

EFFECTIVE DIFFUSION OF MULTICOMPONENT MIXTURES
IN MULTIDIMENSIONAL FLOWS

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The diffusion model of material dispersion is widely used to describe various heat mass transport processes occurring under natural conditions and in technological equipment. A huge range of applications and great simplifications as compared to the complete system of hydrodynamics and mass transport equations are the basic reasons for researchers' interest in dispersion problems. The advantages of dispersion theory lie in the ability to use averaged descriptions of processes, where certain variable characteristics are replaced by constant parameters, as well as in reduced dimensionality of the problem equations.

The diffusion model has long been used in practice, but only since the fundamental studies of Taylor [1, 2] has the technique been justified as (in some sense) a limiting approach, and empiricism avoided. Taylor's studies [1, 2] were a powerful stimulus toward the study of various aspects of dispersion theory, and we may note several original approaches to the problem [3-8], as well as the overview of [9], which extended the theory to more complex cases.

In all those studies, as in many others, only a single convective diffusion equation was considered, while in practice problems are not at all rare in which a mixture consists of several components and (or) one must consider cross-effects such as thermodiffusion, etc. in flow of the mixture in channels and similar regions. A generalization of dispersion theory to the case of flow of a multicomponent system in a circular tube was presented in [10], which also considered the presence of a first order reaction on the channel wall. In the present study we will complicate the analysis by considering dependence of the diffusion coefficients on component concentration and temperature, as well as taking into account the possibility of multidimensional fluid flow in the channel. Thus, in the general case we will commence from a nonlinear formulation of the problem.

As an example of the application of multicomponent mixture dispersion theory we may consider the problem of liquid capillary chromatography. The effect of thermodiffusion on the material dispersion process was studied in [11, 12], although in those studies the temperature profile was determined beforehand independent of the concentration of the target component, i.e., the effect of changes in material concentration gradients upon heat transport was not considered fully, as is demanded by the equations of thermodynamics of irreversible processes, and in particular, the Onsager reciprocity principle [13, 14]. Thus, [11, 12] essentially dealt with a single equation for material concentration, i.e., a certain modification of the conventional single-component dispersion theory [1, 2].

Of definite practical interest is the case of dispersion of material with abrupt decrease in the effective diffusion coefficient in individual regions of the flow, where contact between circulation zones occurs. It has been shown that in such a situation it is desirable to resort to a cellular description of the process, asymptotically justified over a certain time interval.

1. Derivation of the Effective Diffusion Equation. We will consider the motion of a multicomponent mixture in a circular tube with imposition upon the main flow having a mean velocity u of a circulation flow, characterized by velocity components w , v along the z and r axes of a cylindrical coordinate system. We will assume the material distribution is axisymmetric: $\partial C / \partial \varphi = 0$, where C is the material concentration vector-column, and φ is the cyclical coordinate. This leads to the absence in the fundamental system of heat-mass transport equations

$$r \left\{ \frac{\partial C}{\partial t} + u \frac{\partial C}{\partial z} + w \frac{\partial C}{\partial z} + v \frac{\partial C}{\partial r} - \frac{\partial}{\partial z} \left[L(C) \frac{\partial C}{\partial z} \right] \right\} = \frac{\partial}{\partial r} \left[L(C) \frac{\partial C}{\partial r} \right] \quad (1.1)$$

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of a convective term in the direction of the φ axis. Here $L(C)$ is a symmetric, positively defined square kinetic coefficient matrix, as required by the Onsager reciprocity principle and increase in entropy [13, 14]. In the general case L depends on the components c_i of the matrix C . If needed the temperature can be considered one of the components of matrix C . We consider the material in the mixture to be dynamically passive, i.e., having an effect on the hydrodynamic flow parameters, as is characteristic of homogeneous mixtures [15]. We take the components of the circulation velocity to be known functions of the coordinates z and r (there is no φ -dependence, $\partial/\partial\varphi = 0$ for any variable), i.e., we consider the hydrodynamics problems of liquid flow realization in the tube as solved. Such flows develop, for example, in the presence of stirrers or other obstacles in equipment, or in the presence of jets, pockets, etc., in a channel, and are of definite interest in the theoretical, experimental, and practical sense [16-18]. We will also note that we have chosen the channel in the form of a tube of circular cross section to reduce the size of some expressions and simplify calculations. The principles used to obtain the dispersion equations by the method of [19, 20] do not depend on channel form, and similar results are obtained.

Matrix equation (1.1) is supplemented by initial

$$C|_{t=0} = C_*(z, r), \quad z \in (-\infty, +\infty) \quad (1.2)$$

and boundary conditions

$$L(C)\partial C/\partial r|_{r=a} = 0 \quad (1.3)$$

(a is the channel radius). Matrix equation (1.1) is reduced to a dispersion equation in a manner quite similar to the analysis of [19, 20], and in fact, the difference of the multi-component case from the single-component one reduces to accurate "reduction" of the square matrix L and the need to replace division by multiplication by a matrix inverse to L , the matrix L^{-1} from one or the other side of the matrix identity. For example, from Eq. (1.3), expressing the absence of material flow on the channel boundary, it follows in light of symmetry properties and the positive definition of the matrix L that we must have $\partial C/\partial r|_{r=a} = 0$. We consider the liquid flowing in the channel incompressible and the channel boundary $r = a$ impermeable to the liquid. The arguments presented above show that the complications of the analysis in dispersion of a multicomponent mixture in a channel are easily overcome, and the calculations similar to those used in the one-component case [19, 20] can best be omitted.

Limiting ourselves to the first approximation, we arrive at the equation

$$\frac{\partial G}{\partial t} + u \frac{\partial G}{\partial z} = \frac{\partial}{\partial z} \left\{ [L(G) + L^{-1}(G) E(z)] \frac{\partial G}{\partial z} \right\}. \quad (1.4)$$

Here G is the mean concentration over the section (matrix):

$$G = \frac{2}{a^2} \int_0^a r C(z, r, t) dr, \quad (1.5)$$

and $E(z)$ is the "convective portion" of the dispersion coefficient:

$$E(z) = \frac{2}{a^2} \int_0^a \frac{dr}{r} \left[\int_r^a \xi w(z, \xi) d\xi \right]^2. \quad (1.6)$$

Equation (1.4) is applicable at sufficiently large times, more precisely, at $t \geq t_1$, where

$$t_1^{-1} = \frac{2}{L_* a^2} \int_0^a r v^2(0, r) dr,$$

L_* is the characteristic value of the elements of matrix L . The expressions obtained, Eqs. (1.4)-(1.6), refer to established motion in the channel. In the case where the circulation motion is unsteady, the function w , and thus, according to Eq. (1.6), $E(z)$ as well, depend on time.

Exactly as in [19, 20] one can obtain an initial condition for Eq. (1.4) by making use of Eq. (1.2) and merging the two expansions by the perturbation method [21, 22]:

$$G|_{t=0} = G_*(z) = \frac{2}{a^2} \int_0^a r C_*(z, r) dr.$$

In typical situations the convective portion of the dispersion coefficient significantly exceeds the molecular [3, 19] and, moreover, changes in $E(z)$ are insignificant, so that the simplified equation

$$\frac{\partial G}{\partial t} + u \frac{\partial G}{\partial z} = E_* \frac{\partial}{\partial z} \left[L^{-1}(G) \frac{\partial G}{\partial z} \right] \quad (1.7)$$

($E_* = \text{const}$) is of independent interest. But cases exist in which the circulation flow velocity w drops sharply in individual sections of the tube. This occurs, for example, at the borders between zones with different vorticities for flow over pockets by the Lavrent'ev pattern [19, 23]. Since such effects have been studied but little in descriptions of heat-mass transport problems by effective diffusion equations, we will concentrate our attention on analysis of such situations below.

When the function w vanishes on the liquid zone boundary w is of first order smallness ($\partial w / \partial z \neq 0$ on the boundary), which leads to a second order null in the function E , as follows from Eq. (1.6). All the above leads to the necessity of considering a boundary layer equation of the form (see [19, 20] for details)

$$\frac{\partial G}{\partial t} + u \frac{\partial G}{\partial z} = \frac{\partial}{\partial z} \left\{ \left[L(G) + kz^2 L^{-1}(G) \right] \frac{\partial G}{\partial z} \right\} \quad (1.8)$$

($k = E''(0)/2$). Such a simplification, like that previously presented, Eq. (1.7), is based on fulfillment of the corresponding inequalities of [19, 20] for all components of the matrix L . Otherwise, it would be necessary to make special stipulations and refinements for certain components of the vector equations (1.7), (1.8).

The major unique features of the dispersion equations obtained in this section, as compared to the traditional ones, are the nonlinearity of the equations and (even for $L = \text{const}$, when the equations are linear) the presence of a dependence of the dispersion coefficients on the longitudinal coordinate. And we are most interested in cases where this coefficient not only changes, but does so significantly, leading to Eq. (1.8). The simplest case for analysis, yet sufficiently widespread, is the case of a constant matrix L . Therefore, it is desirable to demonstrate the solution of the equations obtained with an example.

2. Analysis of the Linear Problem ($L = \text{const}(G)$). When the components of the matrix L are independent of the vector G the system of equations (1.4), (1.7), (1.8) can be "split" by performing a linear transform on the solution vector G : $G = RT$, where T is the new solution vector, and R is a square nondegenerate matrix, diagonalizing the kinetic coefficient matrix:

$$D = R^{-1}LR, \quad D_{ij} = \kappa_i \delta_{ij}, \quad i, j = 1, 2, \dots, N \quad (2.1)$$

(δ_{ij} is the Kronecker symbol). The existence of a matrix R with such properties follows from the general theories of linear algebra [24] under conditions which the matrix L satisfies (symmetry and positive definition). It also follows from this that $\kappa_i > 0$ for all i . The action of transform (2.1) on all the equations (1.4), (1.7), (1.8) is similar, so that we will now work only with Eq. (1.8), having in mind the problem formulated above.

With consideration of Eq. (2.1) we rewrite Eq. (1.8) in the form

$$\frac{\partial T_i}{\partial t} + u \frac{\partial T_i}{\partial z} = \frac{\partial}{\partial z} \left[(\kappa_i + kz^2 \kappa_i^{-1}) \frac{\partial T_i}{\partial z} \right], \quad i = 1, 2, \dots, N. \quad (2.2)$$

In this equation, as in Eq. (1.8), $z = 0$ is chosen as the coordinate of the boundary between two adjacent circulation zones.

In view of the identical structure of Eq. (2.2) for all i we may limit our study to one equation, omitting the index i where reasonable. It will also be useful to reduce Eq. (2.2) to "canonical" form by choosing the dimensionless variables

$$\zeta = zk^{1/2}/\kappa, \quad \tau = tk/\kappa, \quad n = u/2k^{1/2}. \quad (2.3)$$

We then have

$$\frac{\partial T}{\partial \tau} + 2n \frac{\partial T}{\partial \zeta} = \frac{\partial}{\partial \zeta} \left[(1 + \zeta^2) \frac{\partial T}{\partial \zeta} \right]. \quad (2.4)$$

As follows from Eq. (1.6) the criterion n is formed from the hydrodynamic characteristics of the process - the ratio of the mean transport velocity u to the mean square velocity of the circulation motion on the zone boundary, which follows from the expression $k = \frac{2}{a^2} \int_0^a rv^2(0, r)dr$, obtained from Eq. (1.6) for the function $E(z)$ after certain transformations with use of the liquid incompressibility equation. For identical parameter values to the left and right of the zone boundary, Eq. (2.4) can be considered in the region $\zeta \in (-\infty, +\infty)$. This case is usually realized, since the component of the velocity vector v is continuous on this boundary, so that the value of k is one and the same in the two adjacent zones given the condition that the tube radius is not discontinuous at the point of zone contact. Although in this case the description of heat-mass transport in the boundary region may become complicated, in individual examples it is also justifiable [20] to assume that k is one and the same for the two contacting pockets. This fact leads to equality of the basic similarity criterion n for the two zones, and if the diffusion characteristics of both zones are identical (κ is one and the same), all the variables in Eq. (2.3) can be dedimensionalized identically and can be considered continuous upon transition through the boundary $z = 0$ between the pockets.

Of special interest is the problem of heat-mass transport between the zones with the initial condition, which without loss of generality can be written in terms of the matrix T : $T|_{\tau=0} = f(\zeta)$. If we carry out the transform $T = X \exp[n \tan^{-1}(\zeta)]$, then for the function X we obtain in place of Eq. (2.4) the self-conjugate equation

$$\frac{\partial X}{\partial \tau} + \frac{n^2}{1 + \zeta^2} X = \frac{\partial}{\partial \zeta} \left[(1 + \zeta^2) \frac{\partial X}{\partial \zeta} \right] \quad (2.5)$$

with the obvious transformation of the initial condition: $X|_{\tau=0} = f(\zeta) \exp[-n \tan^{-1}(\zeta)]$. The problem of constructing the solution of Eq. (2.5) for the given initial condition coincides in its structure with the method of searching for expansions of arbitrary functions in integrals (series) in a system of eigenfunctions of the corresponding Sturm-Liouville problem, which is based on operational calculation and has been presented in detail in [25, 26]. Considering this, we will omit calculations making use of the properties of the Legendre functions, etc. [27], and present only the final results for the function T and the integral transforms involved in finding T , which may be useful in consideration of other problems:

$$T = 2 \exp \left(n \operatorname{arctg} \zeta - \frac{\tau}{4} \right) \int_0^{\infty} \frac{r \operatorname{sh}(\pi r) \exp(-\tau^2 r)}{\operatorname{ch}^2(\pi r) + \operatorname{sh}^2(\pi n)} dr \times \quad (2.6)$$

$$\times \sum_{j=1}^2 \left| \Gamma \left(\rho_j + \frac{ir}{2} - \frac{in}{2} \right) \Gamma \left(\rho_j + \frac{ir}{2} + \frac{in}{2} \right) \right|^2 \Phi_j^n(\zeta, r) \int_0^{\infty} \Phi_j^n(\xi, r) B_j(\xi) d\xi,$$

where

$$B_j(\zeta) = \frac{1}{2} \{ f(\zeta) \exp(-n \operatorname{arctg} \zeta) + (-1)^j f(-\zeta) \exp(n \operatorname{arctg} \zeta) \};$$

$$\Phi_j^n(x, r) = \frac{\exp \left(-\frac{\pi n}{2} \right) P_{ir-1/2}^{n_i}(xi) + (-1)^j P_{ir-1/2}^{n_i}(-xi) \exp \left(\frac{\pi n}{2} \right)}{v_j 2^{n_i+1} \Gamma(\rho_j + ir/2 + in/2) \Gamma(\rho_j + in/2 - ir/2)}; \quad j = 1, 2;$$

$v_1 = i$ is the imaginary unit; $v_2 = 1$; $\rho_1 = 1/4$; $\rho_2 = 3/4$; $P_\nu^m(z)$ is a Legendre function [27]; $\Gamma(z)$ is a gamma function. We will note that the functions $\Phi_j^n(x, r)$ are real along the integration line. The expressions for the unknown integral transforms take on the form

$$g(x) = 2 \int_0^{\infty} \frac{r \operatorname{sh}(\pi r) dr}{\operatorname{ch}^2(\pi r) + \operatorname{sh}^2(\pi n)} \left| \Gamma\left(\frac{1}{4} + \frac{ir}{2} - \frac{in}{2}\right) \Gamma\left(\frac{1}{4} + \frac{ir}{2} + \frac{in}{2}\right) \right|^2 \Phi_1^n(x, r) \int_0^{\infty} g(\xi) \Phi_1^n(x, r) d\xi; \quad (2.7)$$

$$g(x) = 2 \int_0^{\infty} \frac{r \operatorname{sh}(\pi r) dr}{\operatorname{ch}^2(\pi r) + \operatorname{sh}^2(\pi n)} \left| \Gamma\left(\frac{1}{4} + \frac{ir}{2} - \frac{in}{2}\right) \Gamma\left(\frac{3}{4} + \frac{ir}{2} + \frac{in}{2}\right) \right|^2 \Phi_2^n(x, r) \int_0^{\infty} g(\xi) \Phi_2^n(\xi, r) d\xi. \quad (2.8)$$

In the special case $n = 0$ the integral transforms of Eqs. (2.7), (2.8) transform into those studied in [28], i.e., generalize the latter. A proof of the corresponding theorems for the expansions of Eqs. (2.7), (2.8) was presented in [29].

Equation (2.6), the solution for the individual components of the matrix T , permits simple construction of the general solution of the problem of heat-mass transport between circulating pockets after application of the transform R . We will note that the parameters κ_i of Eq. (2.1) characterize the rate of approach of the solution to a steady-state value for the corresponding components of the matrix T , or if we may express it so, the "modes" of the matrix G , which follows from both Eq. (2.3) and Eq. (2.6). If in this case the individual κ_i ($i = 1, 2, \dots, N$) differ significantly from each other, we can simplify the solution over certain time intervals by replacing the individual "modes" of Eq. (2.6) by steady-state solutions of the corresponding (for a given number) Eq. (2.4).

3. Construction of a Cellular Heat-Mass Transport Scheme between Circulation Zones.

The solution of Eq. (2.6) constructed in Sec. 2 for the boundary layer equation (2.4) describes the process of heat and mass exchange between adjacent circulation zones near the boundary for time values of the order of t_1 . At longer times the pockets become "depleted" [19, 20] and the treatment of the problem must be refined. Of independent interest is study of the dynamics over time of the mean over the pocket of the material concentration vector. Let ℓ be the length of the circulation zone. Having integrated Eq. (1.4) over z with the limits $(0, \ell)$, we find

$$\ell \frac{d\langle G \rangle}{dt} + \left(uG - L \frac{\partial G}{\partial z} \right) \Big|_{z=\ell} = \left(uG - L \frac{\partial G}{\partial z} \right) \Big|_{z=0}, \quad (3.1)$$

where the mean concentration vector is determined by the expression

$$\langle G \rangle = \frac{1}{\ell} \int_0^{\ell} G dz = \frac{1}{V} \int_V C dV$$

($V = \pi a^2 \ell$ is the cell volume). In deriving Eq. (3.1) use was made of the equality to zero of the function $E(z)$ on the boundary between the zones. For simplicity in the future we will assume all pockets to be the same.

At this point we will consider only the linear problem for a constant matrix L . Use of the linear transform of Sec. 2 ($G = RT$) leads to an equation for the function $\langle T \rangle$, stemming from Eq. (3.1):

$$\ell \frac{d\langle T \rangle}{dt} + \left(uT - D \frac{\partial T}{\partial z} \right) \Big|_{z=\ell} = \left(uT - D \frac{\partial T}{\partial z} \right) \Big|_{z=0} \quad (3.2)$$

[D is the diagonal matrix (2.1)]. It has been shown previously [19, 20] that flows $uT - D\partial T/\partial z$ at sufficiently lengthy times $t \gg t_1$ can be expressed in terms of mean values $\langle T \rangle$ of the cell under consideration and adjacent ones. More precisely, in [19, 20] $u = 0$, although all the methodology of constructing cellular models in [19, 20] remains unchanged for $u \neq 0$, so that we will make use of it without further explanations. It is of importance that at $t \gg t_1$ one can use the steady equations (2.2), which simplifies calculations significantly. Assigning the chosen cell the index j , and the adjacent ones the indices $j - 1$ and $j + 1$ (see Fig. 1), using the algorithm of [19, 20], after some calculations we obtain an expression for the material flux

$$uT - D\partial T/\partial z|_{z=0} = u[(1 + \alpha)\langle T^{j-1} \rangle - \alpha\langle T^j \rangle] \quad (3.3)$$

and a similar one for the boundary $z = \ell$. Here

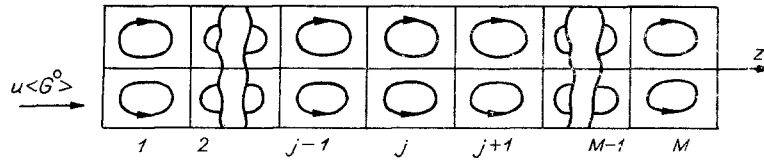


Fig. 1

$$\alpha = [\exp(2\pi n) - 1]^{-1}. \quad (3.4)$$

Substituting Eq. (3.3) in Eq. (3.2), we find

$$\frac{l}{u} \frac{d \langle T^j \rangle}{dt} = (1 + \alpha) \langle T^{j-1} \rangle - (1 + 2\alpha) \langle T^j \rangle + \alpha \langle T^{j+1} \rangle. \quad (3.5)$$

The value of l is one and the same for all cells n , and hence, according to Eq. (3.4), the quantity α is also independent of cell number (see Sec. 1) and component. Therefore, it will be useful to apply to Eq. (3.5) a reverse transform R and transform to the vector $\langle G \rangle$:

$$\frac{l}{u} \frac{d \langle G^j \rangle}{dt} = (1 + \alpha) \langle G^{j-1} \rangle - (1 + 2\alpha) \langle G^j \rangle + \alpha \langle G^{j+1} \rangle. \quad (3.6)$$

The interesting fact that Eqs. (3.6) for the individual components of the vector $\langle G \rangle$ prove to be independent of each other is explained by the fact that Eq. (3.6) is suitable for times large in comparison to t_1 ($t \geq t_2 = l/u$, $t_2 \gg t_1$). A quasisteady description of the process by diffusion equations is characteristic of a given time interval. The components of the matrix L then affect only the rate of approach to equilibrium of the individual "modes" of the matrix G , but not the slower changes of mean concentrations described in Eqs. (3.5) and (3.6).

Equations (3.5), (3.6) deal with the internal circulation zone, where all pockets form a chain of cells following one another (Fig. 1). The end pockets in the heat-mass exchange configuration are under specific conditions, and require certain additional information on the process at the entrance and exit of the zone system. For the first zone we can take the flux from without (at the input) equal to $u \langle G^0 \rangle$ ($\langle G^0 \rangle$ is a specified known function of time), while for the last (M -th) we assume that material flows into a nonexistent cell with number $M + 1$ with the previous concentration, which is a discrete analog of the well-known [30, 31] Dankwerst condition, widely used in heat-mass transport problems. These considerations permit use of Eq. (3.6) to describe heat-mass transport in the end cells:

$$\frac{l}{u} \frac{d \langle G^1 \rangle}{dt} = \langle G^0 \rangle - (1 + \alpha) \langle G^1 \rangle + \alpha \langle G^2 \rangle, \quad \frac{l}{u} \frac{d \langle G^M \rangle}{dt} = (1 + \alpha) (\langle G^{M-1} \rangle - \langle G^M \rangle). \quad (3.7)$$

In the scalar case the system of equations obtained for the cellular model, Eqs. (3.6), (3.7), finds wide use in chemical technology for analysis of heat-mass transport processes [30, 31], in which it is usually formulated on the basis of certain hypotheses as to the structure of heat-mass transport between cells. We have in fact derived these equations from more general principles, more precisely, from the system of equations of convective diffusion, Eq. (1.1). It has also been shown that over a certain time range such a system can be transformed to a vector one and used to independently describe each component of the concentration vector.

The desirability of transforming to a cellular model in our example is a result of the specific behavior of the dispersion coefficient in the general diffusion model of Eq. (1.4), which decreases abruptly near the boundary between zones, making description of heat-mass transport by a single equation of the form of Eq. (1.4) inconvenient.

4. Note. It should be noted that in practical situations the form of the cell configuration and its circulatory motion may be more complex than that shown in Fig. 1. Nevertheless, the technique for deriving cellular model equations presented above is usable with certain modifications for analysis of heat-mass transport in other similar situations.

We will also call attention to the fact that the sequence of equations (1.1), (1.4), and (3.6) forms a unique hierarchical structure, reflecting a gradual coarsening of detailing the description of processes and corresponding simplification of that description. This is related to the spatial and time scales of the phenomena and should be considered depending on the concrete goals of the problem under consideration.

The effective matrix diffusion equations (1.4) obtained above, as well as the simplified variants, Eqs. (1.7), (1.8), satisfy the requirements of nonequilibrium thermodynamics imposed upon the dispersion coefficients. These coefficients form a symmetric, positively-defined matrix, which is easily derived from their functional expressions in terms of the matrix L , which has these properties, and from the condition $E(z) \geq 0$, following from Eq. (1.6).

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EFFECT OF EXCITATION OF INTERNAL DEGREES OF FREEDOM
IN CLUSTERS ON CONDENSATION KINETICS

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At present a number of experimental results have been presented on condensation of vapors of various substances, which cannot be explained by classical theory (see the review [1]). One of the factors not considered in such a theory is the effect of disruption of equilibrium cluster distribution over internal degrees of freedom due to the condensation affecting the kinetics of the process. A method for considering this effect has been proposed in a multimolecular model of condensation kinetics. The presence of internal degrees of freedom in a monomer can lead to an entire series of new condensation regimes. The present study will briefly evaluate such regimes.

The first question which arises upon consideration of internal degrees of freedom in a monomer is related to the method used for defining various types of cluster internal energy. It is clear that even small complexes (trimers, tetramers, etc.) may have a quite large number of oscillatory modes, which can conveniently be divided into two groups. In the first group we have oscillations of molecules entering into the composition of clusters - intermolecular oscillations, while in the second we have oscillations of atoms forming the molecule (monomer) - intramolecular oscillations. Intermolecular oscillations usually are of low energy. Thus, for Van der Waals complexes their characteristic frequencies lie in the range 50-200 cm^{-1} . As for intramolecular oscillations, various situations are possible.

1. If these oscillations are of low frequency, they effectively exchange energy with the intermolecular oscillations, which makes it possible to introduce the total oscillatory energy of the cluster $E_j(k)$ (where j is the number of molecules in the cluster and k is the energy level number). The existence of various types of intermolecular oscillations is not then considered.

2. If the monomers have high frequency oscillation modes, then their interaction with intermolecular oscillations is ineffective. The internal energy of the cluster can then be specified by quantum numbers k and ℓ , characterizing the total internal energy of low frequency intermolecular oscillations $E_j(k)$ and high frequency intramolecular oscillations $\mathcal{E}_j(\ell)$, as well as a quantum number characterizing the distribution of the latter over cluster monomers [the quantum number related to degeneration of the level (k, ℓ)]. Consideration of interaction leads to removal of the degeneration with respect to this number and development of a multiplet of closely spaced levels, while radiationless intracluster transitions [4] rapidly lead to a microcanonical distribution for a given \mathcal{E}_j . Here we will lim-

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