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DIFFUSIONAL MASS TRANSFER IN LIQUID MIXTURES

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The general form of the equations for determining the flow relations in liquid mixtures is obtained. A closed calculation algorithm and an experimental method of holographic interferometry are developed for the identification of the binary-diffusion coefficients. A ternary mixture is investigated by the method of molecular dynamics.

Equation for Determining Flow Relations in Liquid Mixtures

It is known that any closed nonequilibrium macroscopic system passes to a state of statistical equilibrium in the course of its relaxation time. This state of the system is described by an N-particle Gibbs distribution function [1]. For the large canonical ensemble of a v-component system, it takes the form

$$F_0^N = A \exp \left[- \left(E - \sum_{\alpha=1}^v \mu_{\alpha} N_{\alpha} \right) / KT \right],$$

where A is a normalization factor; μ_{α} , N_{α} are the chemical potential and number of particles of component α .

However, in practice, it is necessary to consider the system through times comparable with, or even less than, the relaxation time. In this case, its description may be constructed, as suggested in [2], by reducing the number of parameters characterizing the nonequilibrium macrosystem in the course of relaxation.

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Analyzing the structure of the function F_0^N , it may be asserted that the nonequilibrium distribution function F^N will depend on dynamic variables in the form of the molecular velocities and coordinates, as well as a series of macroscopic functions characterizing the nonequilibrium state. In isobarically isothermal conditions, such functions are the diffusional velocities V_α and the chemical potentials of the components μ_α . This allows the function F^N for the ν -component system to be written in parametric form

$$F^N = F^N(\mathbf{v}_{\alpha i}, \mathbf{r}_{\alpha i}, \mathbf{V}_\alpha, \mu_\alpha, T),$$

where $\mathbf{r}_{\alpha i}, \mathbf{v}_{\alpha i}$ are the position and velocity of particle i of type α .

According to the principle of local equilibrium, the function F^N may be expanded in series in terms of Hermitian polynomials [3], retaining only the first term of the expansion

$$F^N = \left[1 + \sum_{\alpha=1}^{\nu} \sum_{i=1}^{N_\alpha} \mathbf{a}_\alpha \frac{\partial}{\partial \mathbf{v}_{\alpha i}} + \sum_{\alpha, i} \sum_{\beta, j} \sum_{k, l} a_{k l} \frac{\partial^2}{\partial v_{\alpha i}^k \partial v_{\beta j}^l} \right] F_0^N.$$

Satisfying the basic integral relations of the form

$$\int \mathbf{v}_{\alpha i} F^N d^N \mathbf{v} d^N \mathbf{r} = \mathbf{V}_\alpha,$$

$$\int m_\alpha \mathbf{v}_{\alpha i}^2 F^N d^N \mathbf{v} d^N \mathbf{r} = 3KT,$$

it is found that $\mathbf{a}_\alpha = -\mathbf{V}_\alpha$ and hence

$$F^N = F_0^N \left(1 + \sum_{\alpha=1}^{\nu} \sum_{i=1}^{N_\alpha} \frac{m_\alpha}{KT} \mathbf{v}_{\alpha i} \mathbf{V}_\alpha \right). \quad (1)$$

The further construction of the theory involves representing the nonequilibrium system in the form of a hierarchical structure of two characteristic scales. These correspond to the processes of thermal motion of the molecules, with velocity $\mathbf{v}_{\alpha i}$ and interaction time τ_c , and relaxation of the macroscopic fields \mathbf{V}_α with characteristic time T_r ($\mathbf{v}_{\alpha i} \gg \mathbf{V}_\alpha$, $\tau_c \ll T_r$). Analysis of this structure is possible within the framework of the method of conjugate physical and mathematical modeling. The basic idea is that the relation between the schemes in the hierarchical system is parametric, and the parameters may be calculated by satisfying the fundamental conservation laws [4]. In the given case, this conservation law is the fundamental Liouville equation [1].

The irreversibility of diffusion [5] may be taken into account here by averaging the dynamic scale functions $\mathbf{v}_{\alpha i}$ over the time interval of pair interaction τ_c . Substituting the function of Eq. (1) into the Liouville equation, it is found, taking account of irreversibility, that

$$\sum_{\alpha=1}^{\nu} \sum_{i=1}^{N_\alpha} \frac{\mathbf{v}_{\alpha i} \nabla \mu_\alpha - m_\alpha \mathbf{v}_{\alpha i} \mathbf{V}_\alpha}{\tau_c} = 0, \quad (2)$$

where it is taken into account that

$$\frac{\partial \mu_\alpha}{\partial \tau} \ll \mathbf{v}_{\alpha i} \nabla \mu_\alpha,$$

$$\mathbf{v}_{\alpha i} \frac{\partial \mathbf{V}_\alpha}{\partial \tau} \ll \mathbf{v}_{\alpha i} \mathbf{V}_\alpha. \quad (3)$$

Estimating the chemical potential $\mu_\alpha = \mu_\alpha^0 + KT \ln X_\alpha$, where μ_α^0 is the chemical potential of the pure liquid, X_α is the mole fraction of component α , and $\mathbf{v}_{\alpha i} \sim \frac{\mathbf{v}_{\alpha i}}{\tau_c}$, $\frac{\partial \mathbf{V}_\alpha}{\partial \tau} \sim \frac{\mathbf{V}_\alpha}{T_r}$ it is simple to prove Eq. (3).

Multiplying Eq. (2) by the momentum of particle i of type α at time $\tau = 0$ and averaging it over the ensemble, the final system of equations is found

$$3KT\nabla\mu_\alpha + \sum_{\beta=1}^v N_\beta m_\alpha \overline{\langle \mathbf{v}_{\alpha i}(0) \mathbf{v}_{\beta j}(\tau) \rangle}_0 \nabla\tau_\beta - \sum_{\beta=1}^v N_\beta \overline{\langle \mathbf{p}_{\alpha i}(0) \dot{\mathbf{p}}_{\beta j}(\tau) \rangle}_0 (\mathbf{V}_\beta - \mathbf{V}_\alpha) = 0; \quad \alpha = \overline{1 \dots v}, \quad (4)$$

where the relation

$$\overline{\langle \mathbf{p}_{\alpha i}(0) \dot{\mathbf{p}}_{\alpha i}(\tau) \rangle}_0 = - \sum_{\beta=1}^v N_\beta \overline{\langle \mathbf{p}_{\alpha i}(0) \dot{\mathbf{p}}_{\beta j}(\tau) \rangle}_0$$

is used, since the system may be regarded as closed in the course of time τ_c .

Thus, within the framework of the method of conjugate physical and mathematical modeling, the general form of the basic equations for determining some relations in liquid mixtures may be obtained. The coupling parameters of the scales $\mathbf{v}_{\alpha i}$ and \mathbf{V}_α are the momentum and force correlation function (MFCF)

$$\overline{\langle \mathbf{p}_{\alpha i}(0) \dot{\mathbf{p}}_{\beta j}(\tau) \rangle}_0 = \lim_{T_r \rightarrow \infty} \frac{1}{T_r} \int_0^{T_r} \mathbf{p}_{\alpha i}(t) \frac{\mathbf{p}_{\beta j}(t + \tau_c) - \mathbf{p}_{\beta j}(t)}{\tau_c} dt, \quad (5)$$

and the mutual velocity correlation function (MVCF) averaged over time interval τ_c

$$\overline{\langle \mathbf{v}_{\alpha i}(0) \mathbf{v}_{\beta j}(\tau) \rangle}_0 = \lim_{T_r \rightarrow \infty} \frac{1}{T_r} \int_0^{T_r} \frac{1}{\tau_c} \int_0^{\tau_c} \mathbf{v}_{\alpha i}(t) \mathbf{v}_{\beta j}(t + \tau) d\tau dt. \quad (6)$$

The system in Eq. (4) may be significantly simplified for small $\tau_c \rightarrow 0$ (model system of solid spheres). Estimating the terms of the first and second sums in Eq. (4) and using the relations

$$\mathbf{V}_\beta \simeq \frac{n_\beta}{KT} D_\beta \nabla\mu_\beta; \quad D_\beta \simeq \frac{KT}{m_\beta} \tau_{pa}; \quad \dot{\mathbf{p}}_{\beta j} \simeq \frac{\mathbf{p}_{\beta j}}{\tau_c},$$

where τ_{pa} is the "free" path time, it may be found that as $\tau_c \rightarrow 0$

$$m_\alpha \overline{\langle \mathbf{v}_{\alpha i}(0) \mathbf{v}_{\beta j}(\tau) \rangle}_0 \nabla\mu_\beta \ll \overline{\langle \mathbf{p}_{\alpha i}(0) \dot{\mathbf{p}}_{\beta j}(\tau) \rangle}_0 \mathbf{V}_\beta,$$

which is equivalent to the inequality

$$\tau_c \ll \tau_{pa}. \quad (7)$$

Although these inequalities are of model type, they may be valid for real liquids in which the molecular interaction is determined basically by the repulsive forces. A system of equations of simpler form may be used to investigate such media

$$3KT\nabla\mu_\alpha - \sum_{\beta=1}^v N_\beta \overline{\langle \mathbf{p}_{\alpha i}(0) \dot{\mathbf{p}}_{\beta j}(\tau) \rangle}_0 (\mathbf{V}_\beta - \mathbf{V}_\alpha) = 0. \quad (8)$$

In addition, in the case of a model system of solid spheres, an analytical solution may be obtained for the flow relation j_α . In the binary collision of two spheres with diameters σ_α and σ_β , the variation in momentum occurs along the line connecting their centers, in the direction of the unit vector \mathbf{e} :

$$\Delta \mathbf{p}_{\beta j} = (\mathbf{p}_{\alpha i} \mathbf{e} - \mathbf{p}_{\beta j} \mathbf{e}) \mathbf{e}.$$

On passing to the center-of-mass system of the colliding molecules, averaging over the two-particle distribution function

$$F_{\alpha\beta}^{(2)} = (\mu_{\alpha\beta}/2\pi KT)^{3/2} \exp[-\mu_{\alpha\beta} v_{\alpha\beta}^2/2KT] g_{\alpha\beta}(r_{\alpha i} - r_{\beta j})/V$$

gives the following expression for the MFCF

$$\lim_{\tau_c \rightarrow 0} \left\langle p_{\alpha i} \frac{\Delta p_{\beta j}}{\tau_c} \right\rangle_0 = (2KT)^{3/2} (\mu_{\alpha\beta}/\pi)^{1/2} 4\pi \sigma_{\alpha\beta}^2 g_{\alpha\beta}^0 n, \quad (9)$$

where $\sigma_{\alpha\beta} = (1/2)(\sigma_{\alpha} + \sigma_{\beta})$; n is the numerical density of the mixture; $\mu_{\alpha\beta}$ is the reduced mass; $v_{\alpha\beta} = v_{\alpha i} - v_{\beta j}$, $g_{\alpha\beta}^0$ is the radial function at the contact point of the spheres. This function may be obtained from the solution of the Percus-Yevick integral equations [6, 7]

$$g_{\alpha\beta}^0 = (\sigma_{\beta} g_{\alpha\alpha} + \sigma_{\alpha} g_{\beta\beta})/2\sigma_{\alpha\beta},$$

$$g_{\alpha\alpha} = \left[(1 - \xi) + \frac{3}{2} \sigma_{\alpha} \left(\sum_{k=1}^{\nu} \frac{\pi}{6} n_k \sigma_k^2 \right) \right] / (1 - \xi)^2, \quad \xi = \sum_{i=1}^{\nu} \pi n_i \sigma_i^3 / 6. \quad (10)$$

In this case, the solution of Eq. (8) for a binary mixture in the mean-mass coordinate system determined by the coupling equation

$$\sum_{\beta=1}^{\nu} (n_{\beta} m_{\beta} / \rho) V_{\beta} = 0$$

will take the form

$$j_{\alpha} = - \frac{n_{\alpha}}{KT} D_{\alpha\beta} \nabla \mu_{\beta}, \quad D_{\alpha\beta} = 3 \left(\frac{KT}{2\pi \mu_{\alpha\beta}} \right)^{1/2} \frac{1}{8n \sigma_{\alpha\beta}^2 g_{\alpha\beta}^0}. \quad (11)$$

Note also that in the limiting case, for a system of rarefied gases, Eqs. (8) with account of Eq. (9) and also the relation $\mu_{\alpha} = \mu_{\alpha}^0 + KT \ln(n_{\alpha}/n)$ transform to the well-known Stefan-Maxwell equations [7]

$$(\nabla n_{\alpha}/n) = \sum_{\beta=1}^{\nu} \frac{n_{\alpha} n_{\beta}}{n^2} \frac{1}{D_{\alpha\beta}} [V_{\beta} - V_{\alpha}],$$

where $D_{\alpha\beta}$ takes the form in Eq. (11).

Experimental Investigation of Diffusion in Multicomponent Mixtures

The region of applicability of Eq. (11) to a real system is confined to a reduced-density value $\rho_0 \approx \sqrt{2}/n\sigma_{\alpha} = 1.5$ [8], at which there is phase transition to a model system of solid spheres. However, for binary systems, the contribution of attractive forces to the radial function $g_{\alpha\beta}^0$ may be taken into account. The most universal approach here entails investigating the equation of state of solid spheres [6], with the introduction of a term taking account of the contribution of attractive forces to the pressure $f(V)$

$$P + f(V) = nKT \left(1 + \frac{2}{3} \pi n \sum_{\alpha=1}^{\nu} \sum_{\beta=1}^{\nu} X_{\alpha} X_{\beta} \sigma_{\alpha\beta}^3 g_{\alpha\beta}^0 \right).$$

Then Enskog relation [9] may be obtained for $g_{\alpha\alpha}$ - the radial function of the component α at infinite dilution ($X_{\beta} \rightarrow 0$) in Eq. (10)

$$\frac{\pi}{6} n_{\alpha} \sigma_{\alpha} g_{\alpha\alpha} = \left[\frac{V \left(\frac{\partial P}{\partial T} \right)_V}{R} - 1 \right] / 4. \quad (12)$$

Thus, using Eqs. (10)-(12), $D_{\alpha\beta}$ may be determined. The derivative $(\partial P/\partial T)_V$ is determined here from the equation of state of a pure liquid. For example, the Lee-Kessler equation of state [10] ensures a mean error of less than 2% in calculating the thermodynamic properties of hydrocarbons at reduced temperatures of 0.3-4.0 and reduced pressures of 0-10 for the vapor and liquid phases.

For sufficiently dense systems $\rho_0 \approx 1.5$, the Eiring equation is most often used as the equation of state [10]

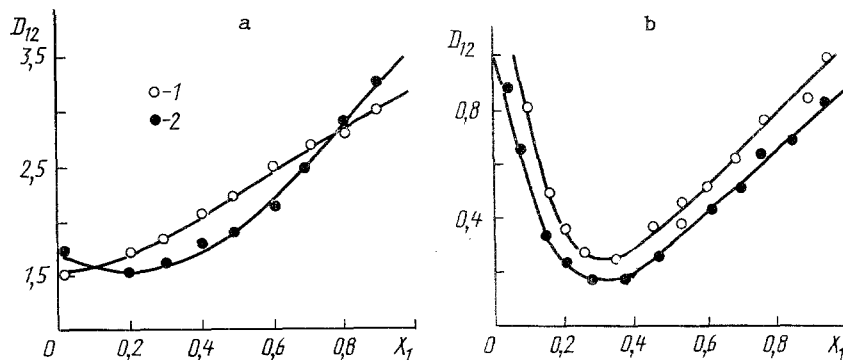


Fig. 1. Concentration dependence of the binary-diffusion coefficient $D_{12} (\cdot 10^9 \text{ m}^2/\text{sec})$ at $T = 298 \text{ K}$: a) theory; 2) experiment; a) the system $\text{C}_6\text{H}_{14}-\text{CCl}_4$, calculation by the Eiring equation; b) the system $\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$, calculation by the Lee-Kessler equation.

$$P + \frac{a}{V^2} = nKT \left[1 + \frac{b}{V} + 0,625 \left(\frac{b}{V} \right)^2 + 0,2869 \left(\frac{b}{V} \right)^3 + 0,1928 \left(\frac{b}{V} \right)^4 \right].$$

Comparison of the numerical values of $g_{\alpha\beta}^0$ obtained from Eq. (10) with those calculated from the Eiring and Lee-Kessler equations of state gives a difference within limits of 30%. This is the basis for application of a version of perturbation theory in constructing the concentration dependence of the binary-diffusion coefficient. To test this hypothesis, calculations and experimental investigations of the dependence of D_{12} on the composition X_1 are undertaken. The method of holographic interferometry is used in the experiment. The optical scheme of the real-time holographic interferometer corresponds to the Mach-Zehnder scheme. In the course of the experiment, one-dimensional non-steady diffusion is organized within a diffusional cell in the form of a narrow plane-parallel parallelepiped. The procedure for deriving the diffusion coefficients is based on numerical integration, in the course of which moments of four orders of the interference-band shift function are established.

The basic advantage of the measurement method is its relative simplicity, both in terms of realization and in the volume of calculations required. In the course of the experiment, weak sensitivity to the form of the initial concentration profile is discovered; this is of fundamental importance. The measurement error, according to estimates, is no more than 5%.

The results of calculating D_{12} from Eqs. (10)-(12) for the binary systems $\text{C}_6\text{H}_{14}-\text{CCl}_4$, $\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$ at $T = 298 \text{ K}$ are shown in Fig. 1, together with experimental data obtained by holographic interferometry. As is evident from Fig. 1, the use of the Lee-Kessler and Eiring equations of state gives the best agreement with experiment, within limits of 20%.

With the aim of verifying the fundamental principles of the theory, a numerical experiment on the investigation of the three-component Lennard-Jones mixture Alimadad (acetone-benzene-methanol) by the method of equilibrium molecular dynamics is developed and undertaken. The matrix elements of multicomponent diffusion $D_{\alpha\beta}$ are calculated on the basis of solution of Eq. (4) in the mean-mass coordinate system. The functions in Eqs. (5) and (6) are determined experimentally. The results for $D_{\alpha\beta}$ are compared with the transfer coefficients obtained earlier by the method of nonequilibrium molecular dynamics (NEMD) [11].

The total number of particles modeled is chosen to be $N = 256$; the integration step $\Delta t = 10^{-14} \text{ sec}$. The number of steps in the thermalization procedure $NK = 400$ completely ensures stability of the temperature $T = 300 \pm 15 \text{ K}$ over the whole time interval $t_r = 10^{-11} \text{ sec}$ of accumulation of the statistics. With the aim of reducing the velocity fluctuations of the molecules, the integration of the equations of motion is by the Moulton-Adams scheme

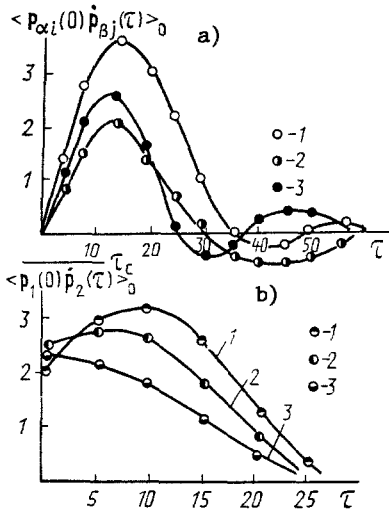


Fig. 2

Fig. 2. Dependence of MFCF ($\cdot 10^{35} \text{ N}^2 \cdot \text{sec}$) on τ ($\cdot 10^{14} \text{ sec}$) for the system acetone-benzene-methanol when $T = 300 \text{ K}$, $X_1 = 0.4$, $X_2 = 0.5$; a) curves of $\langle p_i(0) \dot{p}_j(\tau) \rangle_0$ (1), $\langle p_1(0) \dot{p}_2(\tau) \rangle_0$ (2), and $\langle p_2(0) \dot{p}_3(\tau) \rangle_0$ (3); b) $\tau_c = 10^{-13}$ (1), $2 \cdot 10^{-13}$ (2), and $3 \cdot 10^{-13}$ (3) sec.

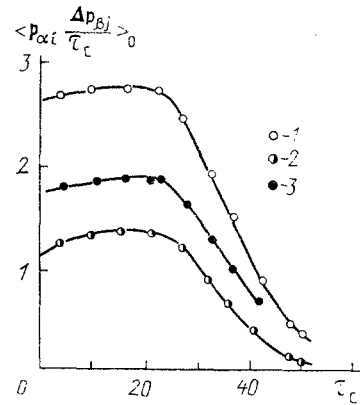


Fig. 3

Fig. 3. Dependence of the function $\langle p_{\alpha i} \frac{\Delta p_{\beta j}}{\tau_c} \rangle_0$ ($\cdot 10^{35} \text{ N}^2 \cdot \text{sec}$) on the averaging time τ_c ($\cdot 10^{14} \text{ sec}$) for the acetone-benzene-methanol system when $T = 300 \text{ K}$, $X_1 = 0.4$, $X_2 = 0.5$; 1) $\langle p_1 \frac{\Delta p_2}{\tau_c} \rangle_0$; 2) $\langle p_1 \frac{\Delta p_3}{\tau_c} \rangle_0$; 3) $\langle p_2 \frac{\Delta p_3}{\tau_c} \rangle_0$.

$$v_{\alpha i}^{(n+1)} = v_{\alpha i}^{(n)} + \frac{\Delta t}{24m_{\alpha}} [55F_{\alpha i}^{(n)} - 59F_{\alpha i}^{(n-1)} + 37F_{\alpha i}^{(n-2)} - 9F_{\alpha i}^{(n-3)}],$$

$$r_{\alpha i}^{(n+1)} = r_{\alpha i}^{(n)} + \frac{\Delta t}{24} [55v_{\alpha i}^{(n)} - 59v_{\alpha i}^{(n-1)} + 37v_{\alpha i}^{(n-2)} - 9v_{\alpha i}^{(n-3)}],$$

where $F_{\alpha i}^{(n)}$ is the Lennard-Jones force acting on molecule i of type α from its nearest neighbor.

Calculation of the function $\langle p_{\alpha i}(0) \dot{p}_{\beta j}(\tau) \rangle_0$ by the formula

$$\langle p_{\alpha i}(0) \dot{p}_{\beta j}(\tau) \rangle_0 = \frac{m_{\alpha} m_{\beta}}{N_p} \sum_{h=1}^{N_p} u_{\alpha}(t_h) \frac{u_{\beta}(t_h + \tau + \Delta t) - u_{\beta}(t_h)}{\Delta t}, \quad (13)$$

where Δt is the integration step, clearly demonstrates the meaning of the pair-interaction time in the liquid.

Graphs of the function in Eq. (13) for the mixture acetone(1)-benzene(2)-methanol(3) when $T = 300 \text{ K}$, $X_1 = 0.4$, $X_2 = 0.5$ (Fig. 2a) have a clearly expressed peak directly characterizing the interaction of the molecules α and β . The width of this peak also determines τ_c .

When $\tau > \tau_c$, the behavior of Eq. (13) is fluctuational in character. To identify the irreversible parameters in Eq. (5) determining the velocity v_{α} in Eqs. (4) and (8), it is expedient to consider the evolution of the following function in terms of τ_c

$$\langle p_{\alpha i}(0) \dot{p}_{\beta j}(\tau) \rangle_0 = \frac{m_{\alpha} m_{\beta}}{N_p} \sum_{h=1}^{N_p} u_{\alpha}(t_h) \frac{u_{\beta}(t_h + \tau + \tau_c) - u_{\beta}(t_h)}{\tau_c},$$

$$t_h = \Delta t k, \quad u_{\alpha} = \sum_{i=1}^{N_{\alpha}} \frac{v_{\alpha i}}{N_{\alpha}}. \quad (14)$$

TABLE 1. Results of Numerical Modeling of Acetone-Benzene-Methanol Mixture

Composition		Equilibrium method ($\cdot 10^9 \text{ m}^2 \cdot \text{sec}$)				Nonequilibrium method ($\cdot 10^9 \text{ m}^2 \cdot \text{sec}$)			
x_1	x_2	D_{11}	D_{12}	D_{21}	D_{22}	D_{11}	D_{12}	D_{21}	D_{22}
0,35	0,3	2,92	-0,8	-0,6	1,95	2,84	-0,52	-0,36	2,27
0,4	0,5	2,73	-1,1	-0,6	2,46	2,7	-0,74	-0,31	2,1
0,2	0,55	2,7	-0,6	-0,3	1,35	2,62	-0,42	-0,12	1,65
0,55	0,19	3,2	-0,2	-0,3	1,9	3,06	-0,16	-0,44	2,48

Graphs of this function for various τ_c in the case of the given mixture with $\alpha = 1$, $\beta = 2$, $X_1 = 0.4$, $X_2 = 0.5$ are shown in Fig. 2b. "Deformation" with increase in τ_c appears here in the motion of the maximum of the basic peak to the left, with decrease and complete disappearance at τ_c greater than some critical value $\tau_c > \tau_{cr}$.

Such behavior of the curves of Eq. (14) forms the basis for determining the parameters in Eq. (5) which do not depend on the time τ_c . Determining the parameters in Eq. (5) as the mean of the function in Eq. (14) with respect to τ in the time interval $[0, \tau_{\max}]$ for fixed τ_c is the clearest example confirming the initial principles of the method of conjugate physical and mathematical modeling. In the case where $\tau_c > \tau_{cr}$, their values are determined when $\tau = 0$. The corresponding graph of this function $\langle p_{\alpha i} \frac{\Delta p_{\beta j}}{\tau_c} \rangle_0$ has a clearly expressed plateau (Fig. 3). The width of this section $\Delta \tau \approx 2 \cdot 10^{-13}$ sec, which is an order of magnitude greater than the integration step and indicates the correctness of the above determination.

The results of modeling an acetone-benzene-methanol mixture in Table 1 indicate good agreement of the diagonal matrix elements obtained by two different methods. The relatively large spread (~60%) with respect to the nondiagonal elements may be explained by the incorrect use of the thermocompensation procedure in the NEMD method.

The error of the numerical experiment obtained from the maximum spread of the function $\langle p_{\alpha i} \frac{\Delta p_{\beta j}}{\tau_c} \rangle_0$ on the plateau (Fig. 3) is no more than 20%. The MVCF, which is calculated from the formula

$$\langle \mathbf{v}_{\alpha i}(0) \mathbf{v}_{\beta j}(\tau) \rangle_0 = \frac{1}{N_p} \sum_{k=1}^{N_p} \frac{1}{N_k} \mathbf{u}_{\alpha}(t_k) \sum_{l=1}^{N_k} \mathbf{u}_{\beta}(t_l),$$

has the character of a correction, and has a weak influence on the experimental accuracy (within limits of 5-10%).

NOTATION

μ , chemical potential of the molecules of the component; \mathbf{v}_{α} diffusional velocity of the molecules of the component α ; \mathbf{u}_{α} mean velocity of the molecules of the component α ; $\mathbf{v}_{\alpha i}$ dynamic velocity of particle i of component α ; $\mathbf{r}_{\alpha i}$ radius vector of particle i of type α in the laboratory coordinate system; $g_{\alpha\beta}$, radial distribution function; F^N , non-equilibrium distribution function; F_0^N , locally equilibrium distribution function; $F_{\alpha\beta}^{(2)}$, two-particle distribution function; τ_c , pair-interaction time; τ , current microscopic time; τ_{pa} , free path time for model system of solid spheres; τ_{\max} , time of a maximum of $\langle p_{\alpha i}(0) p_{\beta j}(\tau) \rangle_0$; τ_{cr} , time of disappearance of the basic peak of the function $\langle p_{\alpha i} \frac{\Delta p_{\beta j}}{\tau_c} \rangle_0$ on averaging with respect to τ ; m_{α} , mass of particle type α ; μ_{α} , reduced mass; σ_{α} , diameter of molecule of type α in model system of solid spheres; V , volume of system; X_{α} , mole fraction of component α ; n_{α} , numerical density of component α ; n , numerical density of mixture; $D_{\alpha\beta}$, matrix of multicomponent diffusion coefficients; D_{12} , binary diffusion coefficient.

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DETERMINING THE TEMPERATURE FIELDS OF MULTILAYER SPHERICALLY SYMMETRIC SYSTEMS

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On the basis of the WKBJ method, approximate relations are obtained for determining the nonsteady temperature field in spherically symmetric multilayer systems.

In calculating the temperature fields of multilayer shells, power plants, and various aircraft, not only computer-based numerical methods may be successfully used, but also approximate analytical methods with the introduction of effective thermophysical characteristics for inhomogeneous media [1-4]. It is very expedient in this case to use the principles of the WKBJ method [5], which is well developed and widely used in theoretical physics. In thermophysical investigations, these ideas have been realized in determining the temperature in plane multilayer systems [6], and estimates have been made for the cylindrical case [7].

Consider a multilayer spherically symmetric system. Its temperature field is determined by the equations

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \kappa(r) \frac{\partial T}{\partial r} \right] + q_v(r, t) = c\gamma(r) \frac{\partial T}{\partial t}, \quad (1)$$

$$\frac{\partial T}{\partial r} = 0, \quad r = 0, \quad (2)$$

$$-\kappa \frac{\partial T}{\partial r} = \alpha (T - T_{me}), \quad r = R, \quad (3)$$

$$T(r, t = 0) = T_{in}(r). \quad (4)$$

where κ , $c\gamma$ are the thermal conductivity and volume specific heat; q_v denotes the heat sources; α , T_{me} are the heat-transfer coefficient with the surrounding medium and its temperature; R is the radius of the system.