SPECTRAL THEORY OF CONCENTRATION OF DISPERSE SYSTEMS

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A continuous function of coordinates and time is introduced to describe the random field of volume concentration of a monodisperse system. The conditions are clarified under which the function ensures a most detailed description, consistent with a physical-intuition description, of the local values of concentration. The variance of this function is computed, and an expression is obtained for the spectral density of the random deviation of the true concentration from its mean value. Some quantities also obtained in a similar manner describe the concentration of individual components of the dispersion phase in a polydisperse system.

The initial stage in the statistical analysis of fluctuating concentrations of components of a polydisperse system consists in obtaining sufficiently representative expressions for the distribution of the numbers of suspended particles of various types in a specified volume of the disperse system. A solution to this problem for rarefied systems in which individual particles can be considered as indistinguishable, noninteracting, and statistically independent particles was already given in the classical works of Einstein [1] and Smoluchowski [2] (see also the exposition of colloidal statistics in [3]). A sound basis has subsequently been provided for the methods used in the above-cited articles by introducing additive measure on the set of elementary events for an individual particle and by a subsequent functional integration over the product of measures for different particles [4].

A generalization of Smoluchowski's combinatorial method to include concentrated monodisperse systems whose particles are, as previously, indistinguishable but need not be statistically independent was proposed in [5]. In particular, an expression was obtained in [5] for the probability $W(n_A)$ of finding n_A particles each of volume σ in some volume A selected in a sufficiently large volume V occupied by the disperse system:

$$W(n_A) = C_{N_A}^{n_A} v^{n_A} (1-v)^{N_A - n_A}, \qquad v = n_V / N_V = \text{const} \tag{0.1}$$

where $n_V = \text{const}$ is the total number of particles in the volume V.

If the particles of a disperse system travel independently, that is, if one considers the fact of finding a particle in the volume A as an event independent of the behavior of other particles and which is only determined by the total number of particles already found in A, then one has

$$N_V = V \frac{\rho_*}{\sigma}, \quad N_A = A \frac{\rho_*}{\sigma}, \quad n_V \leqslant N_V, \ n_A \leqslant N_A \tag{0.2}$$

where ρ_* is the volume concentration of the system in the densely packed state.

The larger is n_A and the bigger the volume A compared with the mean specific volume of a particle $\sigma_\rho = \sigma/\rho$, where $\rho = v\rho_*$ is the mean volume concentration of particles in V, the more accurate becomes the distribution (0.1). From (0.1) one can easily obtain for $n_A \gg 1$, $N_A \gg 1$, $v = \text{const}$ the Gaussian distribution

$$W(n_A) \approx \frac{1}{[2\pi N_A v(1-v)]^{1/2}} \exp \frac{-(n_A - vN_A)^2}{2N_A v(1-v)} \tag{0.3}$$

The first two moments of the distributions (0.1) and (0.2) are the same. We have

$$\langle \delta n_A \rangle = \langle n_A - \nu N_A \rangle = 0, \quad \langle (\delta n_A)^2 \rangle = \langle (n_A - \nu N_A)^2 \rangle = \nu (1 - \nu) N_A \tag{0.4}$$

It is not difficult to see that the nonfulfilment of the assumption of the independence of the behavior of separate particles has no effect on the form of the distributions (0.1) and (0.3). Indeed, let the particles travel in groups each consisting on the average of n_g particles and such that the behavior of particles within a group is completely correlated though different groups are statistically independent. The method used in [5] is also applicable in this case provided not separate particles but separate groups are considered. In this case one should understand, in particular, by n_V and n_A the number of such groups in the volumes V and A, respectively, and

$$N_V = V \frac{\rho_*}{n_g \sigma}, \qquad N_A = A \frac{\rho_*}{n_g \sigma} \tag{0.5}$$

Hence in the particular case of $n_g = 1$ one obtains the relations (0.2).

A serious shortcoming of the theory lies in that the volumes must be measured discretely and be multiples of the "minimal" volume $n_g \sigma / (\rho_* A)$. Therefore any volume A can only be described with a relative error of the order of $n_g \sigma / (\rho_* A)$, which limits the applicability of the theory when dealing with numbers of particles in small volumes. With an unbounded increase of A this error ceases to be of any importance; then the relations given above become accurate.

In the general case it is necessary when analyzing a disperse system within the framework of the mechanics of continuous media to pass on from the discrete method of describing concentration and other quantities which characterize the state of a disperse system to describing them by using some continuous random functions of coordinates and of time (a phenomenological discussion of a number of problems which have a bearing on our problem can be found in [6]). Some concepts pertinent to such transition were previously given when statistical hydrodynamics of disperse systems was formulated and random motions investigated of the particles and of their fluid phase, whose appearance was in point of fact conditioned by the concentration fluctuations (see, for example, [7]). By employing a more rigorous analysis based on a number of methods developed in statistical physics of fluids and dense gases the relations previously used in [7] can be made somewhat more exact.

It should be emphasized that all our subsequent considerations apply to systems in the "equilibrium" state in which all the macroscopic characteristics which describe the state remain constant within the volume V. The analysis is carried out by using a system of coordinates in which the dispersed phase is permeated by the fluid flow and is on the average in the state of rest.

1. Instantaneous Volume Concentration of Particles. One defines first the function

$$\xi_A (x) = \rho + \zeta_A (x) = \frac{1}{A} \int_A \varepsilon (x') d (x' - x) = \frac{\sigma n_A}{A} \tag{1.1}$$

in which the integration is over the volume A, x is the radius vector of the symmetry center of the volume, and the function $\varepsilon (x)$ is equal to unity in the interior of the particles and zero outside them. It can easily be seen that the function $\xi_A (x)$ is continuous and differentiable.

By using the expression (0.4) and the definition (0.5) of the number N_A a representation for the variance of $\xi_A (x)$ is obtained from (1.1) which, in view of what was said above, is valid for $\langle n_A \rangle \gg 1$:

$$\langle \zeta_A^2 (x) \rangle = \frac{\rho^2}{\langle n_A \rangle} \left(1 - \frac{\rho}{\rho_*} \right) \tag{1.2}$$

whence it is seen that statistical characteristics of $\xi_A (x)$ depend to a considerable extent on the size of the volume A appearing in (1.1). In fact, when deriving (1.2) it was assumed that $n_g = 1$.

In particular, for $\langle n \rangle \to \infty$ the function $\xi_A(x)$ approaches the constant ρ; for $\langle n_A \rangle \to 0$ its variance increases without bounds; this does not make sense from the physical point of view. Therefore the question now arises as to what volume A should be selected in (1.1) for a physically adequate definition of $\xi_A(x)$. To answer this question let us consider a realization of a "homogeneous" distribution of particles in space to which a function $\xi (x)$ corresponds identically equal to its mean value ρ. In such state the particles are distributed in a regular manner and are found, for example, at the nodes of a regular lattice. To assume

that such states do exist seems absolutely indispensable at least within the framework of the statistical theory of the type under consideration; for comparison with an analogous case in the statistical physics of fluids see [8].

One assumes, for simplicity, that all particles are of the same shape. Then it is natural to think that the volume A appearing in (1.1) is similar in shape to the volume of a single particle in a system with a specified type of regular packing. It is required that the quantity $\xi_A(x_0)$, where x_0 is the center of gravity of any particle, be exactly equal to ρ. If $A \leq \sigma$, then it is obvious that the volume A is mainly positioned within a particle so that $\xi_A(x_0) > \rho$ and perhaps $\xi_A(x_0) > \rho_*$. The latter, however, does not make sense from the physical point of view since $\xi_A(x_0)$ should not exceed the value ρ_* which corresponds to the densely packed state. If $A > \sigma$, $A < \sigma_\rho$, then again $\xi_A(x_0) > \rho$. Finally, let $A > \sigma_\rho$. Since the particles are regularly positioned, it is clear that if the volume A exceeds only slightly σ_ρ, then within this volume a unique particle can be found with center at the point x_0 such that $\xi_A(x_0) < \rho$. It can thus be inferred that the volume A should be equal to the average volume of a particle in the system σ_ρ.

One can also select $A \gg \sigma_\rho$; then the quantity $\xi_A(x_0)$ is identical with ρ. However, this is a much more crude description of the local concentration values of a monodisperse system than the most detailed possible description which corresponds to the equality $A = \sigma_\rho$. For $A < \sigma_\rho$ the function $\xi_A(x)$ defined in accordance with (1.1) has no straightforward physical sense.

The shape of the volume A is determined by the form of a particle average volume [8] and depends first of all on the form of the particles and also on the type of their regular packing. It can be determined from the equality of $\xi(x)$ to the quantity ρ when the point x is displaced from the center of the particle x_0. In actual disperse systems the packing of particles is usually chaotic; moreover, different particles can be of different shape and can be differently oriented in space. Therefore, for simplicity one can consider the volume A as being a spherical volume.

Even for $A = \sigma_\rho$ the concentration of the disperse system is described only locally by the function (1.1). Indeed, it is not difficult to see that the quantities $\xi_A(x_j)$, where x_j ($j = 1, \ldots, n_V$) are the radius vectors of the particle centers and are equal to or exceed ρ not only for a homogeneous but also for any distribution of particles in space even if the system is locally rarified in the neighborhood of some particles. To eliminate this disadvantage the continuous function $\rho(x) = \rho(t_0, x)$ describing the local volume concentration of a disperse system at a time instant will be defined with the aid of the relation

$$\rho(x) = \rho + \delta\rho(x) = \frac{1}{A}\int_A \xi_A(x' - x)\,dx' \qquad (1.3)$$
$$A = \sigma_\rho, \quad \langle(\delta\rho(x))^2\rangle \equiv \langle\zeta_A^2(x)\rangle$$

The use of the function (1.3) corresponds to a perfectly natural notion that from the macroscopic point of view any quantity describing a local state of a disperse system can only be defined with an accuracy up to the mean volume of an individual particle. The relation (1.3) represents one of the possible formal definitions in statistical physics [8, 9] of the instantaneous specific volume of a particle with subscript j

$$\sigma_j = \sigma / \rho(x_j), \qquad j = 1, \ldots, n_V \qquad (1.4)$$

Thus, the mean specific volume of a particle plays the part of the least "physically small" volume of a disperse system which can be considered within the framework of the continual theory.

The variance will now be calculated of the function $\rho(x)$. To this end, a large volume $A \ll V$, $\langle n_A\rangle \gg 1$ is considered consisting of n_A specific volumes (1.4) where the space distribution of particles at the instant t_0 is completely determined, as stated above, by either the quantities σ_j or the quantities $\rho(x_j)$. Of course, for statistically independent particles these quantities can be regarded as independent. For $\langle n_A\rangle \gg 1$ one has the equality

$$\delta\rho_A = \frac{\sigma\delta n_A}{A} \approx \frac{1}{\langle n_A\rangle}\sum\delta\rho_j, \quad \delta\rho_j = \rho(x_j) - \rho, \quad 1 \leqslant j \leqslant \langle n_A\rangle \qquad (1.5)$$

The quantities $\delta\rho_j$ satisfy all the assumptions whose fulfillment makes the central limit theorem of the probability theory valid for their sum. Consequently, it can be asserted that for $\langle n_A\rangle \gg 1$ the quantity $\delta\rho_A$ has a Gaussian distribution whose variance is equal to the sum of equal variances of the random components $\delta\rho_j/n_A$ in (1.5). By using the relation (0.3) the distribution can be written as

$$W(\delta \rho_A) \approx \left[\frac{\langle n_A \rangle}{2\pi \rho^2 (1 - \rho/\rho_*)} \right]^{1/2} \exp \frac{- \langle n_A \rangle (\delta \rho_A)^2}{2\rho^2 (1 - \rho/\rho_*)} \tag{1.6}$$

Here, as in (0.3), the exact equality has been replaced by an approximate one because the obvious constraints $-\rho \le \delta \rho_A \le \rho_* - \rho$ or $0 \le n_A \le N_A$ have been ignored. This is quite admissible in view of the smallness of the relative fluctuations for $\langle n_A \rangle \gg 1$. From (0.4), (1.5), and (1.6) the formula

$$\langle (\delta \rho)^2 \rangle = \langle (\delta \rho^{(j)})^2 \rangle = \rho^2 (1 - \rho/\rho_*) \tag{1.7}$$

is now obtained and will be used later when one proceeds to a spectral description of concentration fluctuations of a disperse system. Formally, one could have obtained (1.7) from (1.2) and (1.5) using that $\langle n_A \rangle = 1$. However, the latter contradicts the assumption $\langle n_A \rangle \gg 1$ for the validity of the relation (1.2).

2. Partial Spectral Density of Concentration Fluctuations. The quantity $\delta \rho (\mathbf{x})$ of (1.3) will now be considered as a random function of a space point; it is represented in the form

$$\delta \rho (\mathbf{x}) = \int e^{i\mathbf{kx}} dz_\rho \tag{2.1}$$

where the integration is over the entire wave space and dz_ρ is the spectral measure of the field $\delta \rho (\mathbf{x})$. To calculate the spectral density

$$\Phi_{\rho,\rho} (\mathbf{k}) = \lim \langle dz_\rho {}^* dz_\rho \rangle (d\mathbf{k})^{-1} \qquad (d\mathbf{k} \to 0)$$

the methods developed in statistical physics [9, 10] will be employed. Following [10] the "detailed" concentration of a disperse system and its Fourier transformation are represented in the form

$$\nu (\mathbf{x}) = \frac{\sigma}{V} \sum \delta (\mathbf{x} - \mathbf{x}_j), \qquad F\nu (\mathbf{x}) = \frac{\sigma}{V} \sum e^{i\mathbf{kx}_j} \qquad (1 \leqslant i \leqslant n_V) \tag{2.2}$$

In view of the equivalence of particles and statistical homogeneity of the space, the values of $\nu (\mathbf{x})$ at different points can be considered as statistically independent, that is, the random field $\delta \nu (\mathbf{x}) = \nu (\mathbf{x}) - \langle \nu \rangle$, $\langle \nu \rangle = \langle \nu (\mathbf{x}) \rangle$ is white noise. Clearly in this case $\Phi_{\nu,\nu} (\mathbf{k}) = \Phi = $ const, which follows, for example, from the second relation (2.2). From our previous considerations, however, it becomes clear that the description of a system with the aid of the function $\nu (\mathbf{x})$ within the framework of a continual theory does not make much sense, one of the reasons being that its variance does not assume any finite value. This difficulty can usually be avoided by using a method proposed by Massignon [9, 10]. Namely, the δ-functions in the sum (2.2) are replaced by other distributions in the sense of Schwartz; they can be either functions or measures with the property

$$\int_V \Theta (\mathbf{x} - \mathbf{x}_j) d\mathbf{x} \equiv 1$$

From the physical point of view this indicates that the position of the center of any particle can be determined with an accuracy up to a volume σ_0 within which $\Theta (\mathbf{r})$ is different from zero. In statistical physics one employs, as a rule, for $\Theta (\mathbf{r})$ some smooth function which decreases sufficiently rapidly as $\mathbf{r} \to \infty$ (Massignon himself used the Gaussian function [9]). The rate of this decrease as well as the angular dependence $\Theta (\mathbf{r})$ (its deviation from some isotropic function) is determined by the type of intermolecular interaction in the fluid or solid system of many particles and by a short- or long-range order which is present in it.

In view of chaotic packing of real particles in a disperse system the function $\Theta (\mathbf{r})$ can be considered as an isotropic function of $r = |\mathbf{r}|$. To be specific $\Theta (\mathbf{r})$ will be expressed in terms of a Heaviside unit step function, that is, we set

$$\Theta (\mathbf{r}) = \frac{1}{\sigma_0} Y (a_0 - r), \qquad Y (x) = \begin{cases} 1, & x > 0 \\ 0, & x < 0 \end{cases} \qquad \sigma_0 = \frac{4}{3} \pi a_0^3 \tag{2.3}$$

The function

$$\rho (\mathbf{x}) = \frac{\sigma}{\sigma_0 V} \sum Y (a_0 | \mathbf{x} - \mathbf{x}_j |) \qquad (1 \leqslant i \leqslant n_V) \tag{2.4}$$

which is obtained from ν (**x**) in (2.2) by replacing the δ-functions by the functions Θ of (2.3), is subsequently identified with ρ (**x**) of (1.3). Using the relations (2.1), (2.2) and employing a standard approach [10] for determining $\Phi_{\rho,\rho}$ (**k**) by $\Phi_{\nu,\nu}$(**k**), one obtains the relations

$$\langle(\delta\rho)^2\rangle = \int \Phi_{\rho,\rho}(\mathbf{k})\,d\mathbf{k}$$

$$\Phi_{\rho,\rho}(\mathbf{k}) = \frac{\Phi}{\sigma_0}\frac{\sigma}{V}\int e^{i\mathbf{k}\mathbf{r}}Y(a_0-r)\,d\mathbf{r} = 3\Phi\frac{\sigma}{V}\frac{\sin ka_0 - ka_0\cos ka_0}{(ka_0)^3} \qquad (2.5)$$

$$(\Phi = \text{const})$$

Comparing the variance ρ (**x**) computed from (2.7) and the quantity (1.8), one obtains the expression

$$\Phi = \frac{V}{\sigma}\frac{\sigma_0}{8\pi^3}\rho^2\left(1 - \frac{\rho}{\rho_*}\right) \qquad (2.6)$$

The volume σ_0 characterizes the degree of "coarseness" [10] of the particle system under consideration, that is, it describes the size of the minimal "cell" in space and must be the error with which various local properties of the system can be determined; the latter possess a physical meaning from the macroscopic point of view. Hence it follows directly that the volume σ_0 must be equal to the volume $A = \sigma_\rho$ which appears in the definitions (1.1) and (1.3). This assertion represents one of the possible hypotheses with regard to the quantity σ_0.

It would have also been possible to replace the expression (2.2) for ν (**x**) by a more exact formula in which the $\delta(\mathbf{r})$ were correspondingly replaced by the functions $\sigma^{-1}\varepsilon(\mathbf{r})$ introduced in (1.1) and then to attempt to identify $\rho(\mathbf{x})$ with the sum thus obtained. The latter is equivalent to admitting that $\sigma_0 = \sigma$, so that a_0 in (2.3) and (2.4) is identical with the radius a of a sphere whose volume is equal to σ.

Finally, it is admissible to consider a priori σ_0 as a measure of volume within which one may find the center of a particle for a given packing of particles in space, that is, to identify σ_0 with the mean free volume σ_f in the system. The free volume can also be represented approximately by $\sigma_f \approx \sigma_\rho - c_*$, where $\sigma_* = \sigma/\rho_*$ is the minimal value of σ_ρ attained in the state of dense packing [8]. Some relations implied by these hypotheses have already been considered by the author in a number of articles.

To find an adequate definition of the quantity σ_0 the fluctuations of the number of particles are again considered in a large volume A. For simplicity it is assumed that the volume is a parallelepiped with sides l_j (j =1, 2, 3). Using (2.1), the deviation of the number of particles n_A in the volume from the mean value $\langle n_A \rangle$ can bewritten as

$$\delta n_A = \frac{1}{\sigma}\int \delta\rho(\mathbf{x})\,d\mathbf{x} = \frac{1}{\sigma}\int \prod_{m=1}^{3}\frac{e^{ik_m x_m}-1}{ik_m}\,dz_\rho \qquad (2.7)$$

Employing the familiar properties of the representation (2.1), the relation

$$\langle(\delta n_A)^2\rangle = \frac{1}{\sigma^2}\langle|\delta\rho(\mathbf{x})\,d\mathbf{x}|^2\rangle = \frac{8}{\sigma^2}\int \prod_{m=1}^{3}\left(\frac{1-\cos k_m x_m}{k_m^2}\right)\Phi_{\rho,\rho}(\mathbf{k})\,d\mathbf{k}$$

$$= 3\frac{\sigma_0}{\sigma^2}\frac{\rho^2}{\pi^3}\left(1-\frac{\rho}{\rho_*}\right)\int \prod_{m=1}^{3}\left(\frac{1-\cos k_m x_m}{k_m^2}\right)\frac{\sin ka_0 - ka_0\cos ka_0}{k^3}\,d\mathbf{k} \qquad (2.8)$$

is obtained from (2.5)-(2.7).

By selecting l_m such that $l_m \gg a_0$ one obtains from (2.8)

$$\langle(\delta n_A)^2\rangle = \frac{\sigma_0}{\sigma^2}\rho^2\left(1-\frac{\rho}{\rho_*}\right)l_1 l_2 l_3 = \frac{\sigma_0}{\sigma}\rho\left(1-\frac{\rho}{\rho_*}\right)\langle n_A\rangle \qquad (2.9)$$

Finally, comparing the above relation with (0.4), one obtains

$$\sigma_0 = \sigma\rho^{-1} = \sigma_\rho, \qquad a_0 = a\rho^{-1/3} \qquad (2.10)$$

Instead of smoothing the "detailed" concentration (2.3) by "spreading about" each particle over the mean specific volume, the spectrum of concentration disturbances could be cut off from its short-wave region [9, 10]. In fact, this procedure is equivalent to the Massignon method, the difference being that it is not

in the real but in the wave space. On the other hand, it is equivalent to applying the familiar method of Debye for determining the number of harmonics of the Fourier representation of the random quantity $\delta\rho(x)$ from the number of degrees of freedom of the multiparticle system under consideration. In this case the integration over the wave space is, in fact, replaced by the addition over the Brillouin zone for the system.

By introducing the critical wave number k_0 at which the cut off of the spectrum is effected we can write

$$\Phi_{\rho,\rho}(k) = \Phi' \, Y \, (k_0 - k) \tag{2.11}$$

The constants k_0 and Φ' are determined from the previous conditions, that is, by demanding that the values of the variances of the quantities $\rho(x)$ and n_A be equal to those calculated above. In this manner one obtains

$$\Phi' = \frac{3}{4\pi} \frac{\rho^2}{k_0^3} \left(1 - \frac{\rho}{\rho_*}\right), \qquad k_0 = \left(\frac{9\pi}{2}\right)^{1/3} \frac{1}{a_0} = \left(\frac{9\pi\rho}{2}\right)^{1/3} \frac{1}{a} \tag{2.12}$$

The functions (2.3) and (2.11) represent Fourier transformations of each other; in our theory both these functions are equally worthy of being considered; this is due to the arbitrariness in the choice of the smoothing function $\Theta(r)$. In fact, the form of $\Theta(r)$ should be determined by using the properties of the packing of the particles as it is done, for example, for crystal lattices. However, in disperse systems the actual packing of particles does not belong to any specified type, and to be able to apply this method statistical weights of packings of various regular types must be found. It is not known at present how to solve this problem; therefore preference for either the function (2.3) or (2.11) would signify an excess in the precision of the theory. However, in specific calculations preference can be given to the considerably simpler function (2.11).

It is now assumed that the behavior of the neighboring particles is correlated and that $n_g > 1$. The arguments used when deriving the relations in Sections 1 and 2 remain valid also in this case provided that separate particles are replaced in our considerations by separate groups (packets) of particles, each consisting of n_g particles. In particular, the basic form of the formulas (1.8), (2.3), (2.11), and others remains the same even for $n_g \neq 1$; however, the expressions for A, σ_0, a_0, and k_0 obtained previously should be replaced by

$$A = \sigma_0 = \frac{n_g \delta}{\rho}, \qquad a_0 = a\left(\frac{n_g}{\rho}\right)^{1/3}, \qquad k_0 = \left(\frac{9\pi\rho}{2n_g}\right)^{1/3} \frac{1}{a} \tag{2.13}$$

The reason for the increase in the volumes A and σ_0 and in the quantity a_0 is quite obvious since statistical links now appear between the particles; in particular, a_0 can be considered simply as a characteristic linear size of a packet or a particle "correlation radius." The corresponding decrease in k_0 describes the reduction in the system Brillouin zone, that is, a reduction in the number of harmonics in the Fourier representation of the random field $\delta\rho(x)$. The latter is related to the reduction of the total number of translational degrees of freedom of particles when they are combined into packets.

Basically, the quantity n_g depends on the physical properties of the phases of the disperse system and on the type of their mean motion; the latter is not known a priori but can be estimated within the framework of statistical hydromechanics of disperse systems (see, for example, footnotes in [7]).

3. The Dynamics of Concentration Fluctuations of a Monodisperse System. We have considered so far only the characteristics of a random field $\delta\rho(x)$ at some fixed instant t_0. Now the change of the field in time will be investigated; this is absolutely indispensable in studying the internal structure of chaotic local motions (pseudoturbulence) of disperse systems.

The characteristic time of a change in the random field T_ρ is of the same order of magnitude as the external time scale T of the pseudoturbulent motion by which this change is caused [7]. Therefore, to describe the dynamics of concentration fluctuations one does not find it convenient to apply the standard diffusion equation in the Fick form, which is only valid in the limit $T_\rho/T \to \infty$; the problem now arises of finding a generalized diffusion equation which would permit the investigation of diffusion processes with a characteristic duration $t \gtrsim T$.

There are various methods for obtaining such an equation, and one can subdivide them into two kinds. The methods of the first kind reduce to having the diffusion coefficients dependent on t so that for t → ∞ they approach the familiar stationary diffusion coefficients. These methods are based on variances of displacement of an individual particle and are characteristic for the theory of turbulent diffusion, the theory of Brownian motion for small t, etc. In our case it is not expedient to apply this approach since it is difficult then to use the correlation theory of stationary random fields for describing $\rho(t, x)$.

The methods of the second kind reduce to adding terms containing higher time-derivatives to the Fick equation. However, there is no method available which would enable one to estimate accurately (even in the simplest cases) the constant coefficients which appear in these terms. It is obvious that the most rigorous method for deducing a general diffusion equation would involve the introducing of distribution functions for the coordinates, the velocities, and the accelerations of all orders for the suspended particles; it would also involve proceeding from the continuity differential equations for these functions in the corresponding phase space to finite-difference equations [11]. The main disadvantage of such an approach lies in that one has to compute all moments of the distribution functions for the velocities of the particles.

There exists another feasible approach which consists in considering the continuity equations for the last functions only; in the latter the details of disturbances suffered by the moving particles are taken into account phenomenologically by introducing concentrations of "scattering centers" and effective scattering cross section or by mean lengths of free paths of the particles between two consecutive scatter reports. A diffusion equation obtained in this manner was already employed in [7]. Finally, one can also consider a simple simulation of a random walk of a particle in space [3] assuming that the displacement velocity of the particle is finite (this problem was analyzed in detail in [12] for a single-dimensional walk). An element of arbitrariness is also contained in these methods when determining the definite values of the velocity of the walk, of the characteristic duration of motion without a change in its direction, etc. All the described methods lead to the diffusion equation (3.1).

The diffusion equation of particles is written as

$$T_0 \frac{\partial^2 \rho}{\partial t^2} + \frac{\partial \rho}{\partial t} \approx \left(\frac{\partial}{\partial x} D \frac{\partial}{\partial x} \right) \rho \qquad (3.1)$$

In the above D is the tensor of the diffusion coefficients of particles, which can be calculated within the framework of the statistical hydromechanics of disperse systems [7], and the quantity T_0 satisfies the relation

$$T_0 \sim T \sim L \langle w'^2 \rangle^{-1/2} \qquad (3.2)$$

where L is the characteristic linear scale of pseudoturbulent motion and w' is the particle pulsation velocity. With $T_0 \to 0$ Eq. (3.1) becomes Fick equation. Some considerations which follow from (3.1) enable one to adopt (see the footnote to [7])

$$T_0 \approx \text{tr } D \langle w'^2 \rangle^{-1}, \qquad \text{tr } D = D_{ii} \qquad (3.3)$$

It is not convenient to apply the estimates (3.2) and (3.3) since the quantities L and $\langle w'^2 \rangle$ which appear in them are not known a priori. It is therefore better to employ sometimes the approximate relation

$$T_0 \approx T_\rho \qquad (3.4)$$

where T_ρ is the time scale of the concentration fluctuations $\delta \rho$ (t, x) calculated below. The expressions (3.2) and (3.4) are only approximate.

Equation (3.1) for the quantity $\delta \rho$ (t, x) determines a "regular" degeneration of the random field of concentration fluctuations due to particle diffusion. Assuming that the initial distribution of particles and the boundary conditions are given, the problem thus obtained can be considered as a problem with initial data though from physical considerations it is clear that only those solutions need be considered which decrease with time. In reality, such regular damping of fluctuations is compensated by their random accumulation; this, however, has been completely disregarded in Eq. (3.1). To take into account the accumulation one should introduce an additional source term on the right-hand side of (3.1). It is essential that the characteristic time of the varying forces which cause the appearance of fluctuations, that is, the time for a change in this term, is of the same order of magnitude as the internal time scale of pseudotrubulence

τ which characterizes the internal interaction in the system leading to the establishing of local equilibrium [7]. In view of the inequality $\tau \ll T$ the random quantities whose time scale is equal to τ can be regarded as quantities with independent increments if only the processes whose characteristic duration is of order T or more are of primary interest.

The quantity τ represents the characteristic minimum time of local interactions for any statistical system in nonequilibrium statistical mechanics. The use of the inequality $\tau \ll T$ is equivalent to considering this sytem in the familiar random-phases approximation. Some examples will be given to clarify the matter. Thus in the kinetic theory of gases the part of the time τ is played by the time of establishing the state of molecular chaos, that is, the mean time between successive collisions of a molecule. The random-phases approximation is equivalent in this case to the hypothesis of molecular chaos, and instead of the Liouville equation for gas one is able to consider the familiar Boltzmann equation. In the latter case all processes of duration $\sim \tau$ are generally disregarded (that is, one ignores the so-called region of "molecular noise" due to local infringements of the molecular state of chaos); for this reason the equation which describes "regular" approximation of gas to the macroscopic state of maximal entropy is not suitable for describing the generation of fluctuations in gases. In the theory of Brownian motion the quantity τ is identical with the time during which a suspended particle undergoes several molecular impacts. On the other hand, the part of the time T is played in these systems by the time of equalization of macroscopic parameters (temperature, density) of a gas in a physically small volume and as well by the characteristic retardation time of a Brownian particle due to the forces of viscous interaction with the fluid, respectively.

In view of what was said above, the stochastic equation for $\delta\rho$ (t, x) can be written as

$$T_0 \frac{\partial^2 \delta\rho}{\partial t^2} + \frac{\partial \delta\rho}{\partial t} - \left(\frac{\partial}{\partial x} D \frac{\partial}{\partial x}\right) \delta\rho \approx c(t, x) \tag{3.5}$$

where c(t,x) is a random quantity whose spectral density is independent of the pulsation frequency ω.

Similarly as in (2.1) the random variables will now be represented by stochastic Fourier-Stieltjes integrals:

$$\delta\rho = \iint e^{ikx + i\omega t} dZ_\rho, \qquad c = \iint e^{ikx + i\omega t} dZ_c \tag{3.6}$$

Inserting (3.6) in (3.5) one obtains

$$[i\omega + (kDk - T_0 \omega^2)] dZ_\rho = dZ_c \tag{3.7}$$

Hence one obtains the expression for the complete spectral density of the random process $\delta\rho$ (t, x):

$$\Psi_{\rho,\rho}(\omega, k) = \frac{\Psi_{c,c}(k)}{\omega^2 + (kDk - T_0\omega^2)^2}, \qquad \Psi_{c,c}(k) = \lim_{d\omega, dk \to 0} \frac{\langle dZ_c^* dZ_c \rangle}{dk\, d\omega} \tag{3.8}$$

By employing the obvious relation

$$\Phi_{\rho,\rho'_\kappa}(k) = \int_{-\infty}^{\infty} \Psi_{\rho,\rho}(\omega, k)\, d\omega$$

one obtains from (3.8) the representation

$$\Psi_{\rho,\rho}(\omega, k) = \frac{kDk}{\pi} \frac{\Phi_{\rho,\rho}(k)}{\omega^2 + (kDk - T_0\omega^2)^2} \tag{3.9}$$

In the above $\Phi_{\rho,\rho}(k)$ is the partial spectral density evaluated in Section 2. The space-time correlation function of the process $\delta\rho$ (t, x) is expressed in the standard form

$$R_{\rho,\rho}(\tau, r) = \langle \delta\rho(t, x) \delta\rho(t + \tau, x + r) \rangle = \iint e^{ikr + i\omega\tau} \Psi_{\rho,\rho}(\omega, k)\, d\omega\, dk \tag{3.10}$$

Using (3.9) and (3.10), it is not difficult to calculate the quantity T_ρ appearing in (3.4). By using the formula (2.11) one obtains

$$T_\rho = \frac{1}{R_{\rho,\rho}(0,0)} \int_{-\infty}^{\infty} R_{\rho,\rho}(\tau, 0)\, d\tau = \int \frac{\Phi' Y(k_0 - k)}{kDk} dk \left(\int \Phi' Y(k_0 - k)\, dk\right)^{-1} \tag{3.11}$$

Employing the results of [7], it can be assumed that the pseudoturbulence of the phases of a disperse system has an axial symmetry. By adopting suitable coordinate axes and denoting in these axes the eigenvalues of the tensor D by D_1 and $D_2 = D_3$ respectively one obtains from (3.11) that

$$T_\rho = \frac{3(1+\gamma^2)}{\gamma} \arctan\left(\frac{1}{\gamma}\right) \frac{1}{k_0^2 D_1}, \qquad \gamma = \left(\frac{D_2}{D_1 - D_2}\right)^{1/2} \tag{3.12}$$

It should be emphasized that in contrast to the simultaneous statistical characteristics of concentration disturbances which in accordance with the results obtained in Sections 1 and 2 do not depend on the development level of the pseudoturbulence of a disperse system, the quantities by which the behavior of these disturbances is characterized in time are related (via the coefficients of the particle diffusion) to the intensity of the pseudoturbulence.

4. Generalization of Polydisperse Systems. Monodisperse systems of particles which do not differ from each other have only so far been considered by us. In fact, the particles may differ with respect to some attribute (or attributes) so that in the dispersed phase one has to differentiate between different components (fractions).

First, it is assumed that the volume V is occupied by particles of J different fractions, the total number of particles of the j-th type being equal to $n_V{}^{(j)}$ (subsequently, all quantities referring to such particles carry a superscript j). The mean state of such a polydisperse system can be described with the aid of the mean volume concentration ρ and of the partial concentrations of particles of different types $\rho^{(j)}$:

$$\rho^{(j)} = \frac{n_V^{(j)} \sigma^{(j)}}{V}, \qquad \rho = \frac{1}{V} \sum_{j=1}^{J} n_V^{(j)} \sigma^{(j)} = \sum_{j=1}^{J} \rho^{(j)} \tag{4.1}$$

In principle the analysis of fluctuations of the number of particles of different types in a volume $A \ll V$ can be carried out using the method employed in [5]. Thus relations of the same kind as those in the introductory part are obtained. However, in subsequent considerations only the distributions of the numbers of particles in a sufficiently large volume A are of interest to us when $\langle n_A^{(j)} \rangle \gg 1$, $|\delta n_A^{(j)} n / \langle n_A^{(j)} \rangle| \ll 1$ and when the equality

$$n_A^{(j)} \sigma^{(j)} \left(\sum_{i=1}^{J} n_A^{(i)} \sigma^{(i)} \right)^{-1} \approx \alpha^{(j)} = \frac{\rho^{(j)}}{\rho} \tag{4.2}$$

can be assumed approximately, where $\alpha^{(j)}$ is the specific volume content of the particles of the j-th fraction in V. Employing the relations (4.2), one is able to represent formally the volume A as the sum of the volumes $A^{(j)} = \alpha^{(j)} A$ such that the particles of the j-th type are found inside $A^{(j)}$ with very large probability [see also the distribution (0.3)]. In other words, the volume A is interpreted as a superposition of J lattices, the volumes of whose cells are equal to $\sigma^{(j)}/\rho_*$, their total number being

$$N_A^{(j)} = \frac{\alpha^{(j)} A \rho_*}{\sigma^{(j)}} \qquad (j = 1, \ldots, J) \tag{4.3}$$

The entire volume V occupied by the disperse system can be described in a similar manner. If the considerations in [5] are repeated word for word, the distribution is obtained of the particles of the j-th fraction in the form

$$W(n_A^{(j)}) \approx \frac{1}{[2\pi N_A^{(j)} \nu (1-\nu)]^{1/2}} \exp \frac{-(n_A^{(j)} - \nu N_A^{(j)})^2}{2 N_A^{(j)} \nu (1-\nu)} \tag{4.4}$$

In the above the quantity ν, which takes the place of ν in (0.3), is given by

$$\nu = \frac{\langle n_A^{(j)} \rangle}{N_A^{(j)}} = \frac{\rho}{\rho_*}, \qquad \langle n_A^{(j)} \rangle = \nu N_A^{(j)} \tag{4.5}$$

and is the same for particles of different fractions.

Moreover, the distribution of all particles can be written as

$$W(n_A^{(1)}, \ldots, n_A^{(J)}) = \sum_{j=1}^{J} W(n_A^{(j)}) \tag{4.6}$$

From (4.4) and (4.6) the relations

$$\langle \delta n_A^{(j)} \rangle = 0, \qquad \langle (\delta n_A^{(j)})^2 \rangle = v(1-v)N_A^{(j)} = (1-v)\langle n_A^{(j)} \rangle \tag{4.7}$$

are obtained, which replace (0.4).

The functions $\xi^{(j)}(\mathbf{x})$, $\rho^{(j)}(\mathbf{x})$ as well as their variances are determined by analogy with (1.1)-(1.3):

$$\xi^{(j)}(\mathbf{x}) = \frac{1}{\sigma_\rho^{(j)}} \int\limits_{\sigma_\rho^{(j)}} \varepsilon(\mathbf{x}') d(\mathbf{x}' - \mathbf{x}), \qquad \sigma_\rho^{(j)} = \frac{\sigma^{(j)}}{\rho^{(j)}}$$

$$\rho^{(j)}(\mathbf{x}) = \frac{1}{\sigma_\rho^{(j)}} \int\limits_{\sigma_\rho^{(j)}} \xi^{(i)}(\mathbf{x}' - \mathbf{x}) d\mathbf{x}' = \rho^{(j)}(t_0, \mathbf{x}) \tag{4.8}$$

$$\langle \delta \xi^{(j)2}(\mathbf{x}) \rangle = \langle \delta \rho^{(j)2}(\mathbf{x}) \rangle = \rho^{(j)}\rho\left(1 - \frac{\rho}{\rho_*}\right) = \alpha^{(j)}\rho^2\left(1 - \frac{\rho}{\rho_*}\right)$$

The variance $\rho(t_0, \mathbf{x})$, which is the sum of partial concentrations (4.8), is equal to the sum of the variances $\rho^{(j)}(\mathbf{x})$ and can be expressed, as before, by the formula (1.7). By making use of exactly the same considerations as in Section 2 one arrives at expressions for the partial spectral densities which are of the same form as the relations (2.3) and (2.11). By comparing the variance $\rho^{(j)}(\mathbf{x})$ calculated from the expressions for $\Phi_{\rho,\rho}^{(j)}(\mathbf{k})$ and the quantity $\langle \delta \rho^{(j)2}(\mathbf{x}) \rangle$ of (4.8) one can determine the constants $\Phi^{(j)}$ and $\Phi'^{(j)}$ which appear in them. In this manner one obtains two formulas for $\Phi_{\rho,\rho}^{(j)}(\mathbf{k})$ which correspond to the formulas (2.3) and (2.11):

$$\Phi_{\rho,\rho}^{(j)}(\mathbf{k}) = \frac{3\sigma_0^{(j)}}{8\pi^3}\rho^{(j)}\rho\left(1 - \frac{\rho}{\rho_*}\right)\frac{\sin ka_0^{(j)} - ka_0^{(j)}\cos ka_0^{(j)}}{(ka_0^{(j)})^3}$$

$$\Phi_{\rho,\rho}^{(j)}(\mathbf{k}) = \frac{3}{4\pi}\frac{\rho^{(j)}\rho}{(k_0^{(j)})^3}\left(1 - \frac{\rho}{\rho_*}\right)Y(k_0^{(j)} - k) \tag{4.9}$$

The quantities $a_0^{(j)}$, $k_0^{(j)}$ appearing in (4.9) as well as the volume $\sigma_0^{(j)}$ are determined, as before, from the consistency of the expression for the variance of the number of particles of the j-th type obtained from (4.9) and the relations (4.8). Then one has

$$\sigma_0^{(j)} = \frac{\sigma^{(j)}}{\rho} = \sigma_\rho^{(j)}, \qquad a_0^{(j)} = \frac{a^{(j)}}{\rho}, \qquad k_0^{(j)} = \left(\frac{9\pi\rho}{2}\right)^{1/3}\frac{1}{a^{(j)}}$$

It is noted that $\sigma_0^{(j)} \neq A^{(j)}$ in contrast with describing a disperse system with particles of the same type.

The dynamics will now be considered of fluctuations of partial concentrations of particles. It is obvious that in the general case it is not possible for a coordinate system to be selected such that the mean values of all the components of the disperse phase vanish simultaneously. The velocities $\langle \mathbf{w}^{(j)} \rangle$ must therefore be introduced, and the diffusion equations (3.1) replaced by the corresponding equations of convective diffusion for particles of various fractions. Then applying similar considerations, the following relations for the complete spectral densities are obtained:

$$\Psi_{\rho,\rho}^{(j)}(\omega, \mathbf{k}) = \frac{\Phi_{\rho,\rho}^{(j)}(\mathbf{k})}{M^{(j)}(\omega, \mathbf{k})}\left(\int\limits_{-\infty}^{\infty}\frac{d\omega}{M^{(j)}(\omega, \mathbf{k})}\right)^{-1}$$

$$M^{(j)}(\omega, \mathbf{k}) = (\omega + \langle \mathbf{w}^{(j)} \rangle \mathbf{k})^2 + (\mathbf{k}D^{(j)}\mathbf{k} - T_0^{(j)}\omega^2)^2 \tag{4.10}$$

In conformity with the relation (3.4) for a monodisperse system one can assume that the times $T_0^{(j)}$ of (4.9) and (4.11) are approximately equal to the time scales $T_\rho^{(j)}$ of the fluctuations $\delta\rho^{(j)}(t, \mathbf{x})$. The latter can easily be computed using a coordinate system in which the velocity of the mean motion of the particles of the specified j-th fraction is equal to zero. One then comes to the conclusion that $T_\rho^{(j)}$ is given by means of the relation (3.12) with all quantities which describe the physical properties and the particle diffusion carrying the superscript j.

Now, let the particles of the disperse phase be continuously distributed in a parameter (or parameters) denoted below by λ. In practice, one has to deal mostly with the distribution of particles by their size and

by their density. The corresponding distribution function $\psi(\lambda)$ is introduced which is normalized on the total volume concentration ρ, that is,

$$\int \psi(\lambda) d\lambda = \rho \qquad (4.11)$$

If one considers the particles whose parameter λ is in the interval $(\lambda, \lambda + \Delta\lambda)$ as belonging to some discrete fraction, one can see that all the formulas previously obtained retain their form if the index j is replaced by a functional dependence of various quantities on λ [for example, $\sigma^{(j)} \to \sigma(\lambda)$] and $\rho^{(j)}$ is replaced by $\psi(\lambda) \Delta\lambda$. Moreover, if one proceeds to the limit $\Delta\lambda \to 0$ and instead of discrete sequences of spectral densities one introduces their densities in the space λ, the following relations for these densities are obtained:

$$\Phi_{\rho,\rho}(\mathbf{k}; \lambda) = \frac{3}{4\pi} \frac{\psi(\lambda)\rho}{k_0^3(\lambda)} \left(1 - \frac{\rho}{\rho_*}\right) Y(k_0(\lambda) - k), \qquad k_0(\lambda) = \left(\frac{9\pi\rho}{2}\right)^{1/3} \frac{1}{a(\lambda)}$$

$$\Psi_{\rho,\rho}(\omega, \mathbf{k}; \lambda) = \frac{\Phi_{\rho,\rho}(\mathbf{k}; \lambda)}{M(\omega, \mathbf{k}; \lambda)} \left(\int_{-\infty}^{\infty} \frac{d\omega}{M(\omega, \mathbf{k}; \lambda)}\right)^{-1} \qquad (4.12)$$

$$M(\omega, \mathbf{k}; \lambda) = \,_{1}'(\omega + \langle \mathbf{w} \rangle(\lambda)\mathbf{k})^2 + (\mathbf{k}\mathbf{D}(\lambda)\mathbf{k} - T_0(\lambda)\omega^2)^2$$

Neither is it difficult by using the relations (4.10) or (4.12) to consider various correlation functions which are two-time and two-point. To this end it suffices to employ standard relations of the correlation theory of stationary random processes.

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