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Abstract

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O. M. TODES

KINETICS OF FLUCTUATIONS AND DETERMINATION OF KINETIC COEFFICIENTS

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A number of macrokinetic processes—diffusion, thermal conductivity, etc.—are based on the mechanism of chaotic motion (“wandering”) and mixing of microscopic objects—individual molecules or turbulent “eddies.” The statistical analysis of the process is based on introducing the probability of transition of a micro-object from one place in space to another over a given interval of time. In the case of one-dimensional wandering in unbounded space, the probability of transition from a point with coordinate x to the interval dx' in time t is expressed by the dependence

$$dP = \frac{1}{\sqrt{4\pi Dt}} \exp\left[-\frac{(x'-x)^2}{4Dt}\right] dx', \tag{1}$$

which contains the kinetic coefficient of wandering D—the so-called diffusion coefficient.

From relation (1), with certain approximations, one derives the differential equation of macroscopic diffusion for the concentration of micro-objects $n(x,t)$:

$$\partial n/\partial t = D\partial^2 n/\partial x^2, \tag{2}$$

which includes the same kinetic coefficient D.

The statistical (1) and macroscopic (2) approaches, however, are not fully equivalent. Thus, for example, it follows from (2) that, in the absence of sources inside and at the boundary of a closed region, an initially created nonuniform concentration distribution spreads out and tends to a uniform one,

$$n(x, t=\infty) = \text{const} = \bar{n}, \tag{3}$$

and this established distribution does not depend on the kinetic coefficient D. The statistical approach, on the other hand, shows that in the established state local concentrations will fluctuate around their mean value, and the rate of occurrence and dissipation of fluctuations depends on the magnitude of D. From this point of view Smoluchowski (^{1}) was the first to analyze Svedberg' s data on the one-dimensional Brownian motion of particles of a gold hydrosol.

Let us carry out a generalization of Smoluchowski' s method. Suppose N micro-objects are chaotically distributed in a volume V. Let us select within V a certain small volume $v \ll V$ and measure the instantaneous number of objects located in it, $\nu = \nu(t)$. This number will fluctuate around its mean value

$$\bar{\nu} = Np = Nv/V. \tag{4}$$

The instantaneous concentration of particles in the selected volume will be $n = \nu/v$, and in the remaining part of the volume $n^* = (N-\nu)/(V-v)$. Over a sufficiently small time interval τ, the number of particles located inside v will change by the amount

$$\Delta\nu_\tau = \nu(t+\tau) - \nu(t) = \nu_\tau - \nu. \tag{5}$$

During this time, through the surface S, particles located at the surface in a layer of thickness

$$\xi \approx \sqrt{D\tau/\pi}, \tag{6}$$

will pass outward, and particles located outside the surface in a layer of the same thickness will enter it. The total balance will be

$$\Delta v_\tau = n^* S\xi - nS\xi = \frac{\xi}{l}\,\frac{\bar{v} - v}{1-p}, \tag{7}$$

where $l = v/S$ is the mean radius of the given volume.

Carrying out a series of successive measurements of the differences Δv_τ through equal intervals $\tau = \text{const}$ and averaging the squares of these differences (taking into account the classical relation $\overline{(v-\bar{v})^2} = \overline{v^2} - \bar{v}^2 = (1-p)\bar{v}$), we obtain

$$\overline{(\Delta v_\tau)^2} = \frac{D\tau}{\pi l^2 (1-p)}\,\bar{v}. \tag{8}$$

Relation (6), accurate up to a numerical factor of order unity depending on the geometry of the chosen volume v, is valid at small times, while $\xi \ll l$. In the opposite limiting case, when the interval between successive measurements of v and v_τ is large ($D\tau \gg l^2$), these two quantities cease to be dependent on one another. Indeed, for $\xi \gg l$, a particle that was at time t inside the volume v, by the time $t+\tau$, will have time to leave and return many times, and its appearance inside the volume at time $t+\tau$ ceases to be connected with its location at time t. Then from (4) we obtain

$$\overline{(\Delta v_\infty)^2} = \overline{(v_\tau - v)^2} = 2\left(\overline{v^2} - \bar{v}^2\right) = 2(1-p)\bar{v}. \tag{9}$$

Thus, at small times the ratio

$$\overline{(\Delta v_\tau)^2} \,/\, \overline{(\Delta v_\infty)^2} = D\tau/2\pi l^2(1-p) \ll 1, \tag{10}$$

whereas at large times it tends to unity. To describe the full course of the dependence of $\overline{(\Delta v_\tau)^2}$ on τ, one may use the simplest interpolation formula

$$\overline{(\Delta v_\infty)^2} \,/\, \overline{(\Delta v_\tau)^2} \approx 1 + 2\pi l^2(1-p)^2/D\tau. \tag{11}$$

From the slope of this dependence of $1/\overline{(\Delta v_\tau)^2}$ on $1/\tau$, one can determine the kinetic coefficient D from concentration fluctuations in a steady diffusion process, when macroscopic diffusion has in fact already "ended."

The derivation scheme given for relations (6)–(8) is very approximate. For specific configurations v and V, an exact statistical derivation can be carried out. Denoting the probability density for the transition of a micro-object from a point with radius $\mathbf{r}$ to the neighborhood of a point with radius $\mathbf{r}'$ in time

$$P(\mathbf{r}, \mathbf{r}'; D\tau) \tag{12}$$

one can successively compute first the probability for an object to leave, from a given point $\mathbf{r}$ inside v, the limits of this region,

$$\Pi(\mathbf{r}; D\tau) = \int_{(V-v)} P(\mathbf{r}, \mathbf{r}'; D\tau)\, dv', \tag{13}$$

and then the total probability of a particle leaving, during time τ, the volume v for the volume $V - v$:

$$Q_v(D\tau) = \int_{(v)} \frac{dv}{v}\, \Pi(\mathbf{r}; D\tau) = \frac{1}{v}\int_{(v)} dv \int_{(V-v)} P(\mathbf{r}, \mathbf{r}'; D\tau)\, dv'. \tag{14}$$

From the symmetry of the elementary transition probability (12) with respect to the radius vectors of conjugate points $\mathbf{r}$ and $\mathbf{r}'$, after carrying out analogous calculations it follows that the total probability of transition of a particle in the same time τ from the external volume $V - v$ into the internal one v is related to (14) by the simple relation

$$Q_{V-v}(D\tau) = \frac{v}{V-v} Q_v(\tau). \tag{15}$$

The conclusion (7) is then replaced by the probabilistic relation

$$\Delta\nu_\tau = (N-\nu) Q_{V-v}(D\tau) - \nu Q_v(D\tau) =$$

$$= Q_v(D\tau)\nu \left[\frac{N-\nu}{V-v} - \frac{\nu}{v}\right] = \frac{\bar{\nu}-\nu}{1-p} Q_v(D\tau). \tag{16}$$

A concrete calculation for the one-dimensional problem—a plate (^{1})—and the three-dimensional one—a sphere, for small τ, leads to the value

$$Q_v(D\tau) = \frac{S}{v}\sqrt{\frac{D\tau}{\pi}} = \sqrt{\frac{D\tau}{\pi l^2}} \quad \text{for} \quad \tau \ll \frac{l^2}{D}, \tag{17}$$

confirming the numerical factor $1/\pi$ introduced above in expression (6).

Let us note that the quantity to be calculated,

$$\overline{(\Delta\nu_\tau)^2} = \overline{(\nu_\tau - \nu)^2} = 2\,[\overline{\nu^2} - \overline{\nu_t \nu_{t+\tau}}], \tag{18}$$

is evidently related to the correlation function, which is the ratio of the quantities appearing in brackets in expression (18).

Relations of the type (10) and (11) remain valid also for the kinetics of changes in the fluctuations of other physical quantities proportional to the number of particles, such as energy, entropy, etc.

In order that the quantity of interest to us, (9), be practically measurable, its limiting value $\overline{(\Delta\nu_\infty)^2}$ must not be too small, relatively or absolutely. From the relation

$$\overline{(\Delta\nu_\tau/\bar{\nu})^2}_{\tau\to\infty} = 2(1-p)/\bar{\nu} \tag{19}$$

it is clear that direct fluctuations of the number of molecules in a given volume, for which $\bar{\nu} \gg 1$, do not satisfy this requirement. In the case of a pseudo-fluidized layer of solid particles suspended in an ascending flow (^{2}), the particles group into "packets" (^{3}), separated by gas bubbles. In contrast to ordinary turbulence, these microobjects—packets—preserve their individuality and disperse over distances of the order of the scale of the entire layer (^{4}). In this case, the relations (10) or (11) derived above for the number of microobjects unchanged in the whole volume can be practically used to determine the mixing coefficient of the solid phase in a pseudo-fluidized layer.

An experimental check of this possibility was carried out by us with the aid of capacitive sensors.* In this case the output voltage $U(t)$, taken from the measuring circuit (^{5}), is obtained directly proportional to the instantaneous number of packets $\nu(t)$ in the volume of the measuring probe v. In practice, when using analog electronic machines, it proved more convenient to use not the mean-square fluctuation but the proportional mean absolute fluctuation

$$\overline{|\Delta U_\tau|} = \overline{|U(t+\tau) - U(t)|}.$$

* E. L. Bogomaz, V. P. Skvortsov, and I. I. Petrenko took part in the experiment.

The output voltage $U(t)$ from the measuring bridge was fed to the summing unit and, with the opposite sign, the voltage $U(t-\tau)$, passed through a standard constant-delay unit, was also fed to it. The resulting quantity was then passed through a diode, which transmitted a difference of only one sign; to obtain the mean value it was integrated over a sufficiently long time interval $T \gg \tau$. Varying the shift τ from 0.005 to 0.5 sec, the constant value $\overline{|\Delta U_\tau|}_{t\to\infty}$ was reached, and the desired kinetic coefficient was determined from the data $\overline{|\Delta U_\tau|}$ for small τ according to the relation

$$D = \frac{2\pi l^2}{\tau}\left\{\frac{\overline{|\Delta U_\tau|}}{\overline{|\Delta U_\infty|}}\right\}^2. \tag{20}$$

In conclusion, we note that the relations derived can also be generalized to the case of diffusion in an external field, when the stationary concentration distribution depends on the coordinates.

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