2. The method of averaging wall temperatures and membrane concentrations as mean arithmetic quantities is only approximate.

3. The method of calculating concentration distribution over membrane thickness does not take into account the convective component of transfer.

However, despite the shortcomings connected with the approximate nature of the calculations, the method used is correct in principle, and the results obtained do give a qualitatively correct picture, without a doubt. A more refined technique will naturally produce more accurate results.

NOTATION

G, weight flow rate; F, surface area; m, mass transfer coefficient, referred to condenser surface; $p_{r,c}$, partial vapor pressure in mixture; p, total mixture pressure; β, mass transfer coefficient, referred to partial pressure; Δp, partial pressure heat; j, vapor transverse mass flow density; c, electrolyte concentration; t, temperature; δt, temperature variation; i, current density; I, load current. Subscripts and superscripts: r, in reactor; c, in condenser; s, on surface; h, hydrogen in reaction; m, mixture; th, thermostat liquid; in, input; out, output.

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EFFECTIVE CONDUCTIVITY OF HETEROGENEOUS SYSTEMS WITH DISORDERED STRUCTURE

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UDC 536.24

A model reflecting the disordered character of the structure of a heterogeneous system is proposed, together with a method for calculating the coefficients of generalized conductivity* of compounds, eutectics, composites, and solutions.

We will consider the simplest possible two-component heterogeneous system with chaotic structure, formed, for example, by the pressing of a mixture of two different powders of compact particles. We will limit our consideration to the case of mechanical mixture of noninteracting components which preserve their original properties both within the volume and at the phase boundary.

Use of the concept of "disordered" structure assumes that in regions of the system with dimensions significantly exceeding the dimensions of the original particles the values of the volume concentrations of the components m_i, m_j are practically indistinguishable from the average values of those quantities over the entire system volume, while the system properties are isotropic within the limits of the region and over the system as a whole, although local deviations from mean values may occur.

We will attempt to develop a model reflecting the random (probability) character of the distribution of the individual components within the volume of the two-component system with disordered structure, and to determine its effective conductivity.

*The coefficients of generalized conductivity are the coefficients of thermal conductivity, electrical conductivity, dielectric permittivity, and magnetic permeability, the determination of which is the object of the theory of generalized conductivity.

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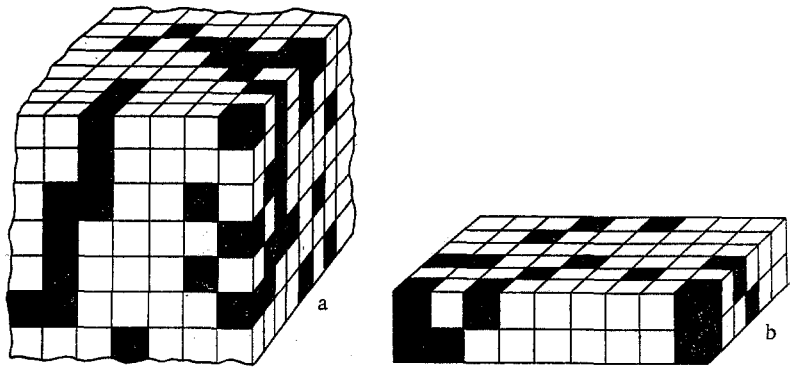

Fig. 1. Model of two-component heterogeneous system: a) volume view of system; b) two-layer mass.

In choosing a model for the system it is necessary to specify the form of the components, their distribution within the volume, the conditions at the boundaries, and the dimensions of the system in the longitudinal (direction of flow) and transverse directions.

Models described in the literature may be divided into two types according to the method used to specify their dimensions:

1. constant dimensions (usually in the form of an elementary cell containing one particle, with a corresponding volume of the second component) [1-3]. The effective conductivity is determined as an analytical function of the concentrations and conductivities of the components;
2. several particles in length in the direction of flow, with the number of particles dependent on the component concentrations [4-5]. Effective conductivity is determined by computer calculation.

The desirability of using this latter type of model depends on the type of structure involved and becomes warranted when there is a sharp difference in conductivity of the components.

An analogous problem has been considered in percolation theory [6], with systems of the type dielectric—conductor ($\lambda \neq 0$, $\lambda_2 = 0$). In percolation theory it was found by computer simulation that there exists in the system a threshold concentration of conductive component m_c ($m_c \approx 0.15$) at which the effective conductivity undergoes an abrupt change: if $m_1 < m_c$, the effective conductivity $\lambda = 0$, while if $m_1 > m_c$, then $\lambda \neq 0$. However, even for a very small yet nonzero conductivity of the second component $1 > \lambda_2/\lambda_1 > 10^{-4}$ the dependence of effective conductivity λ on component concentration is of a monotonic character [7, 8].

We will limit ourselves below to consideration of systems with component properties differing within the limits $1 > \lambda_2/\lambda_1 > 1 \cdot 10^{-4}$, in which there is no discontinuity in the function $\lambda = f(\lambda_1, \lambda_2, m_1)$ over the entire range of component concentrations $0 \leq m_1 \leq 1$.

Since the form of the compact particles has little effect on the effective conductivity of the system, we can replace the real particles by any compact geometric solids (for example, polyhedra) capable of completely (without voids) filling the system volume.

To simulate a structure isotropic in three mutually perpendicular directions we choose as the model for the particles of arbitrary form cubes, arranged such that the planes passing through the cube boundaries intersect no other cubes (Fig. 1a) [9] and so that the mean distance between cube centers equals the mean distance between particle centers in the real system.

Using traditional approaches, we will study the system properties not over its entire volume, but in a model with variable thickness comparable with the mean distance between particle centers in the direction of the flow and extending without limit in the two remaining orthogonal directions.

We define the mean statistical distance between the centers of conductive particles on the same axis $\langle l \rangle$, and on the basis of $\langle l \rangle$ we estimate the size of the model h in the direction of flow.

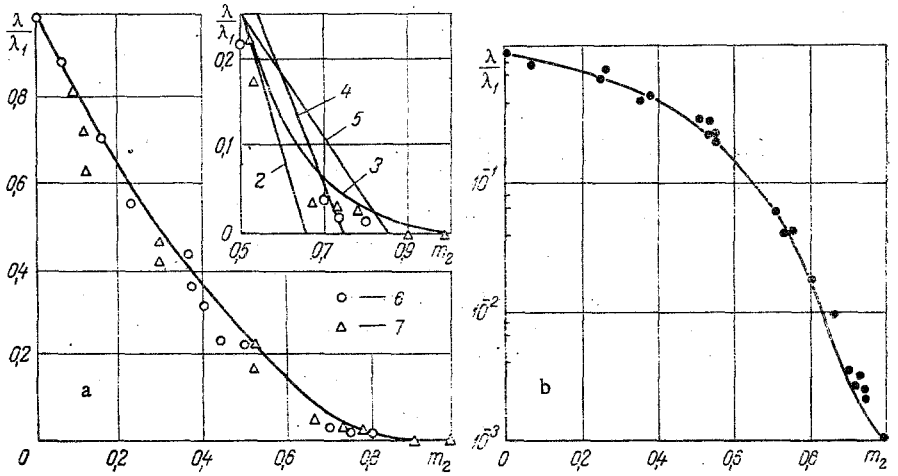

Fig. 2. Comparison of calculated results and experimental data. a) Calculation: 1) Eqs. (16), (21); 2) [9]; 3) [10]; 4) [12]; 5) [13]; experimental data: 6) [10]; 7) [11]. b) Curve, calculation by Eqs. (16), (21); points, experiment [7].

The volume concentration of conductive particles in a system with N particles with identical volume v_0 is equal to

$$m_1 = Nv_0/V. \tag{1}$$

We find in the heterogeneous system some cube such that the particle concentration within it is equal to the particle concentration within the entire system. Then

$$N_V = \frac{N}{V} = \frac{m_1}{v_0} = N_L, \text{ i.e., } N_L = \left(\frac{m_1}{v_0}\right)^{1/3}, \tag{2}$$

where N_L is the number of particles per unit length.

The particle volume v_0 may be represented in terms of a particle form coefficient k_f and a defining linear dimension d in the form

$$v_0 = (k_f d)^3. \tag{3}$$

With consideration of Eq. (3) the expression for N_L may be rewritten as

$$N_L = (k_f d)^{-1} m_1^{1/3}. \tag{4}$$

The reciprocal of Eq. (4) is the mean distance between particle centers

$$\langle l \rangle = k_f d m_1^{-1/3}. \tag{5}$$

For spherical particles (on the same axis) $k_f = 0.805$ and

$$\langle l \rangle = 0.805 d m_1^{-1/3}. \tag{6}$$

With consideration of Eq. (6) the height of a layer may be defined as

$$h = \langle l \rangle + d \quad \text{or} \quad h = d(1 + k_f m_1^{-1/3}), \tag{7}$$

whence

$$\begin{array}{ll} m_1 & 1 \text{ to } 0.53;\ 0.53 \text{ to } 0.06;\ 0{,}06 \text{ to } 0; \\ h & 2d; \qquad (2 \text{ to } 3)\,d; \qquad \geqslant 3d. \end{array} \tag{8}$$

For further simplification of the problem the boundaries of each cube parallel to the common flow direction will be considered as infinitely thin planes impermeable to current lines. We will determine the effective conductivity of a two-layer mass (h = 2d) filled by different cubes (Fig. 1b).

The conductivity of the mass σ may be calculated by summing the conductivities $\sigma_{11}, \sigma_{12}, \sigma_{21}$, and σ_{22} of individual cube pairs, filled by homogeneous and inhomogeneous components with conductivities λ_1 and λ_2 (Fig. 1b):

$$\sigma = n_{11}\sigma_{11} + n_{12}\sigma_{12} + n_{21}\sigma_{21} + n_{22}\sigma_{22}, \tag{9}$$

where

$$\sigma_{11} = \lambda_1 S/h;\ \sigma_{22} = \lambda_2 S/h;\ \sigma_{12} = \sigma_{21} = 2\frac{\lambda_1\lambda_2}{\lambda_1+\lambda_2}\frac{S}{h}. \tag{10}$$

Here n_{11}, n_{22} are the number of pairs of cubes consisting of the same component; $n_{12} = n_{21}$ is the number of pairs of cubes consisting of different components; S is the area of the cube faces.

Then from Eq. (9) we obtain

$$\sigma = \left(n_{11}\lambda_1 + n_{22}\lambda_2 + 4n_{12}\frac{\lambda_1\lambda_2}{\lambda_1+\lambda_2}\right)\frac{S}{h}. \tag{11}$$

We find the conductivity of the mass σ assuming that all $n = n_{11} + n_{12} + n_{21} + n_{22}$ cubes are filled with a homogeneous substance with effective conductivity λ. Equating this value $\sigma = \lambda nS/h$ to Eq. (11) we obtain λ in the form

$$\lambda = \lambda_1\frac{n_{11}}{n} + \lambda_2\frac{n_{22}}{n} + 4\frac{\lambda_1\lambda_2}{\lambda_1+\lambda_2}\frac{n_{12}}{n}. \tag{12}$$

We introduce the notation

$$\frac{n_{11}}{n} = W_{11};\ \frac{n_{12}}{n} = W_{12};\ \frac{n_{22}}{n} = W_{22}, \tag{13}$$

which quantities are none other than definitions of the a priori probabilities W_{ii}, W_{ij} of formation of pairs 11, 12, and 22. Then

$$\lambda = \lambda_1 W_{11} + \lambda_2 W_{22} + 4\frac{\lambda_1\lambda_2}{\lambda_1+\lambda_2}W_{12}. \tag{14}$$

Since in the simplified model all cubes are identical in dimensions, their numerical ratios n_{ii}/n, n_{ij}/n or probabilities W_{ii}, W_{ij} of formation of concrete combinations ii, ij are uniquely related to the volume concentration of components m_i and m_j (expressed as fractions of unity).

In fact, given a random distribution of cubes filled by the different components in each layer, the probability of formation of any pair can be calculated as the probability of the complex event defined by a combination of two independent (for each individual layer) events; i.e.,

$$W_{11} = m_1 m_1 = m_1^2;\ W_{12} = m_1 m_2;\ W_{22} = m_2^2. \tag{15}$$

Substituting the value of the probabilities of Eq. (15) in Eq. (14) we obtain the final expression for calculation of the effective thermal conductivity of the two-layer mass with chaotic component distribution in the very simple form

$$\lambda_{2d} = \lambda_1 m_1^2 + \lambda_2 m_2^2 + 4\frac{\lambda_1\lambda_2}{\lambda_1+\lambda_2}m_1 m_2. \tag{16}$$

Equation (16) undergoes a limiting transformation to a homogeneous material (if $m_i = 1$, then $\lambda_{2d} = \lambda_i$) and permits arbitrary interchange of the component indices, as should be the case for disordered structures (the requirement of symmetry or invariance upon interchange of indices).

Using the same approach of approximate description as for a two-layer model, we obtain an expression for effective conductivity at h = 3d in the form

$$\lambda_{3d} = \lambda_1 m_1^3 + \lambda_2 m_2^3 + 9\lambda_1\lambda_2 m_1 m_2\left(\frac{m_1}{\lambda_1+2\lambda_2} + \frac{m_2}{2\lambda_1+\lambda_2}\right). \tag{17}$$

For the range of volume concentration of conductive particles 0.53–0.06 the values of the effective conductivity coefficient λ will lie between the values calculated from Eqs. (16) and (17, for $m_1 = 0.53$ being defined by Eq. (16), and for $m_1 = 0.06$, by Eq. (17). A quantitative difference between Eqs. (16) and (17) will be observed if $\lambda_2/\lambda_1 \leq 10^{-2}$. Thus we write the expression for the effective conductivity coefficient λ for $m_1 \leq 0.53$ in the form

$$\lambda = f(m_1)\lambda_{3d}, \tag{18}$$

where $f(m_1)$ is found from the boundary conditions

$$\lambda = \lambda_{2d} \quad \text{at} \quad m_1 = 0{,}5;\ \lambda = \lambda_{3d} \quad \text{at} \quad m_1 = 0.06, \tag{19}$$

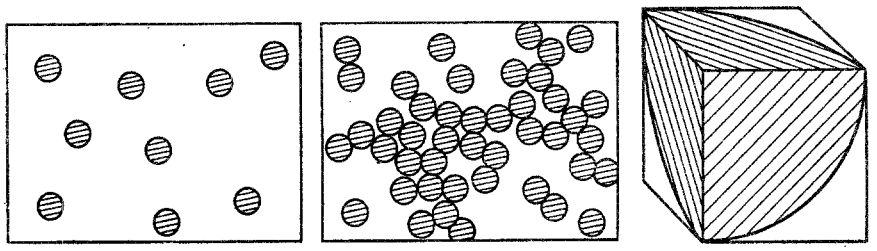

Fig. 3. Schematic representation of compound structure: a) low filler concentration ($m_1 < 0.2$); b) large concentration of filler ($m_1 \geq 0.4$); c) 1/8 part of cube circumscribed about spherical inclusion.

and we also require that the condition

$$\left.\frac{\partial\lambda}{\partial m_1}\right|_{m_1=0,5} = \left.\frac{\partial\lambda_{2d}}{\partial m_1}\right|_{m_1=0,5}$$

be fulfilled. From this, for $\lambda_2/\lambda_1 \leq 10^{-2}$ we obtain

$$f(m_1) = 0.43 + 10.3m_1 - 14.38m_1^2 . \tag{20}$$

Thus, as a second approximation the expression for effective conductivity λ for $0.06 \leq m_1 \leq 0.53$ and $\lambda_2/\lambda_1 \leq 10^{-2}$ may be written in the form

$$\lambda = (0.43 + 10.3m_1 - 14.38m_1^2)\left[\lambda_1 m_1^3 + \lambda_2 m_2^3 + 9\lambda_1\lambda_2 m_1 m_2\left(\frac{m_1}{\lambda_1 + 2\lambda_2} + \frac{m_2}{2\lambda_1 + \lambda_2}\right)\right]. \tag{21}$$

In Fig. 2 experimental data are compared with calculations by Eqs. (16), (21) and also with calculation by the formulas of other authors in the concentration range $m_1 = 0.5$-0, where maximum divergence occurs. The comparison of calculation by Eqs. (16), (21) with experimental data for a system with $\lambda_2/\lambda_1 = 0$ (see Fig. 2a) shows satisfactory coincidence over the concentration range $m_1 = 1$-0.15. Figure 2b presents a comparison of calculation with experimental data on the electrical conductivity of an Li—NH_3 system with $\lambda_2/\lambda_1 = 1.2 \cdot 10^{-3}$ at T = 223°K. In the Li—NH_3 system there is no discontinuity in the function $\lambda = f(\lambda_1, \lambda_2, m_2)$ and the calculation agrees satisfactorily with experiment over the entire concentration range. The mean divergence of calculated and experimental values comprises about 15%, which is comparable to the measurement error involved and to the errors of the approximate methods used for calculating effective properties. This permits recommendation of the disordered structure model and the approximate method of determining its effective conductivity for the entire range of concentrations of components whose properties differ by up to four orders of magnitude, $1 > \lambda_2/\lambda_1 > 1 \cdot 10^{-4}$. With a greater difference in properties of the components $\lambda_2/\lambda_1 < 1 \cdot 10^{-4}$ the region of applicability of the model and calculation method should be limited to the range $0 \leq m_2 \leq 0.85$. The coincidence of experimental and calculated data shows that for the model of a heterogeneous system with disordered distribution of discrete components in calculations or experimental measurements one may choose a layer with the height given by Eq. (7), which depends on the volume concentration of the particles with the higher conductivity.

It should be noted that refinement of the λ value obtained in the two-layer model of Eq. (21) is justified only if $m_1 < 0.5$ and $\lambda_2/\lambda_1 \leq 10^{-2}$.

Generalization to the Case of a Multicomponent Disordered System Consisting of s Components. Using the above approach, we can obtain an expression for calculation of the coefficients of generalized conductivity of a mechanical mixture with any number of noninteracting components in the form (first approximation)

$$\lambda = \lambda_1 m_1^2 + \ldots + \lambda_s m_s^2 + 4m_1 m_2 \frac{\lambda_1\lambda_2}{\lambda_1 + \lambda_2} + \ldots + 4m_s m_{s-1} \frac{\lambda_s\lambda_{s-1}}{\lambda_s + \lambda_{s-1}} \tag{22}$$

or in more compact form

$$\lambda = 2 \sum_{i=1}^{s} \sum_{\substack{j=1 \\ j \neq i}}^{s} \frac{\lambda_i\lambda_j}{\lambda_i + \lambda_j} m_i m_j . \tag{23}$$

If $\lambda_1/\lambda_1 \leq 10^{-2}$ and $m_1 < 0.5$, then in the second approximation

$$\lambda = 3f(m_1)\sum_{i=1}^{s}\sum_{j=1}^{s}\frac{\lambda_i\lambda_j}{2\lambda_j+\lambda_i}m_i^2 m_j. \quad (24)$$

Generalization to the Case of Heterogeneous Systems in Which Contact Phenomena Have a Significant Effect on the Transfer Process. The possibility of using the proposed model of a system with disordered structure and Eqs. (16) and (21) can be expanded to consideration of contact and surface phenomena. We will demonstrate this with the example of compounds with a grainy filler.

Given a low concentration of metallic grains in a binding component (resin) of thermal conductivity λ_2, the grains with thermal conductivity λ_1 are disorderedly distributed in the form of noncontacting inclusions (Fig. 3a). With growth in concentration of filler $m_1 > 0.2$ the individual grains approach each other and form unordered groups or chains (Fig. 3b). It is obvious that the conductivity along the chains of contacting particles will depend on the contact thermal conductivity between filler particles. If the filler grains are close to spherical, then one can circumscribe about them geometric solids forming a solid mass (cubes, prisms) and then assume that these bodies are filled by a homogeneous material with thermal conductivity $\lambda' = f(\lambda_1, \lambda_2, m_2)$, which considers contact conductivity of the grains. Then the heterogeneous system may be represented as a mixture of geometric figures (cubes, prisms) of two types: with conductivities λ_1' and λ_2 (Fig. 3c). The effective conductivity coefficient is defined, according to Eq. (16), in the form

$$\lambda = \lambda' m_{1g}^2 + \lambda_2 m_{2g}^2 + 4\frac{\lambda_1'\lambda_2}{\lambda_1+\lambda_2}m_{1g}m_{2g}, \quad (25)$$

where m_{1g} is the volume concentration of bodies circumscribed about the grains ($m_{1g} = 1 - m_{2g}$).

In the case of the cubes described above

$$m_{1g} = m_1/(1-0.4703) \simeq 1.89m_1. \quad (26)$$

For hexagonal prisms

$$m_{1g} = m_1/(1-0.3995) \simeq 1.67m_1. \quad (27)$$

The value of the thermal conductivity $\lambda' = f(\lambda_1, \lambda_2, m_2)$ can be calculated from known relationships for contacting bodies [1-3]. In an analogous manner we write the expression for λ at $m_1 < 0.53$ with consideration of Eq. (21) for $\lambda_2/\lambda_1' \leq 10^{-2}$.

The proposed structural model and method of calculating generalized conductivity coefficients may be used for prediction of the properties of heterogeneous systems with liquid and gaseous, as well as solid, components.

NOTATION

m_i, volume concentration of components; $\langle l \rangle$, mean distance between particle centers; h, height of representative layer; N, number of particles in volume V; N_V, number of particles per unit volume; N_L, number of particles per unit length; k_f, form coefficient; v_0, volume of single particle; d, diameter of single particle; λ, effective conductivity coefficient; λ_i, conductivity coefficient of the i-th component.

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AN EXPERIMENTAL STUDY OF DIELECTRIC PROPERTIES OF NEMATIC LIQUID CRYSTALS

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Dielectric properties of three successive members of the azomethine homologous series are considered in the liquid crystal and isotropic phases. Experimental values are presented for the relaxation time and the dipole relaxation activation entropy and enthalpy.

The majority of published data on dielectric properties of compounds which possess a liquid crystal phase concerns materials with low dielectric anisotropy and transition temperatures for the liquid crystal—isotropic liquid transition far removed from room temperature.

Practical requirements have recently stimulated the synthesis of series of new liquid crystal compounds with a mesophase region near room temperature. A typical representative of this group is p-methoxybenzylidene-p-butylaniline, a member of the azomethine group, the dielectric properties of which have been studied in the radiofrequency and uhf ranges [1-3].

To systematize data on the dielectric characteristics of azomethines we have studied the dielectric properties and calculated certain characteristics of the molecular motion of three members of the homologous azomethine series in the liquid crystal and isotropic liquid phases.

We have studied p-methoxybenzylidene-p-butylaniline (MBBA), p-ethoxybenzylidene-p-butylaniline (EBBA), and p-propoxybenzylidene-p-butylaniline (PBBA) in the radiofrequency and uhf ranges.

The mesophase transition temperatures of these compounds are presented in Table 1.

All the materials studied were produced by methods described in the literature at the All-Union Scientific-Research Institute of Reagents and Special Purity Materials (IREA). The electrical conductivity of the compounds produced was not more than 10^{-9} $\Omega^{-1}\cdot cm^{-1}$ in the isotropic phase. The impurity content did not exceed 3 mol. %.

The dielectric characteristic measurements in the radiofrequency range were performed with a specially designed low-volume cell and "Tangens-2M" measurement apparatus. The gap between the cell electrodes did not exceed 3 mm. The cell capacitance was 3.2 pF. The error in ε' did not exceed 0.6% and was not greater than 6-7% in ε'' determination in the relaxation range.

Measurements of ε' and ε'' in the uhf range were performed by the cylindrical rod method. The error in ε' determination did not exceed 2%, and in ε'' determination it was not more than 8%.

Temperature was stabilized to an accuracy of ±0.05°.

Experiments were performed over the temperature range 290-355°K and in a magnetic field of intensity up to 4500 G. The experiments revealed that in the rf and uhf ranges in fields of about 2000 G almost complete saturation of ε' and ε'' occurred.

Within the limits of experimental error the results of the MBBA experiments agreed with data in the literature [1-2]. The experimental results were compared with the data from the

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