DIFFUSION OF PARTICLES IN DENSE DISPERSIVE SYSTEMS

Yu. A. Buevich

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We obtain an equation describing the diffusion of particles suspended in a liquid. This equation differs from Fick's by the term $\partial^2 c/\partial t^2$, which takes account of the fact that the particle displacement velocity is finite in the diffusion process.

Particles suspended in the flow of a liquid or gas may undergo chaotic fluctuating motion imposed on the average motion of the dispersed phase as a whole. These fluctuations of individual particles or groups of particles (packets) are particularly intensive in concentrated and comparatively coarse dispersive systems (the pseudoliquefaction or pneumatic transport of large particles, etc.). In many cases they have a definite effect on both the theoretical properties of the dispersive system and the heat and mass transport process in it (a review of experimental investigation on fluctuations and their effect on heat and mass transport in the pseudoliquefied layer is given, for example in [1, 2]).

One of the most important problems in practice is the description of the effect of these fluctuations on the displacement of the dispersed phase in the system. For various applications it is desirable to have a means of continuously describing the displacement using a differential equation, but without any analysis of the random behavior of the actual separate particles. From the analogy between the suspended particles and the molecules of a gas, or from the analogy between the dispersed phase and a turbulent liquid, it is natural to characterize the intensity of the displacement using the effective diffusion coefficients of the particles in the system. This is usually done, the simple Fick diffusion equation, which is strictly valid only as $w_d/w^* \to \infty$, being used, without sufficient justification. That this equation can be applied to the diffusion of gases does not give rise to doubts in view of the high velocities of the molecules in thermal motion. But for suspended particles, the velocities w^* and w_d are usually comparable with each other and in this connection it is necessary both to have a stricter justification for the diffusion analogy and to refine Fick's equation for this case.

The diffusion of suspended particles, determined by their fluctuating motions, has two further characteristics by comparison with the diffusion of the molecules of a gas. First, the fluctuations of the particles are usually anisotropic, so that in general we have to deal not with a unique scalar diffusion coefficient, but a tensor of diffusion coefficients $\mathbf{D} = \|D_{ij}\|$, as occurs, for example, in diffusion in a turbulent field. Second, the spatial scale of the fluctuations ("the mixing length") in many cases is comparable with the dimensions of the apparatus containing the dispersive system. A limitation in the diffusion analogy under these conditions is repeatedly emphasized by Todes and his colleagues is indicated, for example, in [2].

To obtain diffusion equations we use the method below which was developed in [3]. We assume that the particles are in equilibrium in the sense that the total average force on each particle is zero. This implies that the average velocity of any particle is also zero, or can be made zero by an appropriate choice of the coordinate system. In addition, we assume that the disequilibrium of the system is small, i.e., the diffusion flux J of particles is small. In this case the distribution function for the fluctuating velocities **w** of the particles can be written approximately as [3]

$$f(\mathbf{w};\ \mathbf{r},\ t) \approx \frac{1}{4\pi m} c^*(w;\ \mathbf{r},\ t) + \frac{3}{4\pi m w^2} \mathbf{w}\mathbf{J}^*(w;\ \mathbf{r},\ t). \qquad (1)$$

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Here c^*w^2dw and J^*w^2dw are the mass concentration and the mass flux of the particles, the velocity of which lies in the range (w, w + dw) in modulus

$$c^*(w;\ \mathbf{r},\ t) = m\int f(\mathbf{w};\ \mathbf{r},\ t)\,d\,\mathbf{w}_0,\quad \mathbf{J}^*(w;\ \mathbf{r},\ t) = m\int f(\mathbf{w};\ \mathbf{r},\ t)\,\mathbf{w}\,d\,\mathbf{w}_0, \tag{2}$$

$$c(\mathbf{r},\ t) = \int\limits_0^\infty c^*(w;\ \mathbf{r},\ t)\,w^2dw,\quad \mathbf{J}(\mathbf{r},\ t) = \int\limits_0^\infty \mathbf{J}^*(w;\ \mathbf{r},\ t)\,w^2dw.$$

We see that when $f(\mathbf{w};\ \mathbf{r},\ t)$ is given by (1), the first of (2) holds identically.

If we neglect the interaction of the particles with each other and with the random fluctuations in the supporting flow, we can take the equation of continuity as defining the distribution function

$$\frac{\partial f}{\partial t} + \mathbf{w}\frac{\partial f}{\partial \mathbf{r}} = 0, \tag{3}$$

this being a particular case of Liouville's equation when the average force on a particle is zero.

To take account of the interactions we consider the particles in some element of volume of the impurity, taken below as unit volume, and later moving out of that volume. We describe this volume further as a "black box," ignoring the details of the interaction processes in it. To do this we introduce the variable $q(\mathbf{W},\ \mathbf{W}')$ which is the probability that the particles in the box with velocity $\mathbf{w} = w\mathbf{w}_0$, where $W_i \equiv |w_{0i}|$, leave it with velocity $\mathbf{w}' = w\mathbf{w}_0'$, where $W_i' \equiv |w_{0i}'|$. Thus, we consider the scattering of the particles by the "black box" under the condition that the modulus of the particle velocity remains constant.† Obviously this is impermissible if the period in the "black box," i.e., the interaction of the particles with each other and with the fluctuations in the supporting flow do not change the average pulsation energy of the particles (cf. [3]).

The variable $q(\mathbf{W},\ \mathbf{W}')$ can be written as

$$q(\mathbf{W},\ \mathbf{W}') = (1-q)\,\mathbf{I} + q\,(\mathbf{W}'\mathbf{S}\mathbf{W}),\quad \mathbf{S} = \|S_{ij}\|,\quad \sum_{j=1}^{3} S_{ij} = 1,\ S_{ij} \geqslant 0,$$

where **I** is the unit tensor; **S** is the matrix (tensor) of probabilities, normalized by the probability of the certain event, and $q \le 1$ is the probability of an arbitrary scattering of the particles in the "black box."

The elements S_{ij}, with various values of j, are the moduli of the direction cosines of the most probable velocity of a scattered particle under the condition that the particle velocity before scattering was in the direction of the i-axis. The necessity to introduce the angular dependence for the probability $q(\mathbf{W},\ \mathbf{W}')$ is in general associated with the anisotropy of the scattering of the particles in the "black box." The case investigated in [3] when the probability of scattering in a given direction depends only on the angle between the vectors **w** and **w'**, corresponds to the matrix

$$\mathbf{S} = (q_1 - q_2)\begin{Bmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{Bmatrix} + q_2\begin{Bmatrix}1 & 1 & 1\\ 1 & 1 & 1\\ 1 & 1 & 1\end{Bmatrix}. \tag{4}$$

Thus, in particular, we see that the above type of scattering reduces to the simplest isotropic scattering if we change the definition of q. For the scattering of the molecules of a gas we usually have $q = n_tQ$, where n_t is the concentration of the scattering centers and Q is the effective scattering cross section. The quantity $\Lambda = (n_tQ)^{-1}$ is the length of the mean free path of a particle with velocity w between successive scattering events.

Following [3], we obtain the equation

$$\frac{\partial c^*}{\partial t} + \frac{3}{w^2}\,\mathbf{w}\frac{\partial\,\mathbf{J}^*}{\partial t} \approx -\,\mathbf{w}\frac{\partial c^*}{\partial\,\mathbf{r}} - \frac{3}{w^2}\mathbf{w}\,\frac{\partial\,(\mathbf{w}\mathbf{J}^*)}{\partial\,\mathbf{r}} - \frac{3}{w}(\mathbf{w}\underline{\Lambda}^{-1}\mathbf{J}^*), \tag{5}$$

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† This does not imply, of course, the assumption that the modulus of the velocity of any marked particle is constant as it passes through the "black box." We consider only the assemblies of particles entering and leaving and state that if the average pulsation energy of the particles is conserved, the number of them entering the box with velocity w is on the average equal to the number of particles leaving the box with the same velocity.

where we have introduced the new tensor $\underline{\Lambda}$, defined by the equation

$$\mathbf{w}\underline{\Lambda}^{-1}\mathbf{J}^* = (\mathbf{w}\mathbf{J}^*)\int (\mathbf{W}'S\mathbf{W})\,d\mathbf{W}' - \int (\mathbf{W}S\mathbf{W}')\,\mathbf{w}'\mathbf{J}^*\,d\mathbf{W}'. \tag{6}$$

For isotropic scattering, or scattering depending only on the angle between $\mathbf{w}$ and $\mathbf{w}'$, we have $\underline{\Lambda}^{-1} = n_t Q\mathbf{I}$ and $\underline{\Lambda} = (n_t Q)^{-1}\mathbf{I} = \Lambda\mathbf{I}$. Thus, the tensor $\underline{\Lambda}$, defined in (6), can be considered as the tensor of the effective lengths of the "mean free path" of a particle with velocity w.

We see that Eq. (5) contains terms of two types: terms invariant with respect to the transformation $\mathbf{w} \to -\mathbf{w}$, and terms which change their sign under this transformation. From (5) we obtain the following two equations:

$$\frac{\partial c^*}{\partial t} \approx -\frac{3}{w^2}\,\mathbf{w}\,\frac{\partial (\mathbf{w}\mathbf{J}^*)}{\partial \mathbf{r}}, \quad \frac{\underline{\underline{\Lambda}}}{w}\cdot\frac{\partial \mathbf{J}^*}{\partial t} + \mathbf{I}^* \approx -\frac{w\underline{\underline{\Lambda}}}{3}\cdot\frac{\partial c^*}{\partial \mathbf{r}}. \tag{7}$$

The diffusion equation in Fick's form is obtained from this when $\underline{\Lambda} = \Lambda\mathbf{I}$ and when we ignore the term in $\partial\mathbf{J}^*/\partial t$ in the second equation of (7), which corresponds to assuming the changes in the diffusion flow are relatively slow and, conversely that the displacements of the particles are very rapid. The corresponding calculation was made in [3].

If we eliminate $\mathbf{J}^*$ from (7), we obtain a unique equation for c^*:

$$\frac{w}{\underline{\Lambda}(\mathbf{w})}\cdot\frac{\partial c^*}{\partial t} \approx \left(\mathbf{w}\,\frac{\partial}{\partial \mathbf{r}}\right)^2 c^* - \frac{\partial^2 c^*}{\partial t^2}, \quad \underline{\Lambda}(\mathbf{w}) = \mathbf{w}\,(\mathbf{w}\underline{\Lambda}^{-1})^{-1}.$$

This equation depends on the direction of the vector $\mathbf{w}$ which, of course, is connected with the approximate representation (1) for the distribution function. The degree of its validity is not destroyed if in it we average over the directions of $\mathbf{w}$. Then we obtain a new equation:

$$\begin{gathered}\frac{w}{\Lambda(w)}\cdot\frac{\partial c^*}{\partial t} \approx \left(\int w_i w_j f(\mathbf{w};\,\mathbf{r},\,t)\,d\mathbf{w}_0\right)\frac{\partial^2 c^*}{\partial x_i \partial x_j} - \frac{\partial^2 c^*}{\partial t^2},\\ \frac{1}{\Lambda(w)} = \int \frac{1}{\Lambda(\mathbf{w})} f(\mathbf{w};\,\mathbf{r},\,t)\,d\mathbf{w}_0.\end{gathered} \tag{8}$$

The variable $\Lambda(\mathrm{w})$, introduced here, has the meaning of a scalar mean free path length for particles with velocity w. In the isotropic case $\Lambda(\mathrm{w}) = (n_i Q)^{-1}$, i.e., it does not depend on w.

We introduce the average mean free path length of a particle λ and the tensor $\mathbf{D}$ of diffusion coefficients, which are defined by the equations

$$\frac{w^*}{\lambda} = \int \frac{w^3}{\Lambda(w)}\cdot\frac{c^*(w;\,\mathbf{r},\,t)}{c(\mathbf{r},\,t)}\,dw, \quad \frac{w^*}{\lambda}D_{ij} = \int w_i w_j \frac{c^*(w;\,\mathbf{r},\,t)}{c(\mathbf{r},\,t)} f(\mathbf{w};\,\mathbf{r},\,t)\,d\mathbf{w}. \tag{9}$$

The meaning of these equations is obvious. In fact they are similar to the corresponding definitions in [3]. Then, averaging (8) with respect to the modulus of the velocity, we obtain the equation

$$\frac{\partial c}{\partial t} \approx \left[\left(\mathbf{D}\,\frac{\partial}{\partial \mathbf{r}}\cdot\frac{\partial}{\partial \mathbf{r}}\right) - \frac{\lambda}{w^*}\cdot\frac{\partial^2}{\partial t^2}\right] c. \tag{10}$$

By (9), this equation can be rewritten as

$$\frac{\partial c}{\partial t} \approx \left[\left(\mathbf{D}\,\frac{\partial}{\partial \mathbf{r}}\cdot\frac{\partial}{\partial \mathbf{r}}\right) - \frac{\mathrm{tr}\mathbf{D}}{w^{*2}}\cdot\frac{\partial^2}{\partial t^2}\right] c, \quad \mathrm{tr}\mathbf{D} = D_{ii}. \tag{11}$$

Equations similar to (10) or (11) can also be written for the volume concentration of particles in the system, ρ, or for the porosity of the dispersive system $\varepsilon = 1 - \rho$. From (10) and (11) we see that the diffusion equation in Fick's form is valid for

$$\frac{1}{\tau_d}\cdot\frac{\lambda}{w^*} \sim \frac{w_d}{w^*} \ll 1 \quad \text{or} \quad D \ll \tau_d w^{*2}, \tag{12}$$

where τ_d is a characteristic time of the diffusion process; and D is a typical value of the diffusion coefficient.

The relations (12) fail to hold when the mixing length of the particles in the system increases and their fluctuation velocity decreases. Estimates, based on the experimental results in [1, 2], show that Fick's equation is a very rough approximation for the investigation of nonstationary diffusion in dispersive systems and must be replaced by the more accurate Eq. (10) or (11). Moreover, it is this last equation which we must use in calculating many of the variables which are of interest in various technological processes and in conditions of stationary diffusion. As an example we can indicate the calculation of the time a particle spends in the pseudoliquefied layer when the charging rate is constant.

NOTATION

c	is the mass concentration of the particles;
$\mathbf{J}$	is the mass diffusion flux;
w^*	is the mean square velocity of pulsation of the particles;
w_d	is the diffusion rate (the ratio I/c);
$f(\mathbf{w}; \mathbf{r}, t)$	is the pulsation velocity distribution of particles;
$\mathbf{D}$	is the tensor of diffusion coefficients;
$\mathbf{S}$	is the probability matrix;
Λ	is the tensor of lengths of the mean free path of the particles;
$\bar{\Lambda}(\mathbf{w})$, $\Lambda(w)$, λ	are the scalar mean free path lengths introduced in different ways (cf. Eqs. (7)-(9));
τ_d	is the characteristic time of diffusion;
$d\mathbf{w}$	is the volume element in velocity space;
$d\mathbf{w}_0$	is the corresponding solid angle element;
dW	is the solid angle element in first quadrant of velocity space.

LITERATURE CITED

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