the adsorption film may be indicative of a "multiphase" state of the mixture in the pore cross-section. In multicomponent systems, the difference between the diffusion mobilities of the components along the pore axis and along the normal to the pore wall gives rise, at any density, to spatial anisotropy of the flows of molecules of different sorts and to density and molar composition gradients. In this respect, narrow pores differ qualitatively from wide pores in which only the gradients along the pore axis are usually considered.[18]

As the temperature decreases, a liquid may turn into a solid. It is obvious that characteristic times of the molecular transfer in gases and solids are sharply different. Nevertheless, the use of transfer equations either taking or not taking into account the viscosity effects is important also for the simulation of transport phenomena. All the existing numerical procedures of molecular dynamics and the Monte Carlo method leave aside the question of the presence of a solid phase, because the ways for determining the phase content used in these procedures are indirect (analysis of the pair distribution functions or temporal estimates).[13,19] A correct determination is especially important in the case of possible two-phase states of the mixture at low temperatures.

In the low-density limit, the kinetic theory of dense phases should pass into the kinetic theory of gases, which has been rather well-developed. However, the physical statements of the theory of solid and liquid phases differ appreciably from the initial statements of the gas theory; therefore, this transition is impossible at present.

In this study, the diffusion flows for all three aggregation states are described on the basis of a unified kinetic approach, developed previously within the framework of the lattice-gas model (LGM)[20,21] for a static thermostat. This approach allows one to describe the transport processes in the solid bulk, on the solid surface, and in stationary fluid systems. Recently,[22—24] the method has been extended to the case of a mobile thermostat. This opens up the way for investigating all the dissipative coefficients for the transport of atoms and molecules. Let us consider diffusion of a mixture of simple molecules of the spherical shape with approximately the same size. This macroprocess includes adsorption, desorption, and surface migration as elementary steps. The adsorption step will be represented as migration of the molecule from the surface layer on the pore wall into the pore, more precisely, into the second monolayer, with cleavage of the adsorption bond and without association of the molecules. The desorption is the reverse process where the molecule migrates from the central part of the pore to the wall without dissociation. The surface migration means the migration (shift) of the molecule along the surface of the pore wall with overcoming the corresponding activation barrier. Finally, redistribution of the molecules inside the pore implies their migration between the layers (along the normal to the wall) or along the layers (parallel to the wall).

The transfer of molecules in dense phases is described in terms of the mean velocities of jumps (or shifts). On passing to low densities, this description leads to expressions of the elementary kinetic theory of gases (without taking account of the velocity dispersion of molecules),[25,26] which differs in some situations[7,25,26] from the rigorous kinetic theory of gases.[3—6] Therefore, the formal transition from the dense phases to the gas give results that do not necessarily obey the rigorous kinetic theory developed for the gas phase.

The purpose of this study is to derive the equation for determination of the mutual diffusion coefficient of a binary mixture in the gas, liquid, or solid phase by means of a microhydrodynamic approach within the framework of the LGM. It is well known that when the mean migration velocities for an ideal gas mixture are used, the experimental data do not obey the Meyer equation.[26] The Stefan—Maxwell hypothesis[26] resolves this contradiction for an ideal gas. The results obtained for the rarefied and for the dense phase using the microhydrodynamic approach[22,23] for one-component fluids were not at variance with each other. However, the question of whether the mean migrartion velocity can be used to analyze a mixture remains obscure.

Determination of the mutual diffusion coefficient

The use of nonequilibrium thermodynamics results in the same structure of the diffusion equations for molecules in the gas and solid phases, although the mechanisms of the elementary processes of component migration are different. In the gas phase, the diffusion rate depends only on the pair collisions. In the solid phase, the molecules migrate by the vacancy mechanism; for a jump, an atom in an alloy should reach, upon fluctuation, the activation energy needed to overcome the activation barrier. In the latter case, all neighboring atoms influencing the local vibration frequencies and the activation energy of the migrating atom participate directly or indirectly in the jump. The role of the neighboring molecules is equally pronounced in the liquid phase.

We now turn to determination of the mutual diffusion coefficient. Let a gas mixture occur at a constant pressure

(P = const) and temperature (T = const). The molar composition of the mixture is characterized by the ratio $x_i = n_i/n$, where n_i is the numerical density of component i per unit volume, $n = n_1 + n_2$, x_i is the mole fraction of component i, $x_1 + x_2 = 1$. In the nonequilibrium state, the gas molar composition x_i is different on the two sides of some distinguished plane 0. The minimum Gibbs potential corresponds to equal compositions on both sides of plane 0, resulting in mixing of the components. Since components differ by the mass m_i, the lighter and faster molecules rush to the region with an enhanced concentration of heavy particles. In order to counterbalance the local increase in the total concentration of molecules, heavy molecules start to move to the region of higher concentration of light molecules. The difference between the counter-flows of both components creates conditions for the movement of the gas as a whole. This gives rise to a convective flow with the average velocity w_0, depending on the difference between the diffusion coefficients of the components in a fixed reference system D_i. If the number of molecules of sort i = 1 or 2 is designated by N_i, the kinetic equations for their transport will have the form

$$J_i^{\text{tot}} = \mathrm{d}N_i/\mathrm{d}t = w_0 n_i - 0.5\{[n_i w_i l_i]_{\text{I}} - [n_i w_i l_i]_{\text{II}}\}, \qquad (1)$$

where J_i^{tot} is the total flux of the component per unit cross-section, w_i and l_i is the mean thermal rate of transfer and the average free path of component i. The first term in braces refers to half-space I located on the left of plane 0, while the second one refers to half-space II located on the right of plane 0. By expanding the right-hand part of the equation over grad(n_i), $n_i(\text{II}) = n_i(\text{I}) + l_i\text{grad}(n_i)$, we get

$$J_i^{\text{tot}} = \mathrm{d}N_i/\mathrm{d}t = w_0 n_i - D_i(\mathrm{d}n_i/\mathrm{d}z) \quad (i = 1, 2). \qquad (2)$$

For simplicity, we take z to be the coordinate along which the molecules flow. The expressions for the coefficients D_i follow from the elementary kinetic theory with the use of an equilibrium velocity distribution function for molecules.

$$D_i = w_i l_i/2, \qquad w_i = (8kT/\pi m_i)^{1/2}. \qquad (3)$$

Since $\mathrm{d}(N_1 + N_2)/\mathrm{d}t = 0$ and $n = n_1 + n_2$, then

$$w_0 = [D_1(\mathrm{d}n_1/\mathrm{d}z) + D_2(\mathrm{d}n_2/\mathrm{d}z)]/n. \qquad (4)$$

Using relation (4), Eq. (2) can be transformed into the following form:

$$J_i^{\text{tot}} = \mathrm{d}N_i/\mathrm{d}t = -D_{1,2}(\mathrm{d}n_i/\mathrm{d}z), \quad D_{1,2} = x_2 D_1 + x_1 D_2, \qquad (5)$$

where $D_{1,2}$ is the mutual diffusion coefficient of a binary mixture. This gives the so-called Meyer equation for an ideal gas (5).

This relation gives a wrong result for an ideal gas if the l_i value is estimated from a number of collisions of molecule i with both components j = 1 and 2:[26]

$$l_1 = [2^{1/2}n_1\sigma_{11} + n_2\sigma_{12}(1 + m_1/m_2)^{1/2}]^{-1},$$
$$l_2 = [2^{1/2}n_2\sigma_{22} + n_1\sigma_{12}(1 + m_2/m_1)^{1/2}]^{-1}, \qquad (6)$$

where $\sigma_{ij} = \pi d_{ij}^2$, $d_{12} = (d_{11} + d_{22})/2$ is the minimum distance between the molecules, d_{ii} is the diameter of molecule i.

In order to solve the problem of the lack of consistency of Eqs (5) and (6) to experimental data, it was postulated[26] that in estimating l_i, only collisions with molecules of other sort should be taken into account, *i.e.*, $j \neq i$. In this case,

$$l_1^{\text{SM}} = [n_2\sigma_{12}(1 + m_1/m_2)^{1/2}]^{-1},$$
$$l_2^{\text{SM}} = [n_1\sigma_{12}(1 + m_2/m_1)^{1/2}]^{-1}. \qquad (7)$$

As a result, formula (7) is converted into the Stefan—Maxwell formula

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

where $\mu_{ij} = m_i m_j/(m_i + m_j)$ is the reduced mass of the colliding molecules i and j.

Relation (8) is in good agreement with the experiment. This hypothesis is based on the rigorous kinetic theory.[3—6] However, the Stefan—Maxwell formula cannot be just extended to dense phases.

The equation for the mutual diffusion coefficient in solid alloys is constructed in terms of the random walk of atoms. This approach gave fully identical Eq. (5) for the $D_{1,2}$ coefficient within the framework of the Darken theory.[10—12] The essence of the mutual diffusion phenomenon in alloys is that the unequal diffusion mobility of atoms of different sorts results in so-called Kirkendall effect,[10—12] *i.e.*, migration of inert labels placed in a binary alloy by macroscopic distances. The migration of labels attests to the shift of whole crystallographic layers (planes). This is to due to the presence of an uncompensated flow of vacancies whose sink is accomplished through the pore formation in crystals. The collapse of these pores caused by mechanical instability of the solid is responsible for the migration of planes.

For an alloy, the diffusion coefficients are described by the expression

$$D_i = D_i^*(1 + \partial\ln\gamma_i/\partial\ln x_i),$$

where D_i^* and γ_i are the self-diffusion coefficient and the activity coefficient of atom i in the alloy. The lack of cross diffusion terms in Eq. (5) for alloys is usually assumed to simplify the models.

Thus, despite the difference between the mechanisms of particle transport in an ideal gas and a solid alloy, the mutual diffusion coefficient in a mobile reference system is expressed in the same way through the diffusion coefficients of separate components D_i in a fixed reference system.

Modification of the transfer equations

Proceeding from the universal molecular-kinetic theory of condensed phases, we will try to construct a unified system of equations describing the diffusion in systems with different densities. To this end, it is necessary to combine the jump pattern in the LGM for rarefied and dense (in particular, solid) phases with the expression for the mutual diffusion coefficient for an ideal gas. There are two statements that distinguish between the kinetic theories for the gas and for the solid.

(1) The theory of dense systems operates with the probabilities of transitions from one point in space into any other point rather than the probabilities of collisions between the molecules. As applied to the gas phase, this implies considering the motion of molecule *i* after its last collision with molecule *j* inside region I (or II) before crossing the selected plane 0. The elementary kinetic theory considers all collisions of a molecule located in the other region II (or I) after crossing plane 0. This brings about the necessity to take into account the collisions between the molecules. Therefore, instead of the traditional use of the average velocity w_i (3), one should use the motion velocity of molecule *i* after the collision with a molecule of definite sort *j* directly prior to the crossing of plane 0.

(2) From the standpoint of equilibrium, an ideal gas is a rarefied system in which all particles are separated, on average, by the same distance ρ. Otherwise, any deviation from the uniform distribution of molecules should result in fluctuations of the density (relative distribution of components) only due to a difference in the weights of mixture components. However, these differences are impossible without intermolecular interactions, which is ruled out by the concept of ideal gas.

The kinetic gas theory uses two characteristics of linear dimensions: the size of molecules σ, which is related unambiguously to the size of the site in the LGM as $\lambda \approx 2^{1/6}\sigma$ (λ scale), and the free path l_i (*l* scale). Therefore, to bring the equilibrium and the kinetic theory into coincidence, it is necessary to add one more system characteristics, ρ (ρ scale). It is defined as $\rho = v^{1/3}$, where v is the volume per mixture molecule or $\rho = \lambda/\theta^{1/3}$, where $\theta = N/N_s$ is the fraction of sites of the lattice structure occupied by both mixture components, $N = N_1 + N_2$, N_i is the number of sort *i* molecules, N_s is the total number of sites in the structure (equal to the number of sites in a completely filled structure). The relationship between the total concentration of molecules n and the degree of filling θ is given by the formula $n = \theta/v_0$, where $v_0 = V/N_s$ is the average volume of the site. For an ideal gas, the following relations hold: $\lambda \ll \rho \ll l_i$.

In the LGM,[20,21] the self-consistency of the description of process dynamics and the equilibrium state at any density and temperature can be rigorously proved. In order to retain this important feature of the LGM, we will use the ρ scale and describe the processes that occur in the *l* scale on the ρ-scale level. The condition $\rho \ll l_i$ ensures that the processes considered and the conditions of influence of lateral interactions on them at high densities are knowingly met in the *l* scale provided that they are met in the ρ scale.

If we combine both statements when considering the migration of molecules in the ρ-scale, it will turn out that for migration of molecule *i* from site *f* of region I toward site *g* in region II, this molecule has to collide with molecule *j* in site ξ inside region I. Then, instead of the mean thermal velocity (3), the motion of molecule *i* can be described by the relative velocity $w_{i(j)} = (kT/2\pi\mu_{i(j)})^{1/2}$. The second corollary is the conclusion that, if the distance between region I and II at which the density gradients for both components are considered is measured in the ρ-scale sites, it will be equal for all components. This differs from the views on the difference between the path lengths l_i for molecules of different sorts in mixtures, which usually follow from analysis of the number of collisions.

Taking into account these two corrections, we will derive once again the Meyer equation for the case of commensurable sizes of the mixture components. The flow of molecules *i* that crosses plane 0 consists of two parts because after the collision with molecules j = 1 and 2, molecules *i* move at different relative rates $w_{i(j)}$. It is necessary to take into account the fraction x_j of each component *j* which collides with molecule *i*. Therefore, instead of the mean velocity w_i, the relative velocities $(w_{i(1)}x_1 + w_{i(2)}x_2)$ should be introduced into formulas (1)—(3). Then for the flow of the first component, we get

$$J_1^{\text{tot}} = \mathrm{d}N_1/\mathrm{d}t = w_0 n_1 - {}$$
$$- 0.5\{[n_1(w_{1(1)}x_1 + w_{1(2)}x_2)]_{\rm I} - [n_1(w_{1(1)}x_1 + w_{1(2)}x_2)]_{\rm II}\}, \quad (9)$$

where, as previously, the first term in braces refers to half-space I located on the left of plane 0, while the second one refers to half-space II located on the right of plane 0. The expression for the flow of the second component can be written in a similar way.

By analogy with expression (3), we will designate the diffusion coefficients of molecules *i* participating in the transport after the last collision with molecule *j* by $D_{i(j)} = w_{i(j)}l_i/2$ and derive formula (5) once again. This will give the following expression for the mutual diffusion coefficient:

$$D_{1,2} = \{l_1 w_{1(2)} x_2 + l_2 w_{2(1)} x_1 + 2x_1 x_2[l_1(w_{1(1)} - w_{1(2)}) + l_2(w_{2(2)} - w_{2(1)})]\}/2. \quad (10)$$

In view of the fact that $w_{1(2)} = w_{2(1)}$, we replace l_i by l and thus obtain the formula

$$D_{1,2} = D_{1(2)}(x_1 - x_2)^2 + 2x_1 x_2(D_{1(1)} + D_{2(2)}). \quad (11)$$

For the limiting cases of minor contents of either the first or the second component, the contribution of the second term in formula (11) is small and it is transformed directly into expression (8), $D_{1,2} = D_{1,2}^{SM}$, in terms of the Meyer scheme (initial equation (5) does not possess this feature). It can be seen that if the molecular transport is considered from the standpoint of the theory of condensed phases, the expression for the mutual diffusion coefficient in the ideal gas is markedly modified.

Comparison of the structures of expressions for $D_{1,2}$ and $D_{1,2}^{SM}$ at low x_i and the condition for the invariability of l at a given x_i results in replacement of the l_i values by l according to $l = l_1 x_2 + l_2 x_1$. However, Eq. (11) contains a quadratic dependence on the molar composition of the mixture. It is symmetrical with respect to $x_1 = x_2 = 0.5$. For an equimolar composition, the coefficient $D_{1,2}$ is the minimum, as the trend for component mixing is the lowest. The degree of deviation $D_{1,2}(x_1 = 0.5)$ from $D_{1,2}^{SM}$ depends on the ratios of the masses and sizes of the components. For the l value to correspond to formula (8) ($\langle\sigma\rangle = \sigma_{12}$), the equality

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

should hold at any molar composition of the mixture.

In this case, the deviation of formula (11) from formula (8) at any ratio of the component masses and sizes does not exceed the value $(1 - 1/2^{1/2}) < 0.3$ (*i.e.*, it is less than 30%). For molecules with commensurable sizes, these deviations are smaller.

Figure 1 shows the normalized concentration dependences of the mutual diffusion coefficients in a helium—argon binary mixture upon the change in the mole fraction of helium. The experimental data* (curve *5*) do not contain information about temperature; therefore, they are normalized to the limiting value of the mutual diffusion coefficient for the heavier component ($x_{Ar} \to 1$). The experiment shows that the higher the fraction of light atoms, the lower the mutual diffusion coefficient. The limiting $D_{1,2}$ values for $x_{Ar} \to 1$ and $x_{Ar} \to 0$ were obtained from the tabulated data* for mean ratios of the mole fractions of the two components (shown by dots in Fig. 1) by linear extrapolation in accordance with the conclusions of the rigorous theory.[3—6] The analogous normalized ratios shown in Fig. 1 were calculated using the Stefan—Maxwell formula (curve *1*), the Meyer formula (curve *2*), the Meyer formula with the free path (12) common to both components instead of the l_i values (curve *3*), and the new formulas (11) and (12) (curve *4*). Comparison shows that the new equations markedly improve the Meyer formula and are comparable in accuracy with the Stefan—Maxwell formula.

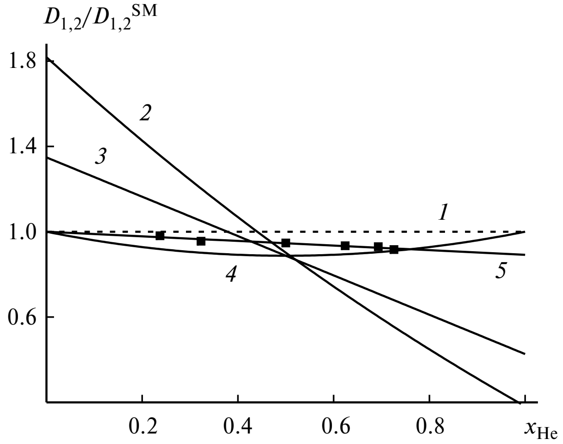

Fig. 1. Normalized concentration dependences of the mutual diffusion coefficient in a helium—argon binary mixture upon the variation of the helium mole fraction calculated by the Stefan—Maxwell (*1*) and Meyer (*2*) formulas, the Meyer formula using free path (12) instead of the l_i values (*3*), and by the new formulas (11) and (12) (*4*), and experimental data (*5*).

Thus, for "practical" sizes and masses of mixtures (such as the He—Ar mixture), the highest deviation of the calculation results obtained using new formulas (11) and (12) from the experimental values[3,5] is 11%. The rigorous theory allows deviations of the same order (~10%).[3—6]

Equilibrium distribution of mixture molecules in a slit-shaped pore

The LGM equations describing the equilibrium distribution of molecules in the pores for any densities have been repeatedly reported.[14—17,27] These equations are needed to find the transfer coefficients, because these are calculated for insignificant deviation of the nonequilibrium distribution function from the equilibrium one. For a mixture of $s - 1$ components, each site of the lattice system has s different occupancy states including the case of the absence of particles (for $i = s$). If the concentration of component i ($1 \le i \le s - 1$) is designated by θ_i (it is equal to the ratio of the number of real particles N_i in some volume to the maximum possible number of the closely packed particles in the same volume N), the local density of particles i in a site with the number f is designated by θ_f^i, $\sum_{i=1}^{s-1}(\theta_f^i + \theta_f^v) = 1$. The average partial fluid concentration θ_i can now be expressed in terms of the local concentrations as $\theta_i = \sum_{f=1}^{t} F_f \theta_f^i$, where F_f is the

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* Experimental data from Table 24 (see Ref. 3) were used.

fraction of type f sites ($1 \le f \le t$), t is the number of site types in the system, $\Sigma_{f=1}^{t} F_f = 1$. The average total degree of pore filling is thus $\theta_i = \Sigma_{i=1}^{s-1}\theta_i$. The character $\{P\} \equiv P_1, ..., P_{s-1}$ stands for the whole set of all partial pressures of mixture components P_i.

To calculate the average partial adsorption isotherms $\theta_i(\{P\})$ and local degrees of filling $\theta_f^i(\{P\})$ on various adsorption centers, we will use the set of equations taking into account the energy nonuniformity of the lattice sites and interactions between the molecules with the coordination spheres separated by distance R:[14—17,20]

$$\theta_i(\{P\}) = \sum_{f=1}^{t} F_f \theta^i_f(\{P\}),$$

$$a^i_f P_i = \theta^i_f \Lambda^i_f / \theta^v_f, \tag{13}$$

$$\Lambda^i_f = \prod_r \prod_g \left\{1 + \sum_{j=1}^{s-1}\left[x^{ij}_{fg}(r) t^{ij}_{fg}(r)\right]\right\}^{z_{fg}(r)},$$

$$x_{fg}{}^{ij}(r) = \exp[-\beta\varepsilon_{fg}{}^{ij}(r)] - 1,$$

where the Λ_f^i function takes into account the intermolecular interactions in the quasichemical approximation, $a_f^i = a_f^{i0}\exp(\beta Q_f^i)$ is the local Henry constant (a_f^{i0} is its pre-exponent, Q_f^i is the energy of bonding of molecule i in layer f with the walls of the slit-shaped pore having the width H, which is calculated as $Q_f^i = E_i(f) + E_i(H - f + 1)$, $1 \le f \le t$, and the interaction potential of the molecule with the pore wall $E_i(f) = \varepsilon_i/f^3$ corresponds to the attraction branch of the Mie (3—9) potential,[28] ε_i is the energy parameter of the potential). Relation (13) takes into account the layer-by-layer distribution of sites of various types in slit-shaped pores: $z_{fg}(r)$ is the number of the neighboring sites in layer g at distance r from the site under interest located in layer f. The fraction of sites F_f in layer f equals $2/H$ for even H and for odd H when $1 \le f \le t - 1$, whereas $F_f = 1/H$ for $f = t$. The subscript g runs through all neighbors of site f separated from it by distance $r \le R$ inside the pore, R is the radius of the lateral interaction potential for the mixture components. In this case, the functions $t_{fg}{}^{ij}(r) = \theta_{fg}{}^{ij}(r)/\theta_f^i$ describe the conventional probability that a neighboring particle j occurs in a type g site at distance r from the central particle i occurring in a type f site, where the functions $\theta_{fg}{}^{ij}(r)$ are defined by the following algebraic set of equations:

$$\theta^{in}_{fg}\theta^{vv}_{fg} = \theta^{iv}_{fg}\theta^{vn}_{fg}\exp(-\beta\varepsilon^{in}_{fg}). \tag{14}$$

Equations (13) and (14) are supplemented by the normalizing relations

$$\theta^{in}_{fg}\theta^{vv}_{fg} = \theta^{iv}_{fg}\theta^{vn}_{fg}\exp(-\beta\varepsilon^{in}_{fg}),$$

$$\sum_{j=1}^{s}\theta^{ij}_{fg}(r) = \theta^i_f. \tag{15}$$

The set of equations (13)—(15) can be solved by the iteration method with a specified set of $\{\theta_i\}$ or $\{P_i\}$. Its solution provides the possibility of calculating all the equilibrium characteristics and the rate of thermal motion in the equilibrium state.

Transfer coefficients

To describe the transport of mixtures in narrow pores, the proposed LGM modification is to be extended to arbitrary mixture densities with retention of the definition of the mutual diffusion coefficient proposed for the gas phase. The ρ scale is taken into account for one component of the forward motion of molecule i toward the collision with molecule j. All other motions of the molecules and consideration of the lateral interactions do not change, being described at the λ-scale level.

Figure 2 shows the shift of molecule in the LGM from site f to neighboring vacant site g (here $\chi = 1$, in the general case the molecule shifts by a distance $\chi > 1$). The scheme shows the sites of two unified coordination spheres around the central sites fg in the lattice with the number of nearest neighbors $z = 6$ (the first coordination sphere includes sites with numbers 1—9 and the site ξ). The molecules in all neighboring sites influence the probability that molecule i will jump from site f into vacant site g through the lateral interactions. With traditional LGM equations,[20,21] the contributions of all of these neighboring molecules located within the first and second coordination spheres are described in the same way in the λ scale. In the LGM modification considered here, contribution of molecules j located in site ξ is described at the ρ-scale level.

Thus the self-consistency of the description of all equilibrium and transport characteristics of the system inherent in the LGM is retained. This self-consistency is present for both the bulk phase and the pores (for example, in the

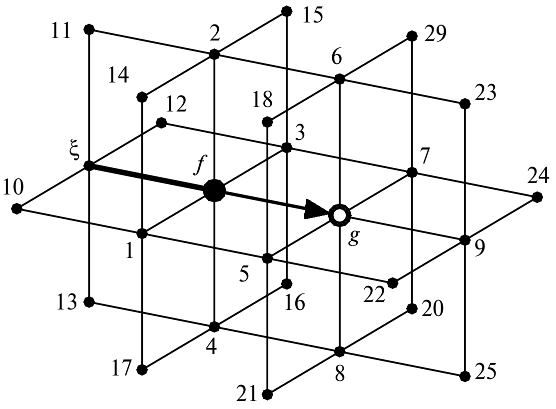

Fig. 2. Scheme of the jump of a molecule from site f into vacant site g and neighboring sites in the first two coordination spheres of the lattice structure with $z = 6$.

calculation of adsorption heats and isotherms with the use of self-diffusion and viscosity coefficients). Below we present, without derivation, the final forms of the new equations for the thermal motion of molecules and for the transfer coefficients.

Thermal velocity of molecules. The velocity of the jump of molecule i from site f into vacant site g by distance χ is described by the expressions

$$U_{\xi fg}{}^{iv}(\chi) = \sum_{j=1}^{s-1} U_{\xi fg}{}^{(j)iv}(\chi),$$

$$U_{\xi fg}{}^{(j)iv}(\chi) = K_{\xi fg}{}^{(j)iv}(\chi) V_{\xi fg}{}^{(j)iv}(\chi), \qquad (16)$$

$$V_{\xi fg}{}^{(j)iv}(\chi) = \theta_{fg}{}^{iv}(\chi) < t_{f\xi}{}^{ij} > \Lambda_{\xi fg}{}^{iv}(\chi),$$

where the subscript ξ refers to a neighboring site in the ρ scale with respect to site f accommodating the neighboring molecule j, which determines the momentum and the jump direction of molecule i from site f into vacant site g. The site ξ is located in one straight line with sites f and g, both on the other side of site f, the distance to this site exceeding the lattice parameter of this structure in the λ scale. The rate constant for the jump $K_{\xi fg}{}^{(j)iv}(\chi) = (2\pi\mu_{ij}\beta)^{-1/2}\exp[-\beta E_{fg}{}^{iv}(\chi)]/\chi$ has its usual form except that the reduced mass μ_{ij} of the colliding molecules i and j is used instead of the mass of one molecule m_i; $E_{fg}{}^{iv}(\chi)$ is the activation energy for a jump by distance χ in the action field of the pore wall potential (for sites remote from the pore walls, $E_{fg}{}^{iv}(\chi) = 0$).

Pay attention to the difference of the desorption in which the motion direction is normal to the pore wall and molecule gets the momentum from the wall atoms (the site ξ refers to the pore wall) from the migration of a molecule in the flow far from the walls or in the surface along the pore the wall in which the molecule gets the momentum from other migrating molecules. In the description of the desorption along the above-mentioned direction, the rate constant contains the reduced mass μ_{iw}, where the subscript w refers to the atom (or group of atoms) of the wall surface.

The concentration dependence of the migration velocity of the molecule is expressed by the factor $V_{\xi fg}{}^{(j)iv}(\chi)$. This factor takes into account three parameters: (1) $\theta_{fg}{}^{iv}(\chi)$ is the probability of existence of a free path from site f to site g with length χ (without other molecules across the path); (2) $\Lambda^{i}{}_{\xi fg}(\chi)$ is the influence of lateral interactions of the neighboring molecules, arranged around this path on the probability of jump along the path; (3) $< t_{f\xi}{}^{ij} >$ is the probability that neighboring particle j is located in site ξ in one straight line with sites f and g (in the ρ scale), which is expressed as

$$< t_{f\xi}{}^{ij} > = t_{f\xi}{}^{ij}(\rho)\exp[\beta\delta\varepsilon_{f\xi}{}^{ij}(1.5\rho)]/\theta_{\xi}, \qquad (17)$$

where $\delta\varepsilon_{fh}{}^{ij}(r) = \varepsilon^{*}{}_{fh}{}^{ij}(r) - \varepsilon_{fh}{}^{ij}(r)$, $\varepsilon^{*}{}_{fh}{}^{ij}(r)$ is the interaction parameter of the activated complex for the migration of molecule i from site f with the neighboring molecule j, which exists at the ground state in site h at distance r, $r \le R$. The coefficient of 1.5 found in the argument of the energy parameters, $r = 1.5\rho$, implies the saddle point coordinate with respect to site ξ. For an ideal gas, $\rho > R$ and $< t_{f\xi}{}^{ij} > = x_i$.

As previously,[20,24] the function $\theta_{fg}{}^{iv}(\chi)$ is constructed in terms of the probability of existence of a sequence of vacant sites $g(1)$, $g(2)$, and so on up to $g \equiv g(\chi)$, which form this path: $\theta_{fg}{}^{iv}(\chi) = \theta_{fg(1)}{}^{iv}(1)\prod_{\psi} t_{\psi\psi+1}^{vv}(1)$. The functions $t_{\psi\psi+1}{}^{vv}(r)$ were defined above. The number of factors over ψ is equal to $\chi - 1$. (For $\chi = 1$, the site $g(1)$ is final.)

The function $\Lambda_{\xi fg}{}^{iv}(\chi)$ is expressed in the quasichemical approach as follows

$$\Lambda_{\xi fg}^{iv}(\chi) = \prod_{r=1}^{R}\prod_{\omega_r=1}^{\pi_r}\prod_{h\in m^{*}(\omega_r)}\sum_{k=1}^{v} t_{fgh}^{ivk}(\omega_r)E_{fgh}^{ivk}(\omega_r), \qquad (18)$$

$$t_{fgh}^{ivk}(\omega_r) = \theta_{fh}^{ik}(r_1)\theta_{gh}^{vk}(r_2)/(\theta_f^i\theta_g^v\theta_h^k),$$

$$E_{fgh}{}^{ivk}(\omega_r) = \exp\{\beta[\delta\varepsilon_{fh}{}^{ik}(r_1) + \delta\varepsilon_{gh}{}^{vk}(r_2)]\}.$$

A specified jump distance χ corresponds to the distance from site h to site f, equal to r_1, and that to site g, equal to r_2. The sites h belong to the set $m(\omega_r)$ with fixed distance r and orientation ω_r. The orientation ω_r describes the position of site h and corresponds to the angle formed by the segment connecting the pair of "central" sites fg and the line connecting site h with the midpoint of the segment fg. The set $m(\omega_r)$ includes the sites located at the distance r from a central site (f or g); the character "*" stands for $m^{*}(\omega_r) = m(\omega_r) - 1$, which implies the lack of a factor at $h = \xi$ in the right-hand part of relation (18). A similar reduction of the multipliers in Eq. (18) takes place for large χ due to a decrease in the contribution of lateral interactions at $r \le R$.

In the absence of lateral interactions and far from the pore walls, relation (16) can be written as $U_{\xi fg}{}^{iv}(\chi) = \sum_{j=1}{}^{s-1}K_{\xi fg}{}^{(j)iv}(\chi)x_j\theta_f(1 - \theta_g)^{\chi}$. Assuming that $\chi \to \propto$ and taking into account the relationship between the jump velocity and the thermal velocity $w_{fg}{}^{i} = \chi U_{\xi fg}{}^{iv}(\chi)/\theta_f{}^{i}$, we obtain that the average relative velocity $w_{fg}{}^{i}$ of component i is equal to $w_{fg}{}^{i} = \sum_{j=1}{}^{s-1}w_{i(j)}x_j$, which fully corresponds to formula (9).

The relations (16)—(18) can be used to calculate various transfer coefficients for the average relative velocity of the thermal motion of the molecules i taking into account their collisions with all neighboring molecules.

Label transfer coefficients. The local mass transfer coefficient for a particular component, which characterizes the redistribution or thermal motion of molecule i ($1 \le i \le s - 1$) between neighboring sites f and g, situated in the neighboring planes at distance χ under equilibrium conditions, is the simplest characteristics of the molecular transport.

In practice, these processes are usually identified on the basis of the migration of an isotope label introduced into some local region of the system. The migration is detected by following the label redistribution with time over the whole solution. In the presence of external fields, in this particular case the field of the surface potential of pore walls, local and average partial label transfer coefficients are distinguished for an inhomogeneous system.[29]

For a labeled molecule of sort i, the following expression is valid for the label transfer coefficient:

$$D_{\xi fg}{}^{*i}(\chi) = z_{fg}{}^{*}(\chi)\chi^2 U_{\xi fg}{}^{iv}(\chi)/\theta_f^i, \tag{19}$$

where $z_{fg}{}^{*}(\chi)$ is the number of possible jumps to the neighboring sites g by distance χ for every site f. This expression shows that the self-diffusion coefficients for all components depend appreciably on the local distributions of the mixture components across the pore cross-section and on the motion direction. It also depends on the total local density of the system and intermolecular interactions.

Apart from the local transfer coefficients, average transfer coefficients are of interest for characterization of the flow. These coefficients are defined for some macroscopic area containing a set of local regions. For slit-shaped pores, the forward motion of the molecules along the pore axis with averaging over the contributions of all sites located in its cross-section is considered most often as the averaged characteristics. In view of the inhomogeneous distribution of molecules over the monolayers in a slit-shaped pore, the following expression is valid for the average label transfer coefficient ($1 \le i \le s - 1$):

$$D_i^* = \sum_{\chi} \chi^2 \sum_{q=1}^{t} F_q \sum_{p=1}^{t} \left\{ \left[z_{qp}^*(\chi) U_{\xi qp}^{iv}(\chi)/\theta_q^i \right] \frac{d\theta_q^{*i}}{d\theta_i^*} \right\}, \tag{20}$$

where $z_{qp}{}^{*}(\chi)$ is the number of bonds along which the jumps by distance χ take place from a site in layer q to neighboring sites in layer p, $d\theta_q{}^{*i}/d\theta_i{}^{*} = d\theta_q{}^{i}/d\theta_i$. The relationship between the jump constants and the local Henry constants is described by the expressions

$$a_q{}^i K_{\xi qp}{}^{(j)iv}(\chi) = a_p{}^i K_{\xi pq}{}^{(j)iv}(\chi).$$

Mutual diffusion coefficient. The local and average mutual diffusion coefficients for a binary mixture at constant pressure and temperature can be introduced in a similar way.

If the local flow of the first component toward site g is represented as $J_{fg}{}^{1}(\chi) = -D_{\xi fg}{}^{12}(\chi)\mathrm{grad}(x_1)$, it is possible to write down the expression for the local mutual diffusion coefficient of a binary mixture

$$D_{\xi fg}{}^{1,2}(\chi) = x_2[D_{\xi fg}{}^{11}(\chi) - D_{\xi fg}{}^{12}(\chi)] + \\ + x_1[D_{\xi fg}{}^{22}(\chi) - D_{\xi fg}{}^{21}(\chi)], \tag{21}$$

in which the addends look as follows:

$$D_{\xi fg}^{ik}(\chi) = \sum_{j=1}^{s-1} z_{fg}^*(\chi)\chi^2 U_{\xi fg}^{(j)iv}(\chi) \times \\ \times \frac{d\{\ln[Y_{fg}^i(\chi) Y_{f\xi}^{ij}(\rho) a_f^{i*} p_i]\}}{dx_k} / (\theta_f v_0), \tag{22}$$

$$Y_{fg}{}^{i}(\chi) = \theta_{fg}{}^{vv}(\chi)/[t_{fg}{}^{iv}(\chi) t_{gf}{}^{iv}(\chi)],$$

$$Y_{fg\xi}{}^{ij}(\rho) = \langle t_{f\xi}{}^{ij}(\rho) \rangle / S_{f\xi}{}^{i}(\rho).$$

The a_f^{i*} value is the density-independent part of the local Henry constant (all the density-dependent contributions to the Henry constant (a_f^i/a_f^{i*}) occur in the right-hand part of Eq. (13) together with the imperfection function Λ_f^i). For macroscopic distances, $Y_{fg}{}^{i}(\chi) = 1$, and formula (22) for the calculation of mean mass transfer coefficients for molecules i upon the change in the mole fractions x_j is transformed into the known expression[11,12] that relates the mass transfer coefficient to the gradient of the chemical potential of component i.

The resulting expression shows that the mutual diffusion coefficient for a dense phase, unlike that for a gas, depends not only on the individual properties of the colliding molecules; in addition, an essential role is played by the intermolecular interactions and, as a consequence, the pattern of their arrangement. This means that the configuration effects (short and long orders) and temperature influence the mutual diffusion coefficients. This formula does not include the so-called correlation factor.[11,30]

The mutual diffusion coefficient averaged across the pore cross-section is described by the expression similar to formula (20):

$$D_{1,2} = \sum_{\chi} \sum_{q=1}^{t} F_q \sum_{p=1}^{t} D_{\xi qp}^{1,2}(\chi). \tag{23}$$

Self-diffusion coefficient. The self-diffusion coefficient describes the migration of the label in one-component substances under an equilibrium distribution of molecules throughout the space. Formally, expressions for these coefficients can be derived from formulas (21)—(23) by equating the properties of both components,[3—6] if the partial densities are replaced by the overall density of the molecules.

Shear viscosity coefficient. The expression for the shear viscosity coefficient of a mixture can be found within the framework of a model that extends the Eyring model for a one-component liquid[31] to the case of an arbitrary density (from gases to liquids) and to a mixture of spherical molecules.[15,16] The final expression for the viscosity coefficient η_{fg} upon the shift of the fluid in site g relative to site f (here $\chi = 1$; therefore, this character is omitted) has the form

$$\eta_{fg} = \left[\sum_{i=1}^{s-1} x_j \left(\eta_{fg}^j\right)^{-1}\right]^{-1},$$

$$\eta_{fg}^j = \theta_f^j / U_{\xi fg}{}^{iv}, \qquad x_f^i = \theta_f^i/\theta_f, \qquad \theta_f = \sum_{i=1}^{s-1} \theta_f^i, \tag{24}$$

where x_f^j is the mole fraction of component j in site f, θ_f is the total filling of site f, and $U_{\xi fg}{}^{iv}(\chi = 1)$ can be found from expression (16). In the case of low densities, this equation turns into the Wilke and Brokaw type approximations[32] for gas mixtures extended to locally inhomogeneous systems. For pure components, this expression implies that the temperature dependence of η is given by $T^{1/2}$ and the dependence of η on the density is linear. At high densities, η depends exponentially on temperature, as in the traditional Eyring model.[31] This expression for pure components was verified in the calculation of the bulk viscosities of gases Ar, He, H_2, N_2, NH_3, and CO_2 and showed good agreement with the experiment.[33] For dense phases, the equations obtained allow one to substantiate a number of experimental correlations between the viscosity and mutual diffusion coefficients of liquid mixtures.[32]

The constructed expressions for the transfer coefficients modify similar equations obtained previously.[20,24] At low mixture densities corresponding to an ideal gas phase, these coefficients are in line with the expressions of the rigorous kinetic theory of gases.[3—6] The proposed relations ensure the calculation of transfer coefficients for a binary mixture of any density. The results of numerical analysis of new equations were reported previously.[34]

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