FLUCTUATION IN THE NUMBER OF PARTICLES IN DENSE DISPERSE SYSTEMS

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A statistical theory is formulated to describe the number of particles in an arbitrarily designated volume of a dense disperse system as a random function of time. This theory is a natural extension to concentrated systems of the Smolukhovskii-Einstein statistic, which they proposed for the Brownian motion of indistinguishable noninteracting particles.

The local random pulsations in the dispersed phase, as well as the related phenomena occurring at the level of individual particles, are of particular interest in contemporary investigations into the motion and physicomechanical properties of various disperse systems. Such a study is even more necessary in the light of the numerous significant features involved in the mechanical behavior of disperse systems which cannot be comprehended without reference to detailed information regarding their internal structures. Thus, for example, a valid explanation for the high transport coefficient in a fluidized bed necessarily calls for the introduction of the concepts of pulsation and self-diffusion in the particles of the solid phase. It is impossible to analyze the horizontal flow of a suspension without introducing the concepts of suspension and the vertical equilibrium distribution of the particles, these concepts being typically statistical in nature. It is clear that a listing of such examples can easily be enlarged. They all lead to the conclusion that the disperse medium must be treated not only from the standpoint of a continuum exhibiting particular properties, but also as a statistical system described by local fluctuations in random parameters.

It follows from the analogy to a rarified gas or a system of noninteraction Brownian particles in a continuous medium that the initial stage of a complete statistical study of disperse systems of arbitrary concentration must involve the derivation of expressions to describe the probability characteristics of the system's density (concentration) regardless of the specific nature of that system.

The solution to the analogous problem for a diluted system, in which the individual particles may be regarded as indistinguishable, noninteracting, and statistically independent, has been presented in the classical writings of Smolukhovskii and Einstein [1]; this solution was subsequently subjected to rigorous verification through the introduction of a totally additive measure to the set of elementary events for an individual particle, followed by functional integration with respect to the product of the measures [2]. With transition from a dilute system to one that is concentrated, we can again treat the particles as indistinguishable, but the property of statistical independence for the behavior of the various particles is lost. For example, the probability of a new particle penetrating into some isolated volume is a strong function of the fraction of the "free" volume, or what is the same, a function of the number of particles that already exist within the isolated volume. This circumstance hinders the introduction of measures into the set of elementary events for a collection of particles, and it makes difficult the application of integration in functional space [2]; in this paper we have therefore used the generalization of the combinatorial Smolukhovskii method [1], which is clearer from the physical standpoint, but which is not as rigorous.

Let us calculate the probability $W_V(n)$ of finding n particles in some volume A, set apart in a rather large volume $V(A \ll V)$ occupied by a disperse system. Without loss of generality, it is convenient to make the transition from a continuous method to one that is discrete for determining the volumes, by measuring the volumes with the aid of particle numbers N which can be contained within these volumes under conditions of dense packing. Thus it is clear that

$$N_V = V(\vartheta/\rho_*)^{-1}, \quad N = N_A = A(\vartheta/\rho_*)^{-1},$$
$$n_V \leqslant N_V, \quad n = n_A \leqslant N_A = N.$$

This method of description corresponds to the network model of a disperse system; the volume of a single cell in the network is equal to ϑ/ρ_*, and the volumes are, in general, divisible by the volume of the cell. We describe the concentration of the system by the quantity $\nu = n_V/N_V$, which represents the fraction of the cells occupied by particles, while the situation within volume A is described by means of the number $\nu_A = n/N = \nu + \delta\nu_A$.

In view of the indistinguishability of the particles (as well as of the cells), the probability of the first n particles from the sequence n_V of particles introduced into the empty lattice from N_V cells into any N of the isolated cells, and of all of the remaining particles entering the "outside" cells whose total number is given by $N_* = N_V - N$ is equal to

$$\frac{N}{N_V}\,\frac{N-1}{N_V-1}\cdots$$
$$\cdots\frac{N-(n-1)}{N_V-(n-1)}\,\frac{N_*}{N_V-n}\,\frac{N_*-1}{N_V-(n+1)}\cdots$$
$$\cdots\frac{N_*-(n_*-1)}{N_V-(n_V-1)}=\frac{N!}{(N-n)!}\,\frac{(N_V-n_V)!}{N_V!}\,\frac{N_*!}{(N_*-n_*)!},$$
$$n+n_* = n_V. \qquad (1)$$

It is obvious that the probability of n particles with arbitrarily fixed numbers (from the previous sequence of n_V particles) entering N cells, and of all of the remaining particles entering N_* cells, is also described by (1). For the unknown probability we therefore derive the relationship

$$W_V(n) = C^n_{n_V}\frac{N!\,N_*!\,(N_V-n_V)!}{(N-n)!\,(N_*-n_*)!\,N_V!} =$$

$$= (C^{n_V}_{N_V})^{-1} C^{n_*}_{N_*} C^n_N. \tag{2}$$

It is easy to see that distribution (2) satisfies the completeness condition. Indeed,

$$\sum_{n=0}^{N} W_V(n) = (C^{n_V}_{N_V})^{-1}\sum_{n=0}^{N} C^{n_V-n}_{N_V-N} C^n_N = 1.$$

The summation is carried out here to the number N which represents the maximum possible number of particles in volume A. In studying diluted systems, we do not encounter the problem of determining the upper summation limit, because the states that are close to the densely packed state are extremely unlikely in diluted systems.

We are primarily interested in the limiting form of distribution (2) for an unbounded increase in V. We introduce the quantities

$$\nu_* = \frac{n_*}{N_*} = \frac{n_V-n}{N_V-N} \approx \nu + \delta\nu_*,$$

$$\delta\nu_* = \frac{\nu N-n}{N_V}, \quad N_V \gg N.$$

Using the Stirling formula for the factorials and the expansion of $C^{n_*}_{N_*}$—a function of ν_*—into a series in powers of $\delta\nu_*$, after simple calculations, for $N_V \gg\gg N$ we will obtain

$$C^{n_*}_{N_*} \approx C^{n_V}_{N_V}\nu^n(1-\nu)^{N-n},$$

$$W(n) = \lim_{V\to\infty} W_V(n) = C^n_N\,\nu^n(1-\nu)^{N-n}. \tag{3}$$

Distribution (3) is similar in form to an analogous distribution for diluted systems [3], but its parameters are completely different in meaning. Instead of the total number of particles n_V in the system, (3) includes only the number of cells N in the isolated volume, and instead of the quantity $p = A/V$, tending toward zero with increasing V, we have the quantity $\nu = n_V/N_V$. In particular, it is impossible in (3) to have the passage to the limit $\nu \to 0$, which leads formally (when $N \gg 1$) to the Poisson distribution for the number n. On the other hand, for dense dispersed systems, the quantity ν is significantly different from zero and the application of the Poisson law for the random quantity n in application to such systems would be a serious error. Unfortunately, among the works known to us, this circumstance has not been taken into consideration in any analysis of the fluctuation phenomena occurring within fluidized beds, pulps, and similar densely packed systems (see, for example, [4]).

Assuming ν = const, $N \to \infty$, and $n \to \infty$, after simple calculation analogous to that performed in [3], we derive the formula

$$W(n) \approx [2\pi N\nu(1-\nu)]^{-1/2}\exp\left[-\frac{(n-\nu N)^2}{2N\nu(1-\nu)}\right],$$

$$N,\ n \gg 1. \tag{4}$$

Thus the fluctuations in the number of particles are subject to a Gaussian distribution, given sufficiently large volumes.

It is easy to find the various moments of distribution (3). In particular,

$$\langle n \rangle = \sum_{n=0}^{N} nC^n_N\,\nu^n(1-\nu)^{N-n} =$$

$$= \nu\frac{d}{dx}(1-\nu+x)^N|_{x=\nu} = \nu N,$$

$$\langle n^2 \rangle = \sum_{n=0}^{N} n^2C^n_N\,\nu^n(1-\nu)^{N-n} =$$

$$= \nu\frac{d}{dx}\left(\nu\frac{d}{dx}+1\right)(1-\nu+x)^N|_{x=\nu} =$$

$$= \nu N(\nu N + 1 - \nu).$$

This also yields

$$\langle \delta n \rangle = \langle n-\nu N \rangle = 0, \quad \langle (\delta n)^2 \rangle = \nu(1-\nu)N,$$

$$\langle n \rangle^{-2}\langle (\delta n)^2 \rangle = (1-\nu)\langle n \rangle^{-1}. \tag{5}$$

We see that the quantities in (5) that have been determined from the exact distribution (3) coincide with the analogous Gaussian moments of distribution (4). For moments of higher order this contention is not valid.

Let us now consider the number of particles in volume A as a random function of time n(t). We introduce the probability $S^{(n)}_i(t)$ of i particles leaving volume A within time t and we also introduce the probability $E_j(t)$ of j particles penetrating into this volume from without during that same period of time. In the usual manner, employing the diffusion analogy, for $S^{(n)}_i$ we derive [1, 2]

$$S^{(n)}_i(t) = C^i_n P^i(t)\left(1-P(t)\right)^{n-i}. \tag{6}$$

Here P(t) is the "aftereffect probability" introduced by Smolukhovskii in [1], which is expressed in the following form [2]:

$$P(t) = 1 - g(t), \quad g(t) = \frac{1}{A}\int_A\int_A G(\mathbf{r}\,|\,\rho,\ t)\,d\mathbf{r}\,d\rho, \tag{7}$$

where the integration is extended to the region A; $G(\mathbf{r}/\rho, t)$ is the Green's function for the diffusion equation

$$\frac{\partial\varphi}{\partial t} = \sum_{i,j=1}^{3} D_{ij}\frac{\partial^2\varphi}{\partial x_i\partial x_j} = \sum_{k=1}^{3} D_k\frac{\partial^2\varphi}{\partial y_k^2}, \tag{8}$$

while y_k and D_k are coordinates in the directions of the principal axes and the eigenvalues of the symmetric diffusion tensor D_{ij}. As $t \to 0$ we have $P(t) \to 0$, and as $t \to \infty$, the quantity $P(t) \to 1$.

Let us note that the coefficients D_{ij} are functions, generally speaking, of the concentration of the disperse system and, in particular, of the number of particles in volume A during the diffusion time. However, distribution (4) makes it possible to evaluate D_{ij} in approximate terms from the values which correspond to the concentration ν .

Assuming statistical equilibrium between the particles in the isolated volume and in the ambient medium, we have $E_j = \langle S_j^{(n)} \rangle$, where the averaging is carried out over the number of particles n = n(0) in the volume A(n ≥ j). Using (3) and (6), we obtain

$$E_j(t) = \sum_{n=j}^{N} C_N^n C_n^j \nu^n (1-\nu)^{N-n} P^j (1-P)^{n-j} =$$

$$= (1-\nu)^N \left(\frac{P}{1-P}\right)^j \times$$

$$\times \frac{N!}{j!} \sum_{n=j}^{N} [(N-n)!(n-j)!]^{-1} \left[\frac{\nu(1-P)}{1-\nu}\right]^n =$$

$$= (1-\nu)^{N-j} (\nu P)^j \times$$

$$\times \frac{N!}{j!} \sum_{m=0}^{N-j} [m!(N-m-j)!]^{-1} \left[\frac{\nu(1-P)}{1-\nu}\right]^m =$$

$$= C_N^j (\nu P)^j (1-\nu P)^{N-j}. \qquad (9)$$

Distributions (6) and (9) represent the expansions of the binomials $[P + (1 - P)]^n$ and $[\nu P + (1 - \nu P)]^N$, respectively, and they obviously satisfy the completeness condition.

The Smolukhovskii formula for $E_j(t)$ is derived from (9) for small t, when it is possible to assume $\nu P \approx 0$ and when it is possible to have the passage to the limit $\nu P \to 0$, $N \to \infty$ and j = const to the Poisson distribution. In this case, the probability of a large number of particles penetrating into volume A is exceedingly small, and the existence of an upper summation bound in (9) is inconsequential.

Formally, the probability $E_j(t)$ can be treated as the probability of certain "quasi-particles" leaving (or entering) the "average" volume j during the time t, given that at the instant t = 0 there were N quasi-particles within the volume; the probability of one quasi-particle leaving the volume during time t is equal to $\nu P(t)$. The introduction of such quasi-particles corresponds to a uniform distribution of particles through the cells, much like the diffusion energy corresponds to the uniform "smearing" of the substance in volume A.

As $t \to 0$, we have $E_0 \to 1$, $E_j \to 0$ (j > 0); with an increase in t, the quantity E_0 diminishes monotonically to zero, E_N increases monotonically to unity, and all the other E_j pass through a maximum when $t = t_j$, with t_j denoting a monotonically increasing sequence. The physical significance of this behavior in the functions $E_j(t)$ is self-evident.

Having represented the event which involves the change in n(t) from n when t = 0 to n + k in the form of a sum of mutually exclusive elementary events involving the leaving of i particles from volume A and the penetration of i + k particles into that volume during the time t [1], for the probability of a change in the number of particles in A by a quantity k we obtain the following:

$$Q_{+k}^{(n)}(t) = \sum_{i=0}^{n} S_i^{(n)} E_{i+k} =$$

$$= \sum_{i=0}^{n} C_n^i C_N^{i+k} P^i (1-P)^{n-i} (\nu P)^{i+k} (1-\nu P)^{N-i-k},$$

$$Q_{-k}^{(n)}(t) = \sum_{i=k}^{n} S_i^{(n)} E_{i-k} =$$

$$= \sum_{i=k}^{n} C_n^i C_N^{i-k} P^i (1-P)^{n-i} (\nu P)^{i-k} (1-\nu P)^{N-i+k}. \qquad (10)$$

We can calculate the average of the various functions of the number k directly with the aid of distribution (10), as is done in [1], or we can use distributions (6) and (9). For example, we will have

$$\langle k \rangle^{(n)} = \langle j-i \rangle^{(n)} = \langle j \rangle^{(n)} - \langle i \rangle^{(n)} = P(\nu N - n),$$

$$\langle k^2 \rangle^{(n)} = \langle (j-i)^2 \rangle^{(n)} =$$

$$= \langle j^2 \rangle^{(n)} - 2 \langle j \rangle^{(n)} \langle i \rangle^{(n)} + \langle i^2 \rangle^{(n)} =$$

$$= P^2 (\nu N - n)^2 - P^2 (\nu^2 N + n) + P(\nu N + n).$$

These formulas are derived exactly as the expressions for $\langle n \rangle$ and $\langle n^2 \rangle$ above. Having also averaged these in accordance with distribution (3), we have

$$\langle k \rangle = 0, \quad \langle k^2 \rangle = 2N\nu P(1-\nu P). \qquad (11)$$

It is interesting that $\langle k^2 \rangle$ exhibits a maximum at $t = t_m$, where t_m is the solution of the equation $P(t) = (2\nu)^{-1}$, while as $t \to 0$ and $t \to \infty$, the quantity $\langle k^2 \rangle$ tends, respectively, to zero and the constant $N\nu(1 - \nu)$.

We are also interested in the Euler time correlation of the function n(t). For this we have the formula

$$R(t) = \langle n(0) n(t) \rangle = \langle n(n+k) \rangle =$$

$$= \sum_{n=0}^{N} C_N^n \nu^n (1-\nu)^{N-n} (n^2 + n \langle k \rangle^{(n)}) =$$

$$= (1-P) \langle n^2 \rangle + P \langle n \rangle^2 =$$

$$= (\nu N)^2 + \nu(1-\nu)(1-P) N. \qquad (12)$$

Using the conventional method [3], we obtain an identical zero for the Euler spatial correlation between the particle numbers in two nonoverlapping [nonintersecting] volumes, if we will only neglect the local phenomena whose spatial dimensions are on the order of the linear dimensions of the particles.

The results of this work enable us to express any parameters which characterize the change in the number of particles in an arbitrary volume of a disperse system as a function of the component D_{ij} of the diffusion tensor and of the concentration ν. In studying the fluctuations in volumes of arbitrary shape, we find that the basic difficulty is caused by the calculation of the aftereffect probability P(t) from (7) and (8). However, for volumes of symmetric shape, the determination of P(t) presents no difficulty. For example, for a flat layer of thickness h, perpendicular to the principal axis of the tensor D_{ij}—which corresponds to the eigenvalue of D—we have [1]

$$P(t) = \operatorname{erfc}\left(\frac{h}{2\sqrt{Dt}}\right) + $$
$$+ 2h^{-1}\sqrt{\frac{Dt}{\pi}}\left[1 - \exp\left(-\frac{h^2}{4Dt}\right)\right].$$

We note that on the basis of the derived relationships we can propose certain variants of experiments to determine the coefficients of diffusion in disperse systems. For example, we can trace the change in the number of tagged particles in some mixed volume over a period of time, and to use distribution (6) to calculate the coefficients of diffusion.

Let us also note that formulas (5) for the absolute and relative fluctuations in n differ from the formulas derived in [5] on the basis of the analogy between a bed of solid particles fluidized by a gas and the gas whose particles exhibited delta-like interaction. This is associated with the fact that unlike a conventional gas, representing a two-parameter system, the state of the fluidized particles is completely determined by the assumption of a single parameter—for example, the liquid-phase filtration rate u, while the effective "temperature" Θ of the particles, introduced in [5], is a function of u and cannot be arbitrarily specified. The formulas in [5] correspond to situations in which the quantity Θ remains constant when u is varied. In principle, this is possible only on introduction of extremely specific forced perturbations in the small-scale motion of the solid and liquid phases. On the other hand, the use of the general method of [5] permits us to express the fluctuations in the phase velocity and in other parameters as a function of the fluctuation characteristics for the number n and the averaged parameters of motion, which naturally represents an independent problem.

NOTATION

V is the volume of the disperse system; A is the separated volume; N_V, n_V, N, and n are the numbers of cells and particles in these volumes, respectively; ϑ is the particle volume; ρ_* is the volume concentration of densely packed system; ν is the fraction of cells occupied with particles; P(t) is the aftereffect probability; D_{ij} and D_k are the components of the diffusion tensor and its eigenvalues.

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