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KINETICS OF THE AGGREGATION OF A DILUTE, FINELY DISPERSE SYSTEM AT LOW SHEAR VELOCITIES

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The formation of doublets of spherical particles in a shear stream due to Brownian motion is considered with allowance for their hydrodynamic interaction and the breakup of doublets with a low binding energy.

The rheological, thermo-, electro-, and magnetophysical properties of colloidal and other disperse systems depend very strongly on the processes of reversible and irreversible structure formation taking place in the system. Therefore, a theoretical investigation of such properties is impossible without a preliminary physical analysis both of the peculiarities of the occurrence of these processes under various conditions and of their influence on the observable properties of the system. The most important stage in the structure formation of a disperse system is the initial stage of its aggregation, i.e., the formation of doublets from single particles (singlets). Under certain conditions, doublets can subsequently grow through the capture of new singlets, up to the formation of small chains or round aggregates containing a large number of particles, which can take part as certain elementary units in the construction of more complicated branched structures. In dilute systems, as well as in systems with sufficiently weak interaction between particles, the formation just of doublets comprises the main observable form of structure formation.

Brownian coagulation (or flocculation) is usually investigated on the basis of Smolukhovskii's classical concepts. In doing this, the following factors are ignored or not correctly taken into account in the majority of reports: 1) the hydrodynamic interaction between converging particles and the resulting decrease in the effective coefficient of relative Brownian diffusion, 2) the finiteness of the interparticle binding energy and the possibility of the breakup of doublets, and 3) the influence of the "macroscopic" (mean) motion of the system. Attempts to allow for the first factor were made in [1, 2], for the second in [3, 4], and for the third in [5]. All three factors are considered below on the example of a dilute, finely disperse system of single spherical particles having a central interaction potential and suspended in an incompressible liquid entrained in shear flow.

The kinetics of the initial coagulation stage is determined by the velocity of convective interdiffusion of individual pairs of particles. Placing the origin of coordinates at the center of one of the particles, we write the Liouville equation controlling the evolution of the probability density $p(t, \mathbf{r})$ of finding the center of the second particle of a given pair near the point $\mathbf{r}$ at the time t,

$$\partial p/\partial t + \nabla\cdot(p\mathbf{V}) = 0, \tag{1}$$

where the effective relative velocity of the centers of the particles can be represented in the form

$$\mathbf{V} = (\mathbf{b}_{11} + \mathbf{b}_{22} - \mathbf{b}_{12} - \mathbf{b}_{21})\cdot\mathbf{F}. \tag{2}$$

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The total particle-interaction force **F** equals the sum of the forces due to, respectively, the harmonic interaction of particles with each other and with the external stream, the potential particle interaction, characterized by the potential u(**r**), and the "thermodynamic" force, which results in the same particle displacement as the real mean diffusional displacement. The latter force was first introduced by Einstein, and the corresponding formal apparatus was successfully applied recently by Batchelor [6] to the problem of the Brownian diffusion of hydrodynamically interacting particles. Thus,

$$\mathbf{F} = \mathbf{F}_h + \mathbf{F}_u + \mathbf{F}_t, \ \mathbf{F}_u = -\frac{du}{d\mathbf{r}}, \ \mathbf{F}_t = -kT\frac{\partial \ln p}{\partial \mathbf{r}}. \tag{3}$$

Introducing the tensor

$$\mathbf{D} = kT(\mathbf{b}_{11} + \mathbf{b}_{22} - \mathbf{b}_{12} - \mathbf{b}_{21}) \tag{4}$$

of effective coefficients of diffusion and the velocity **U** of relative motion of particle centers due only to their hydrodynamic interaction and the motion of the system as a whole, from (1)-(4) we obtain the equation*

$$\partial p/\partial t + \nabla\cdot(p\mathbf{U}) = \nabla\cdot[\mathbf{D}\cdot(\nabla p + p\nabla\varphi)], \ \varphi = u/kT. \tag{5}$$

In the case of single spherical particles in a shear stream under consideration, we have

$$\mathbf{D} = D_0\left[\frac{\mathbf{rr}}{r^2}G\left(\frac{r}{a}\right) + \left(\mathbf{I} - \frac{\mathbf{rr}}{r^2}\right)H\left(\frac{r}{a}\right)\right], \ D_0 = \frac{kT}{3\pi\mu a}, \tag{6}$$

$$\mathbf{U} = \mathbf{r}\cdot\mathbf{\Gamma} + 2\mathbf{E}:\mathbf{C}, \ \mathbf{\Gamma} = \mathbf{E} + \mathbf{\Omega} = \text{const}.$$

There are detailed representations for the third-rank tensor **C** and the scalar functions G and H in [6, 7]. Only the form of the function G and the fact that as $r \to \infty$ the components of **C** tend toward zero as r^{-2} are important for the present work. The following asymptotic forms are valid for G ($\rho = r/a$):

$$G \approx 2(\rho - 2), \ \rho \to 2; \ G \approx 1 - \frac{3}{2\rho} + \frac{1}{\rho^3}, \ \rho \to \infty. \tag{7}$$

It is natural to convert to dimensionless variables in (5). Introducing

$$\tau = Et, \ \rho = \frac{r}{a}, \ \mathbf{d} = \frac{\mathbf{D}}{D_0}, \ \gamma = \mathbf{e} + \omega = \frac{\mathbf{\Gamma}}{E}, \ \text{Br} = \frac{Ea^2}{D_0} \tag{8}$$

and using the number density n of particles in the vicinity of the selected particle instead of p, we obtain

$$\text{Br}\,[\partial n/\partial\tau + (\boldsymbol{\rho}\cdot\gamma + 2\mathbf{e}:\mathbf{C})\cdot\nabla n + 2(\mathbf{e}:(\nabla\cdot\mathbf{C}))n] = \nabla\cdot[\mathbf{d}\cdot(\nabla n + n\nabla\varphi)]. \tag{9}$$

Here differentiation with respect to the components of **ρ** is understood in the ∇ operator. The Brenner number Br (as it is proposed to call it in [8]) has the meaning of the ordinary Peclet number, i.e., it characterizes the ratio between the convective and diffusional components of the total particle flux.

Let the dependence of the dimensionless potential φ, which we take as central, on ρ have the form of the curve in Fig. 1, i.e., let it be characterized by a single minimum $\varphi = -\varphi_m$ at $\rho = 2 + \varepsilon$. We assume that φ declines rather rapidly with an increase in ρ and satisfies all the conditions required for the existence of the integrals written below. For the rest, the function φ(ρ) is arbitrary, and, in particular, the absence of a potential barrier is permissible, so that this function asymptotically approaches the abscissa from below as $\rho \to \infty$, i.e., the potential well is infinitely wide.

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*Usually Eq. (5) is validated using the theory of random walks with a number of elementary steps which goes to infinity. Then (5) is adequate in the case when the temporal and linear scales of the field p(t, **r**) are longer than the time in which a particle undergoes a significant number of molecular impacts and the distance into which a significant number of elementary displacements fit. The alternative course (corresponding to the derivation given above) appeals to a representative Gibbs ensemble of particle pairs and does not require the indicated restriction on the scale. In reality, aggregation in general and doublet formation in particular are mass processes, and the observable results actually correspond to averaging over such an ensemble. These considerations allow us to justify the use of the diffusion equation (5) at distances on the order of the scale of the function u(**r**), which can be small.

Strictly speaking, to calculate the rate constants of the processes of doublet formation and breakup one must solve the nonsteady equation (9) under certain initial and boundary conditions, the formulation of which presents considerable difficulties, since one must determine the probabilities of particle absorption and emission by the potential well and give a fully clear definition of just what two-particle configurations should be considered as doublets (the latter is not trivial in the case when the potential barrier in the curve of Fig. 1 is entirely absent). These difficulties can be avoided if one employs the fact that the behavior of each pair of particles (regardless of whether they are combined into a doublet or not) does not depend on the state of ther pairs and that a representative Gibbs ensemble of such pairs exists. Then one can use the principle of detailed equilibrium and analyze the processes of doublet formation and breakup separately [4]. Here, if the characteristic time of the coagulation process far exceeds the time of relaxation of the concentration field $\Delta t \sim a^2/D_0 \sim \mu a^3/kT$, which usually happens, it is permissible to use quasi-steady-state solutions of Eq. (9).

We assign the boundary conditions for the doublet-formation problem as

$$n^+ \to n_1,\ \rho \to \infty;\ n^+ = 0,\ \rho = 2 + \varepsilon. \tag{10}$$

The first condition in (10) is obvious, while the second can be obtained on the basis of the following considerations. Since it is assumed, from the meaning of the problem under consideration, that particles which come together necessarily form a doublet, we must impose the absorption condition $n^+ = 0$ for a certain $\rho = \rho_*$ within the potential well, and the question comes down to the determination of a concrete value of ρ_* corresponding to such a particle "sink." By analyzing the limit $D_0 \to 0$ ($\mathrm{Br} \to \infty$), we find without difficulty that ρ_* must correspond to a position of stable particle equilibrium in the $\Phi(\rho)$ field in the absence of any random factors. Possible oscillations about this position due to thermal fluctuations have already been taken into account through the introduction of the thermodynamic force into (1) and the corresponding diffusional terms into (5) and (9) and must not, of course, be taken into account twice.

Arguing entirely analogously, for the doublet-breakup problem we obtain the boundary condition

$$n^- \to 0,\ \rho \to \infty;\ 4\pi a^3 \int_2^\infty \rho^2 n^- \delta(\rho - 2 - \varepsilon)\, d\rho = 1, \tag{11}$$

where $\delta(\rho)$ is a delta function. The second condition in (11) essentially consists of a source condition.†

Solving Eq. (9) with the boundary conditions (10) or (11) is difficult in the general case, even when the time dependence is neglected. Here we consider only low shear velocities ($\mathrm{Br} \ll 1$), when the motion of the system results in only small corrections for the concentration fields and the corresponding fluxes, which are established in a stationary disperse system. First of all, we find the fields $n_0^+(\rho)$ and $n_0^-(\rho)$ characterizing the situation for Br = 0, i.e., in a state of rest. With allowance for the spherical symmetry of the problems under consideration, after a simple calculation we obtain

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†It is asserted in [4] that for ρ_* one can take any value of ρ corresponding to the potential well in Fig. 1. Leaving aside the meaninglessness of this statement for potentials for which a potential barrier is altogether absent, we point out that in the region of small $\rho_* - 2$ the solutions of both these problems prove to be very sensitive to the choice of ρ_*, which cannot be made arbitrarily, of course. A variant of the internal condition for n^-, according to which equality of the integral of $n^-(\rho)$ over the region of the potential well to unity was required, was analyzed in the same report. The latter is meaningless in the case when the well has an infinite extent (a potential barrier is absent). Moreover, in an equilibrium situation the particle distribution density in the well ought to obey a Boltzmann distribution, while in an analysis of an essentially nonequilibrium diffusion process the randomness of the particle positions is taken into account through the diffusion equation itself, and the coordinate corresponding to the determinate position of stable equilibrium must figure as their "initial" coordinate. The analogy with random-walk problems is entirely obvious here, and it is clear that the position of the absorbing or emitting boundary must not depend on the intensity or other characteristics of the walks themselves.

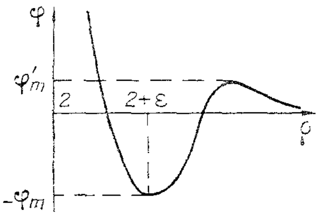

Fig. 1. Characteristic dependence of the dimensionless particle-interaction potential on the dimensionless distance between their centers.

$$n_0^+(\rho) = n_1 \frac{e^{-\varphi}}{K} \int\limits_{2+\varepsilon}^{\rho} \frac{e^{\varphi}}{G\rho^2}\, d\rho, \quad K = \int\limits_{2+\varepsilon}^{\infty} \frac{e^{\varphi}}{G\rho^2}\, d\rho,$$

$$n_0^-(\rho) = \frac{e^{-\varphi_m-\varphi}}{4\pi a^3 (2+\varepsilon)^2 K} \int\limits_{\rho}^{\infty} \frac{e^{\varphi}}{G\rho^2}\, d\rho. \tag{12}$$

The corresponding fluxes in dimensional form are written as

$$J_0^+ = \frac{4\pi D_0 a n_1}{K}, \quad J_0^- = \frac{e^{-\varphi_m} D_0}{(2+\varepsilon)^2 K a^2} \tag{13}$$

These fluxes are equal in magnitude to the number of doublets appearing or disappearing, as a result of spontaneous breakup, respectively, per unit time, normalized to the total number of singlets.

If the kinetic equation for the singlet concentration in the system is introduced in the standard way in the form

$$dn_1/dt = -\alpha n_1^2 + 2\beta n_2, \quad n_1 + 2n_2 = n_0, \tag{14}$$

then the rate constants of the doublet formation and breakup processes for Br = 0 are defined as follows on the basis of (13):

$$\alpha_0 = \frac{4\pi (2+\varepsilon) D_0 a}{W}, \quad \beta_0 = \frac{e^{-\varphi_m} D_0}{(2+\varepsilon) W a^2}, \quad W = (2+\varepsilon) K; \tag{15}$$

here the quantity W plays the role of the well-known "moderation factor" (for $\varphi = 0$ and $G = 1$ we have $W = 1$). Even in the case of $\varphi \approx 0$ this factor can differ significantly from unity if ε is small: $W \sim |\ln \varepsilon|$ for $\varepsilon \ll 1$. The dependence of W on ε is shown in Fig. 2a; the influence of W on $n_0^+(\rho)$ is illustrated by the curves in Fig. 2b. As follows from (14) and (15), however, the equilibrium state of a system containing only singlets and doublets does not depend on the value of W.

Equations (15) allow one to determine the average "lifetime" $t' = 1/\beta$ of a doublet, which depends essentially on the depth φ_m of the potential well, and the characteristic time $t'' = 1/\alpha n_1$ of formation of a new doublet. The relation between these times characterizes the level of development of the aggregation process in a dilute disperse system. The main physical conclusions about the influence of the quantity φ_m and other parameters on this process which follow from the above analysis are in agreement, on the whole, in a qualitative respect, with those obtained in [4].

We note that when the dependence of the size of the gap εa between particles corresponding to their stable equilibrium configuration on a is weak, the quantity ε will grow while W will decrease with a decrease in particle size. The latter fact promotes an increase in the stability of the system when its degree of dispersion is stronger. According to the well-known theory of the aggregative stability of colloids, in which purely hydrodynamic "moderation" is ignored, a decrease in particle size promotes a drop in stability (due to the increase in D_0, for example). From this it is clear that certain colloidal systems should reach maximum stability at a certain finite particle size, which is confirmed experimentally [9, 10].

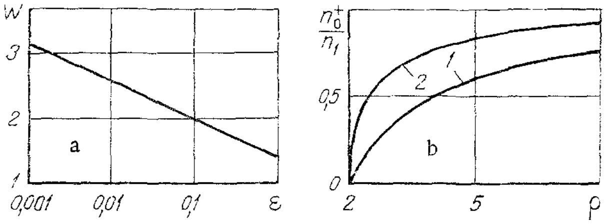

Fig. 2. Dependence of the moderation factor W on ε in a macroscopically stationary system (a) and its influence on the distribution $n_0^+(\rho)$ (b) for $\varphi \approx 0$; 1, 2) $\varepsilon \to \infty$ ($W \to 1$), 0.01.

For nonzero but small Br it would seem natural to apply the perturbation method to the solution of both problems, as in the solution of one problem for the steady-state equation (9) in [7], i.e., seek corrections $\Delta n^{+,-}(\rho) \sim \mathrm{Br}$ to the quantities in (12). It turns out, however, that problems for $\Delta n^{+,-}$ whose formulation follows from (9)-(11) have no solution at all. This is connected, as in the case of the well-known Stokes and Whitehead paradoxes, with the uneven validity of direct expansions with respect to powers of Br of the solutions sought in the region of $2 + \varepsilon \leqslant \rho < \infty$ due to the infinite extent of this region. (Far from an isolated particle there is essentially no Br, while the number $\mathrm{Br}_\rho = Er^2/D_0 = \rho^2 \mathrm{Br}$ can be as large as desired.)

Therefore, we use the method of joined asymptotic expansions [11] here, writing the inner asymptotic expansions of the sought functions satisfying the steady-state equation (9) in the form

$$n^{+,-}(\rho) = n_0^{+,-}(\rho) + \sum_{i=1}^{\infty} f_i^{+,-} n_i^{+,-}(\rho), \quad \lim_{\mathrm{Br}\to 0} \frac{f_{i+1}}{f_i} = 0, \tag{16}$$

where f_i is a certain system of comparison functions. The boundary conditions for the quantities in (16) follow from the internal conditions in (10) and (11):

$$n_i^{+,-} = 0, \ \rho = 2 + \varepsilon, \ i \geqslant 1. \tag{17}$$

In the outer region we introduce the new coordinate $\xi = \rho\sqrt{\mathrm{Br}}$; then the steady-state analog of Eq. (9) takes the form

$$(\boldsymbol{\xi}\cdot\boldsymbol{\gamma} + 2\mathbf{e} : \mathbf{C})\cdot\nabla N + 2(\mathbf{e} : (\nabla\cdot\mathbf{C}))N = \nabla\cdot[\mathbf{d}\cdot(\nabla N + N\nabla\varphi)], \tag{18}$$

with differentiation with respect to $\boldsymbol{\xi}$ being understood in ∇, while **d** and **C** are considered as functions of $\boldsymbol{\xi}$ depending on Br as on a parameter. The outer asymptotic expansions are written as

$$N^{+,-}(\xi) = N_0^{+,-}(\xi) + \sum_{i=1}^{\infty} F_i^{+,-} N_i^{+,-}(\xi), \quad \lim_{\mathrm{Br}\to 0} \frac{F_{i+1}}{F_i} = 0, \tag{19}$$

where F_i is a new system of comparison functions; $N_0^+ = n_1$, $N_0^- = 0$. On the coefficients in (19) we impose only the external boundary conditions

$$N_i^{+,-} \to 0, \ \xi \to \infty, \ i \geqslant 1. \tag{20}$$

In addition, we need to satisfy the joinability conditions in the region of intermediate $\boldsymbol{\rho}$, which define $f_i^{+,-}$ and $F_i^{+,-}$ [11].

For the purposes of this work it is enough to find $f_1^{+,-}$ and $n_1^{+,-}$ and $n_1^{+,-}(\rho)$, i.e., only the first terms of the series in (16), for which we must determine $F_1^{+,-}$ and $N_1^{+,-}(\xi)$, i.e., the first terms of the series in (19). The quantity $N_1^{+,-}(\xi)$ satisfies, obviously, the equation which follows from (18) as $\mathrm{Br} \to 0$ and the conditions (20). Since the tensor **d** is reduced to the unit tensor while **C** is reduced to the null tensor as $\mathrm{Br} \to 0$, and $\varphi(\rho) = \varphi(\xi/\sqrt{\mathrm{Br}}) \to 0$ as well, from (18) we obtain

$$(\boldsymbol{\xi}\cdot\boldsymbol{\gamma})\cdot\nabla N_1 = \nabla\cdot(\nabla N_1 + N_1\nabla\varphi) = \Delta N_1, \tag{21}$$

with the discarded terms having the order of smallness $\sqrt{\mathrm{Br}}$ or higher. This equation describes steady-state convective diffusion in an undisturbed stream characterized by a uniform tensor of velocity derivatives with respect to the $\boldsymbol{\gamma}$ coordinates. It is easy to see that a full solution of (21) satisfying the conditions (20) is not needed for joining the outer with the inner expansion: One needs only two leading terms of the asymptotic expansion of the outer solution as $\xi \to 0$.

Solving the problem (20), (21) for an arbitrary γ is also very laborious. Here we consider as an example only simple shear flow ($\Gamma_{ij} = E\delta_{i1}\delta_{j2}$), for which Eq. (21) was investigated in detail in [12, 13]. As $\xi \to 0$ we have [13]

$$N_1^{+,-}(\xi) \approx N_0^{+,-} + F_1^{+,-}\left(\frac{1}{\xi} - \sigma\right), \quad \sigma = 0.2568. \tag{22}$$

Joining the leading terms in (22) with the corresponding inner solutions (12) using the usual procedures [11], we obtain

$$F_1^{+} = -\sqrt{\mathrm{Br}}\,\frac{n_1}{K}, \quad F_1^{-} = \sqrt{\mathrm{Br}}\,\frac{e^{-\varphi_m}}{4\pi a^3(2+\varepsilon)^2 K}\,. \tag{23}$$

The fact that the first terms of the series (19) have the order $\sqrt{\mathrm{Br}}$ justifies the a posteriori use of Eq. (21) to obtain (22).

From (23) it also becomes clear that the quantities $f_1^{+,-}$ in (16) also have the order $\sqrt{\mathrm{Br}}$, i.e., that $n_1^{+,-}(\rho)$ must satisfy the same Eq. (9), with the left side discarded, as $n_0^{+,-}(\rho)$. From this it is easy, using the conditions (17), to obtain

$$n_1^{+,-}(\rho) = f_1^{+,-} e^{-\varphi}\int\limits_{2+\varepsilon}^{\rho} \frac{e^{\varphi}}{G\rho^2}\,d\rho. \tag{24}$$

Joining (24) with second-order terms in (22), we obtain

$$f_1^{+,-} = -\frac{\sigma}{K}F_1^{+,-}, \tag{25}$$

which completes the solution of the problems of doublet formation and destruction in a finely disperse system in a simple shear stream formulated here. In particular, from (12), (16), and (23)-(25) we have the following expressions for the inner asymptotic expansions to within terms of order $\sqrt{\mathrm{Br}}$:

$$\begin{aligned} n^{+}(\rho) &\approx \frac{e^{-\varphi}}{K}\left(1 + \sqrt{\mathrm{Br}}\,\frac{\sigma}{K}\right)\int\limits_{2+\varepsilon}^{\rho}\frac{e^{\varphi}}{G\rho^2}\,d\rho, \\ n^{-}(\rho) &\approx \frac{e^{-\varphi_m-\varphi}}{4\pi(2+\varepsilon)^2 K a^3}\left[K - \left(1 + \sqrt{\mathrm{Br}}\,\frac{\sigma}{K}\right)\int\limits_{2+\varepsilon}^{\rho}\frac{e^{\varphi}}{G\rho^2}\,d\rho\right]. \end{aligned} \tag{26}$$

The first equation in (26) with $\varepsilon = 0$ was obtained earlier in [5], where it has meaning in the case when there exists an integral defining the quantity K in (12), for which $\varphi(\rho)$ must satisfy the limiting condition as $\rho \to 2$ formulated in [5].

After calculations using (26), we have the following representations for the corrections $\Delta J^{+,-}$ to the fluxes $J_0^{+,-}$ in (13):

$$\Delta J^{+} = \frac{4\pi\sigma}{K^2}\sqrt{\mathrm{Br}}\,D_0 a n_1, \quad \Delta J^{-} = \frac{\sigma e^{-\varphi_m}}{(2+\varepsilon)^2K^2}\sqrt{\mathrm{Br}}\,\frac{D_0}{a^2}\,. \tag{27}$$

The corresponding corrections to the rate constants of the doublet formation and breakup processes defined in (15) are expressed as

$$\Delta\alpha = \frac{4\pi\sigma(2+\varepsilon)^2}{W^2}\sqrt{\mathrm{Br}}\,D_0 a, \quad \Delta\beta = \frac{\sigma e^{-\varphi_m}}{W^2}\sqrt{\mathrm{Br}}\,\frac{D_0}{a^2}\,. \tag{28}$$

The singlet and doublet concentrations in a dilute system which is in an equilibrium state are fully determined, as is easy to see, by the ratio α/β, for which

$$\frac{\alpha}{\beta} = \frac{\alpha_0 + \Delta\alpha}{\beta_0 + \Delta\beta} \approx \frac{\alpha_0}{\beta_0}\left(1 + \frac{\Delta\alpha}{\alpha_0} - \frac{\Delta\beta}{\beta_0}\right) = \frac{\alpha_0}{\beta_0}\,. \tag{29}$$

An analogous problem in a mathematical respect was investigated in [14] in the case of $\mathbf{D} = D\mathbf{I}$, $\mathbf{C} = 0$, and $u = 0$ in connection with the problem of heat or mass transfer from a spherical particle in a simple shear stream.

From (27) and (28) it is seen that the imposition of external shear flow, as one would expect, results in a certain increase in both the rate of formation of doublets and their breakup rate. As follows from (29), however, this does not affect the characteristics of the equilibrium state reached after a long time following the start of the coagulation process. This conclusion pertains only to the situation when $\mathrm{Br} \ll 1$, and physically it means that the variation of these characteristics due to motion of the system has a higher order of smallness than $\sqrt{\mathrm{Br}}$. To find this variation, one must calculate the following series terms in (16), which is a considerably more complicated task than that under consideration: the fields $n_2^{+,-}(\boldsymbol{\rho})$ will no longer be isotropic, while the fields $N_2^{+,-}(\boldsymbol{\rho})$ will depend on the disturbances introduced into the average flow by the isolated particle with the center at the point $r = 0$.

Concrete results on the influence of the external flow on the aggregation process were obtained above only for a simple shear stream, but they are not qualitatively altered for other types of streams. It is clear from the above analysis that corrections of the type (28) to the streams (13) which occur in a state of rest can also be obtained easily for any other flow if one is able to solve the problem of convective diffusion from a point source in this flow undisturbed by the source itself, and to construct the asymptotic forms of the fields $N_1^{+,-}(\boldsymbol{\xi})$ as $\xi \to 0$ which are needed for determining $n_1^{+,-}(\boldsymbol{\rho})$. Such a problem has recently been solved for many important types of shear streams and for plane Poiseuille flow [15, 16], and an elegant method of calculating the diffusion fluxes without a detailed analysis of the concentration fields was also given in [15]. Therefore, obtaining equations replacing Eqs. (26)-(29) for such flows offers no fundamental difficulties.

In conclusion, we emphasize that we made no limiting assumptions above concerning the form of the particle-interaction potential except for the most general ones. Therefore, the results obtained are equally applicable to the analysis of processes of fast and slow, reversible and irreversible aggregation at primary and secondary minima.

NOTATION

a, particle radius; $\mathbf{b}_{ij}$, mobility tensors; $\mathbf{C}$, tensor introduced in (6); $\mathbf{D}$, $\mathbf{d}$, dimensional and dimensionless diffusion tensors; D_0, coefficient of relative Brownian motion; E, characteristic value of shear velocity; $\mathbf{E}$, $\mathbf{e}$, dimensional and dimensionless deformation-rate tensors; $\mathbf{F}$, total particle-interaction force; f_i, F_i, coefficients in (16) and (19): G, H, functions introduced in (6); K, constant defined in (12); k, Boltzmann constant; $\mathbf{I}$, unit tensor; J, particle flux; N, n, external and internal concentration fields; n_0, n_1, n_2, initial number concentration of particles and concentrations of singlets and doublets, respectively; p, probability density; $\mathbf{r}$, dimensional coordinate vector; T, Kelvin temperature; t, time; u, interaction potential; $\mathbf{V}$, relative velocity of the centers of two particles; $\mathbf{U}$, relative velocity due only to the hydrodynamic interaction between particles and the external stream; W, moderation factor; α, β, rate constants of doublet formation and breakup processes; Γ, γ, dimensional and dimensionless tensors of velocity derivatives with respect to the coordinates; ε, dimensionless distance between interacting particles, corresponding to the minimum of the potential; μ, viscosity of the liquid; $\boldsymbol{\xi}$, $\boldsymbol{\rho}$, external and internal coordinate vectors; σ, constant introduced in (22); τ, dimensionless time; φ, dimensionless interaction potential; φ_m, dimensionless depth of potential well; $\boldsymbol{\Omega}$, $\boldsymbol{\omega}$, dimensional and dimensionless vorticity tensors; Br, Brenner number, defined in (8). Indices: + and - pertain to problems of doublet formation and breakup, respectively.

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CONTROLLING DEPOSITION OF A SUBSTANCE ONTO THE INNER SURFACE OF A CYLINDRICAL CHANNEL

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The problem of material deposition on the inner surface of a channel with free-molecular gas flow is considered.

Deposition of material from the gaseous phase is one of the basic methods of producing thin layers of material [1]. This method permits production of layers with thickness varying according to a specified rule. At sufficiently low pressures of the vapors of the material to be deposited, a free-molecular flow regime is created in the gas, and the thickness of the layer deposited is dependent only on system geometry, the molecular flux incident on the surface, and the interaction conditions between gas molecules and solid surface.

At the present time external problems have been studied thoroughly. In these cases, the deposition process can be controlled either by changing the position of the material source relative to the substrate or by changing the geometric parameters of the source itself. More complicated and less well studied are internal deposition problems. Thus, for example, in the case of deposition of a thin layer of material on the inner surface of a cylindrical channel, where the source of material to be deposited lies outside the channel, the deposition process can be controlled only by varying the gas pressure at the channel ends and the temperature distribution along the channel.

In the present study we will examine questions of deposition of material layers on the inner surface of a cylindrical channel for a specified material deposition rule along the channel at arbitrary values of the molecular condensation (adhesion) coefficient α.

Let it be required to deposit a thin layer of condensate along the inner surface of a cylindrical channel, with the layer thickness varying along the channel length by a specified rule. Naturally, the rule for change in layer thickness along the channel must determine the resulting molecular flux into the condensate.

We will make some simplifying assumptions. We assume that at the start of the process the entire inner surface is coated by a layer of condensate (i.e., we will not consider the process of condensate formation on the bare substrate). The condensate formed is assumed solid. We will consider the problem in the quasistationary approximation. We assume that the growing

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