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Abstract

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On the Theory of Brownian Motion in the Critical Region

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As a result of the experimental establishment of the fact that diffusion ceases in the critical region of stratification (^{1,2}), the nonlinearity of the diffusion equation became clearly apparent. It leads to a concentration dependence of the diffusion coefficient, which practically falls to zero at the critical point (^{1,3}).

Since the diffusion coefficient is not a constant quantity, attention should be paid to the behavior of a Brownian particle in the critical region. As is known, the mean square displacement of a particle is proportional to time, i.e.

$$\overline{S^2} = 2Dt. \tag{1}$$

Since the coefficient D has the meaning of a diffusion coefficient, at the critical point a Brownian particle must tread water in place, i.e., in practice there should be observed an effect of cessation of Brownian motion. Experimental proof of the latter assertion is contained essentially in the results of work (^{4}). It is shown there that iodine molecules forming an infinitely dilute solution with CO_2 in its critical phase (one may assume that an infinitely small addition of a second component does not change the state of the critical phase of the pure solvent) practically, in a macroscopically noticeable way, do not mix, in contrast to what takes place outside the critical region.

The study of thermodynamic effects makes it possible to reveal microscopic features of the critical state of a substance. Such a possibility is indicated, for example, in work (^{5}), in which the relaxation time of concentration fluctuations is determined.

The features of the fluctuation mechanism in the critical region must affect the character of the motion of a Brownian particle. The assumption of a possible "stopping" of the particle in the critical state of a pure substance has serious grounds.

The determining equation in the theory of Brownian motion is the Smoluchowski integral equation (^{6})

$$\omega(t_0, \overline{R}_0; t+\tau, \overline{R}) = \int \omega(t_0, \overline{R}_0; t, \overline{r})\omega(t, \overline{r}; t+\tau, \overline{R})\, d\overline{r}, \tag{2}$$

where ω is the probability density for the transition of a particle during the time $t - t_0$ from the state $\overline{R}_0$ to the state $\overline{r}$. The integration extends over the entire region of variation of $\overline{r}$.

Since outside the critical region the rate of change of concentration fluctuations is large, it may be assumed that the particle moves in a homogeneous medium (the latter implies a certain averaging). However, in the critical region the rate of fluctuations practically falls to zero. Stable fluctuations of density with a strong correlation connection determine also the behavior of the Brownian particle. It should be considered that in this case the motion already takes place in an inhomogeneous medium.

If in fact everything is as described, then this necessitates a certain generalization of equation (2) to the region of the critical point. The latter may be verified by invoking the following model representations of random walks.

Let us consider the one-dimensional case. We are interested in the possibility of displacement of a particle along a straight line in the form of a series of steps of two kinds. Each displacement may be made either to the right or to the left. The probability of displacement in either direction is the same and is equal to 1/2, if the neighboring steps are of the same kind. If, however, for example, to the right there is a step of the second kind, then the probability of displacement from a step of the first kind to the right will be $p_2 > 1/2$ (the probability of displacement to the left, toward the step of the same name, is $p_1 = 1 - p_2$).

The probability that the particle will be displaced continuously to the right by N steps, if among them there are n steps of the second kind (not extreme ones and separated by no fewer than 2 steps of the first kind), is

$$P = (1/2)^{N-2n} p_1^n p_2^n. \tag{3}$$

This value will be greatest if $p_1 = 1/2$, which corresponds to the case of homogeneous steps.

Let us extend the example given. Suppose that along a length L there are N steps of the second kind. Let us compute the probability of displacement over a length $l < L$ continuously to the right for an arbitrary arrangement on the chosen segment of m and n steps, respectively, of the first and second kinds. The density of steps of the second kind will be distributed according to the Poisson law $f_\lambda(n)$,

where $\lambda = \dfrac{N}{L} l$, $m > n$, and $n \gg 1$. Then the required probability is

$$P_{\mathrm{I}} = \sum_{n} f_{\lambda}(n) \sum_{\beta=0}^{n} \sum_{\gamma=0}^{[n/2]} \varphi(n)\,(1/2)^{m+n-4\gamma-2\beta}(p_1p_2)^{\beta+2\gamma} \quad (\beta \leqslant n-2\gamma), \tag{4}$$

where $\varphi(n)$ is the probability of the given arrangement of n steps of the second kind over the length l. In what follows we shall regard any arrangement as equally probable. γ is the number of groups in which there are no fewer than two steps of the second kind; β is the number of single steps, to the right and to the left of which there are no fewer than two steps of the opposite (first) kind. If to the left and to the right of a step of the second kind there is one step of the first kind each, then there is essentially no distinction between them. Therefore we exclude this case: such a restriction on the number of possible arrangements of steps does not narrow the content of the problem. In this case

$$\varphi(n) = \left\{ 1 + \sum_{\gamma=1}^{n/2} (n - 2\gamma + 1) \right\}^{-1}. \tag{5}$$

Carrying out the summation in expression (4), we obtain

$$P_{\mathrm{I}} = \sum_{n} f_{\lambda}(n)\,\varphi(n)\,\frac{1-(4p_1p_2)^n\left[2+\frac{1}{2}n-16\left(\frac{1}{2}n+1\right)p_1^2p_2^2\right]}{2^{m+n}(1-4p_1p_2)^2(1+4p_1p_2)}. \tag{6}$$

Along with the general case (4), let us consider the particular arrangement for which $\gamma = 0$. Then the required probability is

$$P_{\mathrm{II}} = \sum_{n} f_{\lambda}(n)\,(1/2)^{m-n} p_1^n p_2^n. \tag{7}$$

There will be an analogy between the actual walk of a Brownian particle and the model examples given if a step of the first kind is put in correspondence with denser regions of the volume, and a step of the second kind with rarefied places. Expression (4) corresponds to the case,

when the relaxation time of the density is small and the Brownian particle moves in a homogeneous medium. Expression (7), however, pertains to the case of a critical state: regions of increased and decreased density alternate in a strictly stable order. p_2 denotes the probability of transition of the particle from an elementary volume of higher density into a rarefied elementary volume; therefore we set $p_2 > 1/2$. Comparison of the probability values (6) and (7) shows that $P_I \gg P_{II}$.

The model problems presented can also be formulated in the Markov method (^{7}), which will make it possible to present them in the most general form.

The sharp difference between the displacement probabilities in homogeneous and inhomogeneous media gives grounds to believe that the original equation describing the motion of a Brownian particle in the critical region must take into account the value of the local density. It is natural to assume that the latter must be taken into account in equation (2), which we rewrite in the form

$$\omega(t_0, \overline{R}_0, \rho_0;\, t+\tau, \overline{R}, \rho_R) =$$

$$= \int \omega(t_0, \overline{R}_0, \rho_0;\, t, \overline{r}, \rho_r)\, \omega(t, \overline{r}, \rho_r;\, t+\tau, \overline{R}, \rho_R)\, d\overline{r}\, d\rho_r, \tag{8}$$

where $\rho_r = \rho(\overline{r})$ is the value of the density.

We use the expansion of the function ω in a series in the neighborhood of the critical density of the medium

$$\omega(t_0, \overline{R}_0, \rho_0;\, t, \overline{r}, \rho_r) = \omega(t_0, \overline{R}_0, \rho_{\text{cr}};\, t, \overline{r}, \rho_r) + \left.\frac{\partial \omega}{\partial \rho_0}\right|_{\rho_{\text{cr}}} (\rho_0 - \rho_{\text{cr}}) + \ldots \tag{9}$$

Restricting ourselves to the first two terms of the expansion (9), and then multiplying equation (8) by the distribution function $f(\rho_0, \rho_R)$ and integrating over the entire volume (the latter integration does not pertain to the Brownian particle), we obtain:

$$\int \omega(t_0, \overline{R}_0, \rho_0;\, t+\tau, \overline{R}, \rho_R) f(\rho_0, \rho_R)\, dV\, d\rho_0\, d\rho_R =$$

$$= \int \omega_{0r}(\rho_{\text{cr}}, \rho_r)\, \omega_{rR}(\rho_{\text{cr}}, \rho_R)\, f(\rho_0, \rho_R)\, d\overline{r}\, dV\, d\rho_0\, d\rho_r\, d\rho_R + \ldots$$

$$\ldots + \int \left.\frac{\partial \omega_{0r}}{\partial \rho_0}\right|_{\rho_{\text{cr}}} \left.\frac{\partial \omega_{rR}}{\partial \rho_R}\right|_{\rho_{\text{cr}}} (\rho_0 - \rho_{\text{cr}})(\rho_R - \rho_{\text{cr}}) f(\rho_0, \rho_R)\, d\overline{r}\, dV\, d\rho_0\, d\rho_r\, d\rho_R. \tag{10}$$

In general form, equation (10) can be written as

$$A = B + C \int_V \overline{(\rho_0 - \rho_{\text{cr}})(\rho_R - \rho_{\text{cr}})}\, dV. \tag{11}$$

The quantities A and B cannot become infinite, whereas the integral on the right-hand side of (11) at the critical point of a pure substance becomes infinite (^{8}). The equation can be satisfied if C, i.e., the first derivatives of ω with respect to density, vanish.

Taking into account the subsequent terms of the expansion (9), one can show that the higher derivatives must likewise vanish. In doing so we use the fact that at the critical point the volume integral of the statistical moment $\overline{(\rho-\overline{\rho})^{\alpha}}$ ($\overline{\rho}=\rho_{\mathrm{cr}}$) is equal to infinity for any even degree α and to zero for an odd one ($\Delta\rho$ obeys the normal law of distribution).

Consequently, in the neighborhood of the critical point the density of the probability of displacement of the Brownian particle vanishes. This also leads to the fact that relation (1) is no longer fulfilled here. Indeed, relation (1) was obtained from the condition of independence of events.

It is assumed that

$$\overline{S^2}=\overline{(S_1+S_2)^2}=\overline{S_1^2}+\overline{S_2^2}.$$

All this is valid for a homogeneous medium. Conversely, in an inhomogeneous medium $\overline{S_1 S_2}\neq 0$, and consequently one cannot obtain the functional equation

$$f(t)=f(t_1)+f(t-t_1),$$

from which (1) followed.

An experimental study of the behavior of a Brownian particle, as well as of diffusion in the critical region, is of great interest and opens up additional valuable possibilities for the study of relaxation microscopic processes.

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Note: Figure translations are in progress. See original paper for figures.