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Abstract

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THE RATE OF BROWNIAN COAGULATION OF AEROSOLS IN THE THIRTEEN-MOMENT APPROXIMATION

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As is known, the problem of the coalescence of particles upon collision was first considered by Smoluchowski ([1]), who calculated the coagulation rate in colloidal solutions. The satisfactory nature of the results he obtained is explained by the circumstance that for colloidal particles the mean Brownian free path l is always much smaller than the particle radius a, and formally may be set equal to zero. This last condition is precisely the condition for applicability of the diffusion equation to the description of the phenomenon of coagulation. In considering the coagulation of aerosols, the situation becomes considerably more complicated. The reason is that in the case of aerosol coagulation the ratio $k = l/a$ may be any number. The first attempt to modify Smoluchowski' s theory with allowance for this circumstance was made in the work of Fuchs ([2]), where, in order to determine the dependence of the coagulation rate on k, it was proposed to regard the motion of particles at small distances between them as if the medium were absent altogether, while at large distances the diffusion equation was to be used, after which the two solutions were matched. In the present work we attempt to determine the dependence of the coagulation rate on the parameter $k = l/a$ in the region of small k, using for this purpose the Fokker–Planck equation.

It is easy to see that the problem of coalescence of Brownian particles of radius a can be reduced to the problem of adsorption of point particles on the surface of a sphere, fixed in space, of radius $R = 2a$, which we shall conventionally call the absorber. We shall seek the stationary solution of this problem. This means that we are interested in the behavior of the system after the lapse of a certain time interval, of the order of the time required for establishing the process of particle motion toward the absorber. We shall start from the stationary Fokker–Planck equation, which determines the distribution function of Brownian particles $f(\mathbf{r}, \mathbf{v})$

$$v_i \frac{\partial f}{\partial r_i} = \beta \frac{\partial}{\partial v_i}(v_i f) + q \frac{\partial}{\partial v_i} \frac{\partial f}{\partial v_i}. \tag{1}$$

In equation (1)* $\beta = \tau^{-1}$ is the Stokes friction coefficient; τ is the relaxation time, $q = \beta\varkappa T/m$, where m is the particle mass, $\varkappa$ is Boltzmann' s constant, and T is the temperature of the medium. If we form the moments of the function

$$n(\mathbf{r}) = \int f(\mathbf{r},\mathbf{v})\,d\mathbf{v};\quad \mathbf{j}(\mathbf{r}) = \int \mathbf{v}\,f(\mathbf{r},\mathbf{v})\,d\mathbf{v};\quad P_{ij\ldots s}(\mathbf{r}) =$$

$$= \int v_i v_j \ldots v_s f(\mathbf{r},\mathbf{v})\,d\mathbf{v},$$

* Summation is assumed everywhere over twice-repeated indices.

distribution, then, using equation (1), it is easy to obtain an infinite system of coupled equations for the moments

$$\frac{\partial j_i}{\partial r_i} = 0, \tag{2a}$$

$$\beta j_i + \frac{\partial P_{ij}}{\partial r_j} = 0, \tag{2b}$$

$$2\beta P_{ij} + \frac{\partial P_{ijk}}{\partial r_k} = 2q\delta_{ij} n, \tag{2c}$$

$$3\beta P_{ijk} + \frac{\partial P_{ijkl}}{\partial r_l} = 10 q j_k. \tag{2d}$$

We have written out only the first few equations of this system. In order to break the chain of equations (2), we shall parametrize the distribution function with the aid of the following first moments [3]

$$n(\mathbf{r});\quad j(\mathbf{r});\quad p(\mathbf{r}) = \frac{1}{3}P_{kk}(\mathbf{r});\quad p_{ij} = P_{ij}(\mathbf{r}) - \frac{1}{3}\delta_{ij}P_{kk}(\mathbf{r});$$

$$S_k(\mathbf{r}) = \frac{1}{2}P_{llk}(\mathbf{r}).$$

The physical meaning of these quantities is evident. In this approximation $f(\mathbf{r},\mathbf{v})$ has the following form:

$$f(\mathbf{r},\mathbf{v}) = \left[\left(\frac{5}{2}n - 3h^2 p\right) + (7h^2 j_i - 4h^4 S_i)v_i + 2h^4 p_{ij} v_{iv} j +\right.$$

$$\left. +(2h^4 p - h^2 n) v_{kv} k\right] f_0, \tag{3}$$

where $f_0 = (h^2/\pi)^{3/2} \exp -h^2 v_{kv} k$ is the Maxwellian distribution function describing a stationary, spatially homogeneous system of Brownian particles, $h^2 = m/2\varkappa T$. Carrying out the closure in equations (2c), (2d) with the aid of function (3), we obtain the following closed system of equations:

$$\frac{\partial j_i}{\partial r_i} = 0, \tag{4a}$$

$$\beta j_i + \frac{\partial p}{\partial r_i} + \frac{\partial p_{ij}}{\partial r_j} = 0, \tag{4b}$$

$$2\beta p_{ij} + \frac{7}{4h^2}\left(\frac{\partial j_i}{\partial r_j} + \frac{\partial j_j}{\partial r_i}\right) - \left(\frac{\partial S_i}{\partial r_j} + \frac{\partial S_j}{\partial r_i}\right) = \delta_{ij}\left(\frac{\beta}{h^2} n - 2\beta p + \frac{\partial S_k}{\partial r_k}\right), \tag{4c}$$

$$6\beta S_i + \frac{5}{h^2}\left(\frac{\partial p}{\partial r_i} - \frac{1}{4h^2}\frac{\partial n}{\partial r_i}\right) + \frac{7}{2h^2}\frac{\partial p_{ij}}{\partial r_j} = \frac{5}{h^2}\beta j_i, \tag{4d}$$

$$p_{ii} = 0. \tag{4f}$$

It should be emphasized that the solutions of equations (4) will describe the physical situation sufficiently well only in the case of a system of Brownian particles with weak spatial inhomogeneity, since the approximation of the exact distribution function f by expression (3) will be valid when the deviation of f from f_0 is small. It is easy to see that the parameter characterizing the degree of spatial inhomogeneity is the ratio $g = \tau/t_0$, where t_0 is the characteristic time of the problem, which may be defined as $t_0 = R/u$, where u is the mean Maxwellian velocity. One can easily verify the latter if, in the system of equations (4), one passes to the dimensionless variable $\xi = (1/R)\mathbf{r}$ and expresses all unknown quantities in terms of new ones whose dimensions coincide with the dimension of concentration according to the rule $P_{\alpha_1 \dots \alpha_m} = u^m \Pi_{\alpha_1 \dots \alpha_m}$, $m = 1, 2, 3$. Thus we arrive at a system of equations in which all first derivatives will be quantities of order g, whereas the second derivatives will be of order g^2. Hence it follows that the determination of the coagulation rate

using the system of equations (4) will be correct only in the case of small $g = \tau/t_0 = l/R = k/2$, where l is the mean Brownian free path. If from equations (4b), (4d), (4f) one eliminates p_{ij} with the aid of (4c) and, in the resulting system of equations, neglects all terms containing second derivatives, i.e., if one assumes $g \ll 1$, then it is easy to obtain the following result:

$$j_i(\mathbf{r}) = -D\frac{\partial n(\mathbf{r})}{\partial r_i}; \qquad S_i(\mathbf{r}) = -\frac{5}{2}D^2\beta\frac{\partial n(\mathbf{r})}{\partial r_i};$$

$$p(\mathbf{r}) = D\beta n(\mathbf{r}), \qquad p_{ij}(\mathbf{r}) = 0, \tag{5}$$

where $D = \chi T/m\beta$ is the well-known diffusion coefficient of Brownian particles. Thus, in this approximation we obtain the diffusion coagulation rate. Taking into account the terms neglected in deriving (5) will make it possible to obtain a correction to the diffusion coagulation rate.

To isolate the solution we need, which takes into account the absorption of particles on the surface of the absorber, the system of equations (4) must be supplemented by the necessary boundary conditions. To obtain the latter, we note that in our approximation the presence of particle absorption is equivalent to the absence of transport of mass, of the normal component of momentum, and of the energy of Brownian particles at the surface of the absorber from the absorber into the medium ([4],[5]). If we introduce scalar functions $j(r)$, $S(r)$, $\mu(r)$, defining them by the relations

$$\mathbf{j}(\mathbf{r}) = \frac{\mathbf{r}}{r} j(r); \qquad \mathbf{S}(\mathbf{r}) = \frac{\mathbf{r}}{r} S(r); \qquad p_{ij}(\mathbf{r}) = \left[\delta_{ij} - \frac{3r_i r_j}{r^2}\right]\mu(r),$$

then for the values of these functions at the boundary of the absorber we obtain the following definitions:

$$j(R) = \frac{1}{R}\int_G (\mathbf{R}\cdot\mathbf{v})\, f(\mathbf{R},\mathbf{v})\, d\mathbf{v},$$

$$\mu(R) = \frac{1}{2}\left[p(R) - \frac{R_{iR} j}{R^2} P_{ij}(R)\right] = \frac{1}{2}\left[p(R) - \frac{1}{R^2}\int_G (\mathbf{R}\cdot\mathbf{v})^2 f(\mathbf{R},\mathbf{v})\, d\mathbf{v}\right], \tag{6}$$

$$S(R) = \frac{1}{2R}\int_G v_{kv} k(\mathbf{R}\cdot\mathbf{v}) f(\mathbf{R},\mathbf{v})\, d\mathbf{v},$$

where the region G contains only those $\mathbf{v}$ for which $(\mathbf{R}\mathbf{v}) < 0$. Substituting expression (3) into equalities (6) and carrying out the necessary integrations, we obtain the following relations:

$$j(R) = \frac{1}{3\sqrt{\pi}\,h} n(R) + \frac{2h}{3\sqrt{\pi}} p(R) + \frac{4h^2}{3} S(R) - \frac{4h}{3\sqrt{\pi}} \mu(R),$$

$$\mu(R) = \frac{1}{2} p(R) + \frac{7}{2\sqrt{\pi}\,h} j(R) - \frac{2h}{\sqrt{\pi}} S(R),$$

$$S(R) = \frac{1}{9\sqrt{\pi}\,h^3} n(R) - \frac{2}{3\sqrt{\pi}\,h} p(R) + \frac{2}{3\sqrt{\pi}\,h} \mu(R) + \frac{35}{36h^2} j(R). \tag{7}$$

Together with the condition at infinity $\lim_{|\mathbf{r}|\to\infty} f = n_0 f_0$, whence it follows that $n(\infty) = n_0$, where n_0 is the unperturbed concentration, $p(\infty) = n_0/2h^2$, conditions (7) uniquely determine the solution of the system of equations (4). If we note that, in the spherically symmetric case, the vectors $\mathbf{j}(\mathbf{r})$ and $\mathbf{S}(\mathbf{r})$ are potential, then, introducing two auxiliary functions $\varphi(\mathbf{r})$ and $\psi(\mathbf{r})$, and defining them by the relations $\mathbf{j} = (-1/2h^2\beta)\nabla\varphi$, $\mathbf{S} =$

$= (-1/2h^2\beta)\nabla\psi$, it is easy to obtain the solution of the system of equations (4). Omitting the uncomplicated calculations, we give the final result:

$$\begin{gathered}
j(r) = \frac{\alpha}{2h^2\beta}\cdot\frac{1}{r^2},\\
n(r) = n_0 + \frac{1}{r}\{\alpha - 3h^2\gamma\sin(\lambda r+\delta)\},\\
S(r) = \frac{1}{r^2}\left\{\frac{\beta\gamma}{\lambda^2}\sin(\lambda r+\delta) + \frac{5\alpha}{8h^4\beta}\right\} - \frac{1}{r}\frac{\beta\gamma}{\lambda}\cos(\lambda r+\delta),\\
p(r) = \frac{n_0}{2h^2} + \frac{1}{r}\left\{\frac{\alpha}{2h^2} - \frac{2\gamma}{3}\sin(\lambda r+\delta)\right\},\\
\mu(r) = \frac{1}{r^3}\left\{\frac{\gamma}{\lambda^2}\sin(\lambda r+\delta) - \frac{\gamma}{4h^4\beta^2}\right\} - \frac{1}{r^2}\frac{\gamma}{\lambda}\cos(\lambda r+\delta) - \frac{1}{r}\frac{\gamma}{3}\times\\
\times\sin(\lambda r+\delta).
\end{gathered} \tag{8}$$

In the equalities (8) the conditions at infinity have already been taken into account, $\lambda^2 \simeq 2.18h^2\beta^2$, and α, γ, δ are constants that must be determined from the conditions (7). Substituting the solution (8) into the relations (7) and finding α, for the coagulation rate

$$v = \int j dS,$$

where the integral is taken over the surface of the absorber, we obtain the following expression:

$$v = 4\pi R D n_0 Q(k),$$

$$Q(k) = \frac{1+0.08k}{1+0.56k+0.21k^2+0.015k^3}. \tag{9}$$

From equality (9) it is seen that for small k, $Q(k) \approx 1 - 0.48k$, and as $k \to 0$, v goes over into the expression obtained by Smoluchowski.

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Note: Figure translations are in progress. See original paper for figures.