THE CORRELATION THEORY OF CONCENTRATION FLUCTUATIONS IN DISPERSED SYSTEMS

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The fluctuations in the volume concentration of the dispersed phase are considered via the correlation theory of stationary random processes; the formula is derived for the rms perturbation in the concentration, which corresponds to a two point two-time correlation function, which is expressed as a simple integral.

The random pulsating motions of particles in the real dispersed system lead to concentration fluctuations resembling the density fluctuations due to the thermal motion of gas molecules. If the individual particles are satistically independent (this is equivalent to the hypothesis of molecular chaos in the kinetic theory of gases), then the spatial and time scales of these fluctuations are of the order of the mean distance between particles and the mean time to pass across this distance respectively. In fact, the suspended particles interact not only by direct collision but also via random pressure fields and velocities on account of the dispersion medium, which perturbs the random motions of the particles. The result is correlation between the behavior of the particles placed fairly close together, and consequent large-scale concentration fluctuations. Examples of these are found in the dense aggregates or clumps containing a fairly large number of particles and cavities filled with uniform dispersion medium. On the whole, such fluctuations resemble the critical fluctuations in density in an ordinary gas or the fluctuations in systems with long-range forces, e.g., in a cloud of charged particles. The position is made even more complicated by the scope for disturbance in the hydrodynamic stability of a spatially uniform flow in a dispersed system and the occurrence of purely hydrodynamic perturbations.

Quantitative evaluation of this nonuniformity, in particular for fluidized beds, is of interest in relation to the marked effect of the degree of nonuniformity on important technological processes in such systems [1]. Also, statistical description of the local concentration in such a system is extremely important in constructing a statistical theory of dispersed systems and formulation of hydrodynamic models for them [2].

The density of dispersed system is characterized below by means of the bulk particle concentration ρ, which is related to the porosity ε by $\rho = 1-\varepsilon$; we put

$$\rho = \rho_0 + \rho', \quad \rho_0 = <\rho>, \quad <\rho'> \equiv 0. \tag{1}$$

Consider the concentration perturbation ρ' as a random function of t and $\mathbf{r}$, which we represent as the following integral [3, 4]:

$$\rho'(t, \mathbf{r}) = \iint e^{i\omega t + i\mathbf{k}\mathbf{r}}\, dZ,$$

where the integration is extended to the entire frequency axis ω and the entire wave space $\mathbf{k}$. A spectral measure dZ of the random process $\rho'(t, \mathbf{r})$ has a number of properties that have been considered in detail [3], the most important of which is expressed by

$$\lim_{d\omega, d\mathbf{k}\to 0} \frac{<dZ^*(\omega, \mathbf{k})\, dZ(\omega', \mathbf{k}')>}{d\omega dk_1 dk_2 dk_3} = \Psi(\omega, \mathbf{k}), \quad d\omega = \omega' - \omega,$$
$$dk_i = k_i' - k_i,$$

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where $\Psi(\omega, \mathbf{k})$ is the spectral density of process $\rho'(t, \mathbf{r})$; there is a theorem [3] that the correlation function of of $\rho'(t, \mathbf{r})$ may be put as

$$R(\tau, \xi) = \langle \rho'(t, \mathbf{r})\, \rho'(t+\tau, \mathbf{r}+\vec{\xi}) \rangle = \iint e^{i\omega\tau + i\mathbf{k}\vec{\xi}}\, \Psi(\omega, \mathbf{k})\, d\omega d\mathbf{k}, \tag{2}$$

which enables us to determine $R(\tau, \vec{\xi})$ for any τ, $\vec{\xi}$, if we know $\Psi(\omega, \mathbf{k})$.

Consider the partial spectral density $\Phi(\mathbf{k})$, which is defined by analogy with (2) for the one-time ($\tau = 0$) two-point ($\vec{\xi} \neq 0$) correlations of process $\rho'(t, \mathbf{r})$; by definition we have

$$\Phi(\mathbf{k}) = \int \Psi(\omega, \mathbf{k})\, d\omega.$$

We assume that the particles are statistically independent, and their positions in space may be defined with any required accuracy; then n', which is the deviation of the true instantaneous number of particles in unit volume from the mean n_0, may be expressed as a sum over δ functions, which correspond to the positions of the centers of the particles [5]. As all the particles are on the same footing and the system is statistically uniform, we can treat as independent the values of n' in any intersecting volumes for any given instant of time, i.e., the spectral density of process $n'(t, \mathbf{r})$, as defined via one-time correlation functions, is not dependent on $\mathbf{k}$ [3]. An analogous result can be obtained directly by expanding the δ functions as Fourier series. It is clear the same statement applies to the random process $\rho'(t, \mathbf{r})$, i.e., we have

$$\Phi(\mathbf{k}) = C = \text{const.} \tag{3}$$

In fact, the particles each have a finite volume, and the position of the centers can be defined only with the accuracy represented by a certain volume σ_f, which is not zero. Formally this means that a particle must be represented not by a δ-function but by the function

$$\Theta(\mathbf{r} - \mathbf{r}_j(t)) = \sigma_f^{-1}\, Y(b_f - |\mathbf{r} - \mathbf{r}_j(t)|), \quad Y(x) = \begin{cases} 1, & x > 0, \\ 0, & x < 0, \end{cases} \tag{4}$$

where $Y(x)$ is a Heaviside function, $\mathbf{r}_j(t)$ is the radius vector of the j-th particle, and b_f is the radius of the sphere having volume σ_f. The particle is, as it were, smeared out over a volume σ_f. We use the functions of (4) in place of the functions $\delta(\mathbf{r} - \mathbf{r}_j(t))$, which is equivalent to the procedure for smoothing out short-wave details of the spectrum, which has been proposed [6] in the statistical mechanics of liquids, although in that particular case the author used a Gaussian function in place of a Heaviside one. As a result, instead of (3) we get [5]

$$\Phi(\mathbf{k}) = 3C\, \frac{\sin kb_f - kb_f \cos kb_f}{(kb_f)^3}. \tag{5}$$

To determine the constant C in (5) we use the result of [7], which gives

$$\langle n'^2 \rangle = \rho_0\, (1 - \rho_0/\rho_*)\, n_0. \tag{6}$$

From (5) we get as follows by representing $\rho'(t, \mathbf{r})$ in the following integral form:

$$\begin{aligned} \langle n'^2 \rangle &= \frac{1}{\sigma^2} \left\langle \left| \int \rho'(t, \mathbf{r})\, d\mathbf{r} \right|^2 \right\rangle = \frac{8}{\sigma^2} \int d\mathbf{k} \prod_{j=1}^{3} \left(\frac{1 - \cos k_j l_j}{k_j^2} \right) \Phi(\mathbf{k}) \\ &\approx 8\pi^3 C l_1 l_2 l_3 \sigma^{-2}, \quad l_1 l_2 l_3 = V = 1, \quad k_j l_j \gg 1. \end{aligned} \tag{7}$$

Comparison of (6) and (7) gives us an expression for C, and in place of (5) we have

$$\Phi(\mathbf{k}) = \frac{3\sigma}{8\pi^3}\, \rho_0 \left(1 - \frac{\rho_0}{\rho_*} \right) \frac{\sin kb_f - kb_f \cos kb_f}{(kb_f)^3}. \tag{8}$$

We also consider what b_f equals in a system of statistically independent particles. The mean specific volume in the system for any individual particle is clearly $\sigma_0 = \sigma\rho_0^{-1}$; but the center of the particle may then not be at any point in the volume σ_0 but only within some other volume $\sigma_f < \sigma_0$, because of the finite volume of the particles and the screening effects of adjacent particles on the displacement of any one particle within its specific volume. By analogy with the terminology used in the statistical physics of liquids, it is convenient to call σ_f the free volume of a particle in the system, which may be determined as the difference between the specific volumes in the actual state and in the close-packed state, when $\rho_0 = \rho_*$, i.e., we have

$$\sigma_f = \sigma_0 - \sigma_*, \quad \sigma_* = \sigma\rho_*^{-1}, \quad b_f = \frac{a}{\rho_0^{1/3}}\left(1 - \frac{\rho_0}{\rho_*}\right)^{1/3}. \tag{a}$$

In the close packed state, σ_f and b_f are zero.

Instead of smoothing out the short-wave part of the spectrum for the local perturbations in concentration by smearing a particle over its free volume, we could use essentially different arguments by considering the truncation of the short-wave part of the spectrum directly in wave space; this operation is in fact an extension of Debye's method of defining the number of harmonics in the Fourier representation of a random process with respect to the number of degrees of freedom in the system. We assume that $\Phi(\mathbf{k}) = 0$ for $k > k_0$ and put

$$\Phi(\mathbf{k}) = C'Y(k_0 - k), \quad C' = \text{const.}$$

We naturally define k_0 and the constant C' such that the integral of $\Phi(\mathbf{k})$ over wave space is equal to the corresponding integral of the function of (8), while $< n'^2 >$ is calculated according to (7), which also would coincide with (6). Then simple steps for a system of statistically independent particles give

$$\Phi(\mathbf{k}) = \frac{3}{4\pi}\frac{\rho_0^2}{k_0^3}\left(1 - \frac{\rho_0}{\rho_*}\right) Y(k_0 - k), \quad k_0 = \left(\frac{3\pi}{2}\right)^{1/3}\frac{1}{b_f}. \tag{10}$$

Equation (10) represents a certain approximation to the spectral density of (8), and it is particularly convenient in practical definition of the pulsation rate in the system, the transport coefficients, etc.(see [2], for example). It is readily verified that, apart from a constant cofactor, functions (8) and (10) are Fourier transforms one of the other; this is not surprising, since Debye's approximation is just simply the method due to Messignon quoted above, but applied not to actual space but in wave space.

We now assume that the random behavior of adjacent particles is correlated, and that the particles perform pulsation motions in groups, each of which consists of several particles: it is readily seen that the arguments leading to (8) and (10) still apply, but (9) for b_f and (10) for k_0 now become incorrect, because they were obtained from a discussion of the free volume of a single particle. The true b_f must be greater than the b_f given by (9), while the corresponding k_0 must be less than the k_0 from (10), and so b_f may be considered as a measure of the mean linear size of a group of particles involved in pulsating motion. The reduction in the number of harmonics in the Fourier representation of $\rho'(t, \mathbf{r})$, i.e., reduction in k_0, reflects a reduction in the number of independent degrees of freedom when there are correlations between particles, which are linked into groups.

From (8) or (10) we have the mean-square fluctuation as

$$<\rho'^2> = \int \Phi(\mathbf{k})\, d\mathbf{k} = \rho_0^2\left(1 - \frac{\rho_0}{\rho_*}\right). \tag{11}$$

This quantity, if considered as a function of ρ_0, has a maximum at $\rho_0 = 2/3\rho_*$. It is of interest to compare (11) with experimental evidence [1, 8] for a fluidized bed; at the core of the bed, i.e., the main part in the height, as ρ_0 approximately linear and very close to ρ_*, i.e., $< \rho'^2 > \approx C\Delta\rho$, where $\Delta\rho = \rho_* - \rho_0$, and C is approximately constant, which agrees qualitatively with observations [1.8]. In the upper zone of the bed, where there is a sharp fall in ρ_0, the fluctuation $< \rho'^2 >$ at first rises sharply to a maximum, and then it falls sharply, which also corresponds with experiment. Unfortunately, direct comparison with the experiments of [1, 8] is difficult in view of the absence of exact numerical data on $\Delta\rho$ and the variation in this with height in the experiments.

The quantity of (11) is dependent only on ρ_0 and ρ_*, and it is not dependent, for instance, on b_f or k_0 and the other parameters that define the behavior of the local pulsations.

It is of interest for applications to consider also the correlation function of $\rho'(t, \mathbf{r})$, which relates the values of this quantity at two points in space at different instants in time. The one-time two-point correlation is easily expressed as an ordinary integral [3] over wave space with respect to $e^{i\mathbf{k}\vec{\xi}} \cdot \Phi(\mathbf{k})$, by analogy with the integral of (2). To obtain the expression for the two-point two-time correlation function, we need the dynamic equation for $\rho'(t, \mathbf{r})$; the simplest assumption would correspond to the hypothesis that this quantity satisfies the ordinary diffusion equation in Fick's form. This is the point of view adopted as regards the dynamics of concentration perturbations in the classical statistical treatment of Brownian motion by Smoluchowski and Einstein, and also in the theory of concentration fluctuations for dense disperse systems in [7]. The after-effect probability introduced there was calculated via Fick's equation; but it has been shown [9] that it is a very crude approximation to apply Fick's equation to a dispersed system, and one should use the equation

$$\frac{\partial\rho'}{\partial t} = \left[\left(\mathbf{D}\frac{\partial}{\partial \mathbf{r}}\cdot\frac{\partial}{\partial \mathbf{r}}\right) - \frac{\operatorname{tr}\mathbf{D}}{w^{*2}}\cdot\frac{\partial^2}{\partial t^2}\right]\rho', \quad \operatorname{tr}\mathbf{D} = D_{ii},$$

where $\mathbf{D}$ is the tensor for the effective diffusion coefficients, and w^{*2} is the mean square of the pulsation velocity of the particles.

This equation describes a regular degeneration of the random distribution $\rho'(t, \mathbf{r})$ given at some initial moment in time. This degeneracy is accompanied by random accumulation of fresh concentration perturbations, which of course is not described by this equation. However, the random occurrence of perturbations may be taken into account by introducing on the right an additional random term, in which the time for substantial change is much less than the characteristic time of the degeneration (see discussion in [2]). Then this term may be considered roughly as a Markov time function whose spectral density is not dependent on the frequency ω. We use the above representation for $\rho'(t, \mathbf{r})$ in this supplemented equation to get in the usual way [3] a relationship for $\Psi(\omega, \mathbf{k})$:

$$\Psi(\omega, \mathbf{k}) = \Phi_0(\mathbf{k})\left[\omega^2 + \left(\frac{\operatorname{tr}\mathbf{D}}{w^{*2}}\,\omega^2 - \mathbf{Dkk}\right)^2\right]^{-1}.$$

The unknown $\Phi_0(\mathbf{k})$ appearing here may be derived from the condition

$$\int \Psi(\omega, \mathbf{k})\,d\omega \equiv \Phi(\mathbf{k}),$$

so finally we have

$$\Psi(\omega, \mathbf{k}) = \frac{\mathbf{Dkk}}{\pi}\left[\omega^2 + \left(\frac{\operatorname{tr}\mathbf{D}}{w^{*2}}\,\omega^2 - \mathbf{Dkk}\right)^2\right]^{-1}\Phi(\mathbf{k}). \tag{12}$$

Substitution of (12) into (2) gives us the space-time correlation function $R(\tau, \vec{\xi})$ in terms of the effective diffusion coefficients for the particles in the mixture and the mean square of the pulsation velocity.

All the above relates to the case where one can assume the most accurate possible definition of the local values of $\rho'(t, \mathbf{r})$ via the elucidation of situations in individual specific volumes; in fact, in experiments one can use devices that somewhat smooth out the local concentration perturbations, for instance, that perform averaging over a definite volume of the mixture, which contains on average N particles. All the above formulas are suitable for describing such an experiment provided that we remember than in (6) in this case there appears a factor N^{-1}, and consequently the value of $\Phi(\mathbf{k})$, $\Psi(\omega, \mathbf{k})$, $<\rho'^2>$, etc. from such an experiment are also reduced by a factor N.

NOTATION

ρ	is the volume concentration of disperse system;
a	is the radius of particle;
σ, σ_0, σ_f	are volume, specific volume in a dense packed system;
b_f	is the radius of volume σ_f;
ω	is the frequency;
$\mathbf{k}$	is the wave vector;
$\mathbf{D}$	is the tensor of diffusion coefficients;
w^{*2}	is the mean square fluctuation velocity;
τ, ξ,	are arguments of correlation function;
< >	means averaging.

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