

Brownian motion

Suspension of magnetic nanoparticles

1. Brownian motion. Langevin's theory

In 1827, the English botanist R. Browne, while looking through a microscope at plant particles immersed in liquid, observed that, if plant particles were small enough, they would continuously move chaotically in different directions. Brownian motion is the random movement of particles in a fluid due to their collisions with other atoms or molecules of liquids. The trajectories of the Brownian particles have a chaotic (random) character in magnitude and direction (Fig. 1).

A. Einstein (1905) and M. Smolukhovski (1907), independently of each other, developed the molecular-statistical theory of Brownian motion and proved that the mean square value (fluctuation) of the displacement of a chaotically moving Brownian particle is directly proportional to the time of motion

$$\overline{x^2} (t \rightarrow \infty) \sim t \quad (1)$$

Formula (1) is valid for very long times. During this time, there are many collisions of liquid molecules with Brownian particles, and its trajectory should be represented by many broken sections in Fig. 1 - much more than shown in Fig. 1. It can be said that formula (1) describes the "echo" of short-term fast random processes over long times.

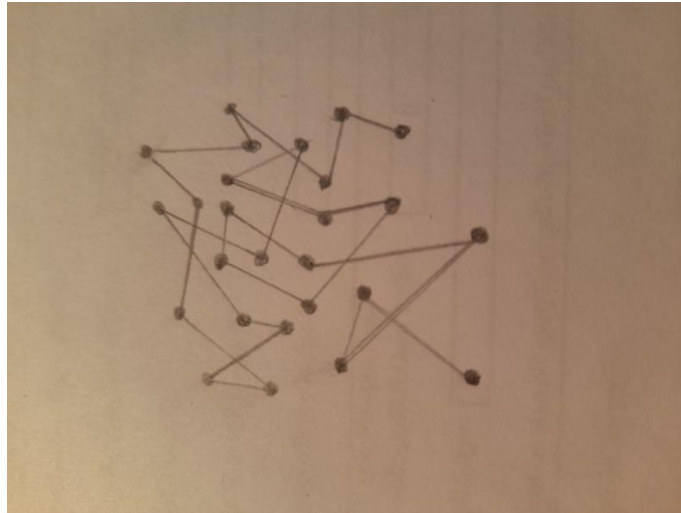


Fig. 1. Chaotic motion of a Brownian particle

The force $F(t)$ with which liquid molecules act on a Brownian particle was presented by Paul Langevin (1908) as the sum of two, qualitatively different, forces:

$$F(t) = f(t) - \gamma \frac{dx}{dt} \quad (2)$$

$f(t)$ is a random force caused by unbalanced collisions of liquid molecules with Brownian particles (Fig. 2). In order to estimate τ , characteristic time of variation of the random function $f(t)$, the average distance between the liquid molecules $\ell = 10^{-10}\text{m}$ should be divided by the average speed of the thermal motion of the liquid molecules: $\tau = \ell/v$. Here, the average speed is computed by using the formula: $\frac{\mu v^2}{2} = \frac{3kT}{2}$ and is equal to $v = \sqrt{3kT/2\mu}$. If we insert into the last formula the Boltzmann constant $k = 1,38 \cdot 10^{-23}\text{J/K}$, the room temperature $T = 300\text{K}$ and the mass of the water molecule $\mu_{H_2O} = 3,1 \cdot 10^{-26}\text{kg}$ numerical values, then we get the characteristic time of the random force: $\tau = \ell/v \approx 2 \cdot 10^{-13}\text{s}$. This is a very short time, and during this time it is not possible to experimentally observe the processes taking place in the liquid. In our discussion, τ plays the role of the smallest time scale of the processes taking place in the system. That's why we consider the function $f(t)$ as a random and rapidly changing function. However, the time spent in

chaotic collisions of molecules is still much smaller than τ . Due to the macroscopic nature of the system, a mechanical description of the processes taking place at these times is completely impossible.

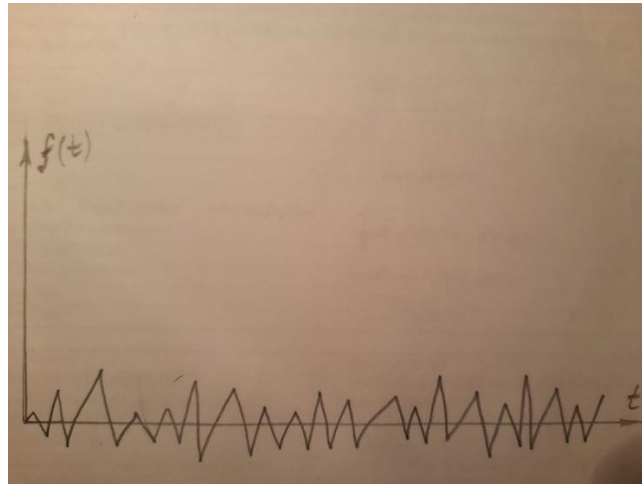


Fig. 2. Random rapidly varying $f(t)$ -force caused by unbalanced collisions of fluid molecules.

$\gamma \frac{dx}{dt}$ is the resistance force proportional to the speed, caused by the viscosity of the liquid. γ - is the "wet" friction coefficient. γ is proportional to the viscosity coefficient η . So the speed of the Brownian particle is proportional to the frictional force:

$$v_x = \frac{dx}{dt} \sim \frac{1}{\gamma} \cdot$$

The resistance force $\gamma \frac{dx}{dt}$ can be considered as the hydrodynamic force of fluid friction.

Langevin's presentation of the total force $F(t)$ as the sum of two forces (Fig. 3) is an important assumption and at the same time an interesting finding for the theory of Brownian motion.

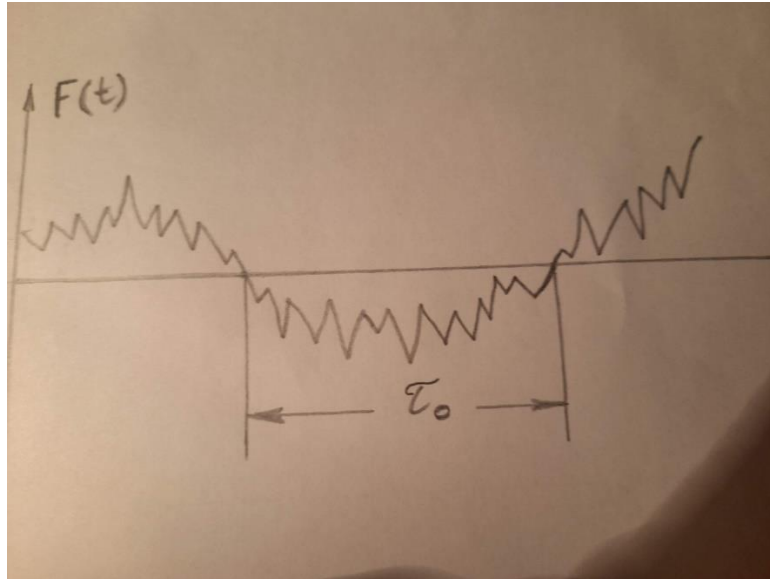


fig. 3. $F(t)$ is the total force of the environment acting on the Brownian particle. τ_0 is the characteristic time for the slow process caused by viscosity.

The dynamical equation of motion of a Brownian particle is:

$$m \frac{d^2x}{dt^2} = f(t) - \gamma \frac{dx}{dt} \quad (3)$$

where m is the mass of the Brownian particle. Since $f(t)$ is a random force, its explicit form cannot be given. Therefore, equation (3) has only a symbolic meaning, and it is meaningless to solve it. But we can write a formal solution to this equation. This procedure is nothing but the transformation of a differential equation into an integral equation. Now we will use such a formal solution to find the average speed of the Brownian particle $\overline{v_x}$.

If equation (3), which is a first-order equation with respect to $v_x = dx/dt$, is formally integrated, we get:

$$v_x(t) = v_x(0)e^{-\gamma t} + \frac{1}{m} \int_0^t e^{-(1/\tau_0)(t-s)} f(s) ds \quad (4)$$

where $\tau_0 = m/\gamma$ is the characteristic decay time of the flow velocity due to viscosity. To calculate the average speed of the Brownian

particle $\overline{v_x}(t)$, let's average the equation (4) over times t , which is many times greater than the characteristic time τ ($t \gg \tau$) of the random variation of the $f(t)$ force. We did the averaging in the usual (standard) way:

$$\overline{\mathcal{A}}(t) = \frac{1}{t} \int_0^t \mathcal{A}(t^*) dt^* \quad .$$

(5)

Since the integrand $f(s)$ on the right-hand side of equation (4) is a rapidly changing random function, the average value of which is zero $\overline{f(s)} = 0$, we get the expression for the average speed:

$$\overline{v_x}(t) = v(0)e^{-t/\tau_0}$$

(6)

which indicates that the average velocity is decayed in τ_0 time. If we assume that Brownian particles have a spherical shape and use the dependence of the coefficient of resistance γ on the coefficient of viscosity η

$$\gamma = 6\pi r\eta, \quad (7)$$

where r is the radius of the particle, we finally get that the time of decay:

$$\tau_0 = \frac{m}{6\pi r\eta}, \quad (8)$$

From which it can be seen that the time of decay of Brownian particle velocity is inversely proportional to viscosity. When studying the Brownian motion J. Perrin used particles of radius $r = 10^{-5}$ cm and mass $m = 10^{-14}$ g. For such particles in a water emulsion ($\eta = 10^{-2}$ (g/cm.s) using formula (8) we get $\tau_0 = 10^{-8}$ sec. As one can see, the time τ_0 is much greater than the characteristic variation time τ of the random force $f(t)$ ($\tau_0 \gg \tau$). Therefore, τ_0 a characteristic time of a relatively slow process in the system is long time. Nevertheless, as

we will show below, the time (1) for observing the movement of the Brownian particle is longer than the "big" time τ_0 ($t \gg \tau_0$).

Now, based on equation (3), let's try to get a closed equation for mean square fluctuation of Brownian particle $\overline{x^2}$. This is possible if we use the law of equal distribution of energy according to the degrees of freedom for the Brownian particle. To get this equation, we need to multiply equation (3) by x and perform simple transformations using the following formulas (identities)

$$x \frac{d^2 x}{dt^2} = \frac{1}{2} \frac{d^2}{dt^2} (x^2) - \left(\frac{dx}{dt} \right)^2 \quad (\#)$$

$$x \frac{dx}{dt} = \frac{1}{2} \frac{d}{dt} (x^2) .$$

As a result, we get

$$\frac{m}{2} \frac{d^2}{dt^2} (x^2) - m v_x^2 = f x - \frac{\gamma}{2} \frac{d}{dt} (x^2) . \quad (9)$$

From this point we begin to introduce the elements of statistical theory.

Let's average the equation (9) over time t using the formula (5). Suppose that the time t is many times greater than the characteristic time τ of the variation of random $f(t)$ force ($t \gg \tau$).

Here we have to take into account that under the influence of $f(t)$ -random force, $x(t)$ -function also turns into a random function. Although the random variation of $x(t)$ is caused by the $f(t)$ function, we assume that these two functions are statistically independent of each other and that there is no correlation between them. This means that if we imagine the graph of Fig. 2 type for $x(t)$, we will "see" that it will not repeat the shape of the function $f(t)$ at any point in time. Therefore, the product of $f(t) x(t)$ is a random function with the same properties as each of them. This assumption is considered valid in the theory of random functions, where it is proved on the basis of intuitive considerations.

As a result of this averaging, the quantities related to the $f(t)$ force ($\bar{f} \approx \bar{x} \approx 0$), which vary rapidly in τ time, "disappear", and only the quantities related to the slow τ_0 - the time of decay of Brownian particle velocity remain ($\bar{F} \neq 0$). These quantities, caused by the viscosity of the liquid, lead to the slowing of the Brownian particle movement down.

When averaging the equation (9), we deal with the correlation function of type $\overline{f(t)x(t)}$, which is the average of the product of two random functions. Since $f(t)$ and $x(t)$ are statistically independent of each other, as we said above, it is possible to "separate" the correlation function $\overline{f(t)x(t)}$, which ultimately leads to its equalizing to zero:

$$\overline{f(t)x(t)} = \overline{f(t)} \cdot \overline{x(t)} = 0, \quad (t \gg \tau). \quad (10)$$

Using the extremely important properties of random functions expressed by formula (10), we get:

$$\frac{m}{2} \frac{d^2}{dt^2} (\overline{x^2}) - \overline{mv_x^2} = -\frac{\gamma}{2} \frac{d}{dt} (\overline{x^2}). \quad (11)$$

Now in the equation (11) we somehow have to get rid of the term $\overline{v_x^2}$.

Using the "separation" formula (10), we got an equation that no longer contains random $f(t)$ forces at large times $t \gg \tau$. At small τ -times, these forces have already done their "job" - under their influence, the Brownian particle's coordinate $x(t)$ has also become a random function. Therefore, for $\overline{v_x^2}$ we can use the law of equal distribution of energy according to the degrees of freedom:

$$\frac{1}{2} m \overline{v_x^2} = \frac{1}{2} kT. \quad (12)$$

Using equation (12) and eliminating $\overline{v_x^2}$ from equation (11), we finally get a closed equation with respect to

$$\frac{m}{2} \frac{d^2}{dt^2} (\overline{x^2}) - mkT = -\frac{\gamma}{2} \frac{d}{dt} (\overline{x^2}). \quad (13)$$

Using the law (12) of statistical physics for equilibrium macroscopic systems and also the correlation separation formula (10), we finally considered the system consisting of Brownian particles as a statistical object. From this point on, we abandon the usual (Cartesian) coordinates and introduce a new "good" variable $\overline{x^2}$ called the root mean square fluctuation. In the later stages of system evolution, it will play the role of a "dynamic" variable. It can be seen from equation (13) that the variation in time of the fluctuation resembles the variation in time of some hypothetical particle - the fluctuation moves like a particle.

Equation (13) can provide information about the displacement of a Brownian particle only within its average value (i.e. - approximate, imprecise, truncated) and also only for large t times (asymptotic $t \gg \tau$). In other words, due to the complexity of the problem (the existence of random forces), we had to give up finding the exact solution to the problem and were forced to settle for finding an approximate solution (incomplete information).

Now let's find the solution of equation (13). If we introduce the notation for the rate of change of mean square fluctuation:

$$\frac{d}{dt}(\overline{x^2}) \equiv \alpha, \quad (14)$$

From (13) we get the equation:

$$\frac{d\alpha}{dt} - 2kT = -\frac{\alpha}{\tau_0}. \quad (15)$$

The solution of equation (15) is

$$\alpha = \frac{2kT}{\gamma} + c \cdot \exp(t/\tau_0), \quad (16)$$

where c is the integration constant. At long times $t \gg \tau_0$, the second term in the right-hand side of (14) can be neglected, as a result of which we get:

$$\alpha = \frac{d}{dt}(\overline{x^2}) = \frac{2kT}{\gamma}. \quad (17)$$

By integrating equation (17), we get

$$\overline{x^2} = \frac{2kT}{\gamma} t.$$

If we use here the formula (7) for spherical Brownian particles, we finally get

$$\overline{x^2} = \frac{t}{t_0}, \quad \frac{1}{t_0} = \frac{kT}{3\pi r\eta}. \quad (18)$$

The equations (18) show that the change in mean square fluctuation is proportional to time, and the rate of change $1/t_0$ is proportional to temperature and inversely proportional to viscosity.

As it was said at the beginning, the result shown by formulas (18) was obtained by Einstein and Smolukhovsky, and experimentally it was checked by J. Peren (1908). If we take the square root from both sides of equation (18) for the s -displacement of a randomly wandering Brownian particle, we get

$$s \equiv \sqrt{\overline{x^2}} \sim \sqrt{t/t_0}. \quad (19)$$

According to formula (19), an important conclusion can be made: at long times ($t \gg \tau_0$), the displacement of a particle caused by a random force is proportional to \sqrt{t} . Such a dependence on the time of movement can only be caused by the impact of a random force. A similar dependence does not exist in classical mechanics, which only studies motion caused by regular (non-random) forces. The opposite is also true: If the system moves according to the \sqrt{t} rule, then the driving force of the motion is random.

The collision of liquid molecules with Brownian particles can cause random translational motion and its random rotational motion as well. Such movement is called Brownian rotational movement (diffusive rotational movement) and it was investigated by I. Frankel. If we denote the angle of rotation of the particle around the z-axis by ϕ in the Cartesian coordinate system and perform the same procedures as we performed to obtain formula (18), in the case of Brownian rotational motion for the mean square value of the ϕ -angle and for a spherical particle with r-radius, we obtain

$$\overline{\phi^2} = \frac{kT}{4\pi r^3 \eta} t. \quad (20)$$

We get a formula similar to (20) for "free-random" rotation around x and y-axes. If we introduce the so-called Brownian relaxation rate

$$\frac{1}{\tau_B} = \frac{kT}{3V\eta} \quad (20a)$$

Where V is the volume of the Brownian particle, we get $\overline{\phi^2} = t/\tau_B$, from which it can be seen that $1/\tau_B$ represents the propagation speed of the mean square fluctuation of the rotation angle. As one can see from (20a), the viscosity prevents the propagation of the fluctuation.

It should be noted that, in addition to the similarities between translational and rotational movements, there is also an important difference. In particular, for translational Brownian motion $\sqrt{x^2}$ - the displacement is an unlimited quantity, while for rotational Brownian motion $\sqrt{\phi^2}$ - the turning angle cannot be more than π (or 2π). After reaching this value, it starts to increase again (from zero value) and therefore $\sqrt{\phi^2}$ has a periodic, "sawtooth" shape, similar to the one shown in (Fig. 5). It is possible to induce an even slower, directed, resonant motion by impacting any of its spectral components with an alternating magnetic field. We will discuss this issue in the 3rd part.

2. Suspension of magnetic nanoparticles.

The elements of the transition (iron) group of the periodic system of elements (Fe-iron, Ni-nickel, Co-cobalt) have a spin moment different from zero. The atoms of these substances in a solid state interact with each other through the exchange interaction U_{ex} .

$$U_{ex} = -2J(\vec{s}_1 \cdot \vec{s}_2) \quad (21)$$

Here \vec{s}_1, \vec{s}_2 are spin operators, J -exchange integral. If $J > 0$, the exchange interaction leads to the polarization of atomic spins (the spins of all atoms are directed in one direction). Such a state of a solid body is called a ferromagnetic state. Actually, the exchange interaction polarizes not the spins of the whole (massive) body, but some of its parts, which are called domains. The dimensions of the domain are several nanometers. The domains contain approximately $N \cong 10^4 \div 10^5$ atoms. The massive pattern of iron consists of many such domains, which are polarized, but chaotically directed towards each other.

If we crush a massive body of iron and grind it to the size of a few nm, we get single-domain iron flakes - iron nanoparticles. The magnetic moment of such a nanoparticle is equal to $\mathcal{M} = N\mu_B$, where $\mu_B = 9,2 \cdot 10^{-24} \text{ A}\cdot\text{m}^2$ - Bohr magneton. Since N is a large number, a nanoparticle is considered as a macroscopic object.

A massive piece of iron has the property of magnetic anisotropy, which is that it is easier to magnetize in one direction than in other directions. This direction is called the axis of easy magnetization. According to phenomenological theory of magnetic anisotropy

developed by L. Landau a massive iron sample has an internal magnetic anisotropy energy

$$U_A \cong A(\sin \beta)^2 \quad ,$$

where β is the angle between the anisotropy axis and the magnetic moment. Minima of U_A energy at 0 and π determine the direction of easy magnetization. Liquid consisting of small solid particles in Brownian motion suspended in it is called a suspension. If the particles sizes are in the range of $1 \div 10^3$ nm, Brownian motion does not allow them to settle to the bottom.

Suspension of magnetic nanoparticles (magnetic nanofluids) is used in medicine. A liquid containing magnetic nanoparticles is a medicine. This kind of suspension is injected into the injured area of the patient's muscle, and from the outside, with the help of magnets, they localize the drug in the injured area and prevent it from spreading throughout the body.

3. Effects of resonant electromagnetic field on rotational Brownian motion

If a magnetic nanoparticle is exposed to a magnetic field, then its total magnetic energy is:

$$U(\theta, \psi) = A \sin^2(\psi - \theta) - mB(t) \cos \theta, \quad (22)$$

$$A > 0, \pi \geq \theta \geq 0, \pi \geq \psi \geq 0.$$

$U_A = A \sin^2(\psi - \theta)$ is the energy of magnetic anisotropy,

$mB(t) \cos \theta$ is the energy of interaction of a magnetic nanoparticle with a magnetic field.

If the internal magnetic anisotropy energy did not exist, the same kind of "random-free" rotation around all three axes of Cartesian coordinates would take place, and the rotation around all

three axes would be expressed by formula (20). And now, due to the presence of magnetic anisotropy, a different situation is occurred when there is rotation around the directed axis (ψ and θ -angles) perpendicular to $B(t)$ - magnetic field (Fig. 4)

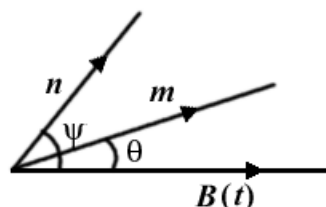


Fig. 4. The orientation of m -magnetic moment and n -anisotropy axis are plotted with respect to $B(t)$ -magnetic induction vector.

Here θ is the angle between the direction of the magnetic moment and the magnetic induction vector, ψ is the angle between the anisotropy axis and the direction of the magnetic field (Fig. 4), $A = KV_m$ is the anisotropy constant, $m = |m| = M_s V_m$ is the magnitude of the magnetic moment, K and M_s are the densities of the anisotropy constant and the magnetic moment, $V_m = \frac{\pi}{6} d_m^3$ is the volume of the central magnetic sphere, d_m is the "magnetic" diameter of the particle, $B(t) = b e^{-\gamma t} \sin \omega t$ - alternating magnetic field, b , ω and γ - amplitude, frequency and frequency broadening of this field, respectively. Anisotropy energy density for magnetite ($Fe_3 O_4$) nanoparticles - $K = 4.8 \cdot 10^4 \text{ J/m}^3$. "Magnetic" and external diameters are $d_m = 7 \text{ nm}$ ($V_m = 0.2 \cdot 10^{-24} \text{ m}^3$) and $d = 2r = 10 \text{ nm}$ ($V = 0.5 \cdot 10^{-24} \text{ m}^3$), the anisotropy constant is $A = 10^{-20} \text{ J}$, the moment of inertia of a spherical nanoparticle is $I = 4 \cdot 10^{-36} \text{ kg} \cdot \text{m}^2$.

$$\begin{cases} I\ddot{\theta} = -2I \frac{1}{\tau_s} \dot{\theta} - \frac{\partial U_A}{\partial \theta} - mB(t) \sin \theta + f(t), \\ I\ddot{\psi} = -2I \frac{1}{\tau_s} \dot{\psi} - \frac{\partial U_A}{\partial \psi} + f(t), \end{cases} \quad (23)$$

where $\frac{1}{\tau_s} = \frac{3V\eta}{I}$ - «viscous» relaxation speed, τ_s - is the rotational analogue of the time of the speed decay caused by viscosity, which we have noted for translational movement τ_0

$$\frac{\partial U_A}{\partial \theta} = -A \sin 2(\psi - \theta) = -\frac{\partial U_A}{\partial \psi}$$

- the moment of the anisotropy rotating force acting on the Brownian particle.

Magnetite is an iron oxide $\text{Fe}_2\text{O}_3 \cdot \text{FeO}$ which is widely used in pharmacology and medicine.

Taking into account the anisotropy forces, the dynamic equations of the rotational motion of the Brownian particle have the form

$$\begin{cases} \ddot{\theta} + 2\frac{1}{\tau_s}\dot{\theta} + \frac{A}{I}\sin 2(\psi - \theta) + \frac{mB(t)}{I}\sin \theta = \frac{f(t)}{I}, \\ \ddot{\psi} + \frac{2}{\tau_s}\dot{\psi} - \frac{A}{I}\sin 2(\psi - \theta) = \frac{f(t)}{I}. \end{cases} \quad (24)$$

Let's introduce generalized coordinates - $\xi = \theta + \psi$ and $\zeta = \theta - \psi$. Then from (24) we get

$$\begin{cases} \ddot{\xi} + \frac{2}{\tau_s}\dot{\xi} + \frac{mB(t)\sin \theta}{I} = \frac{f(t)}{I}, \\ \ddot{\zeta} + \frac{2}{\tau_s}\dot{\zeta} + \frac{A}{I}\sin 2\zeta + \frac{mB(t)\sin \theta}{I} = \frac{f(t)}{I}. \end{cases} \quad (24a)$$

If we multiply equations (24a) by ξ and ζ , respectively, and use (#) type transformations, we get

$$\begin{cases} \frac{1}{2}\dot{\xi}^2 - |\dot{\xi}|^2 = -\frac{1}{\tau_s}\dot{\xi}^2 - \frac{mb}{I}\xi \sin \theta \cdot e^{-\gamma t} \sin \omega t + \frac{\xi f(t)}{I}, \\ \frac{1}{2}\dot{\zeta}^2 - [\dot{\zeta}]^2 = -\frac{1}{\tau_s}\dot{\zeta}^2 - \frac{A}{I}\zeta \sin 2\zeta - \frac{mb}{I}\zeta \sin \theta \cdot e^{-\gamma t} \sin \omega t + \frac{\zeta f(t)}{I}. \end{cases} \quad (25)$$

Now if we average equations (25) according to formula (5), using

$$\frac{I}{2}\overline{\dot{\xi}^2} = \frac{kT}{2}, \quad \frac{I}{2}\overline{\dot{\zeta}^2} = \frac{kT}{2}, \quad (26)$$

the law of equal distribution of rotational energy according to the degrees of freedom (26), and also that

$$\begin{aligned} \overline{\xi f(\xi)} = \bar{\xi} \cdot \overline{f(\xi)} = 0, \quad \overline{f(\xi)} = 0, \\ \overline{\zeta f(\zeta)} = \bar{\zeta} \cdot \overline{f(\zeta)} = 0, \quad \overline{f(\zeta)} = 0, \end{aligned} \quad (27)$$

The properties of the separation of correlations of random functions, we get a system of equations

$$\begin{cases} \ddot{\xi}^2 + \frac{2}{\tau_s} \dot{\xi}^2 + \frac{2mb}{I} \cdot \overline{\xi \sin \theta} \cdot e^{-\gamma t} \sin \omega t = \frac{2kT}{I}, \\ \ddot{\zeta}^2 + \frac{2}{\tau_s} \dot{\zeta}^2 + \frac{A}{I} \overline{\zeta \sin 2\zeta} + \frac{2mb}{I} \cdot \overline{\zeta \sin \theta} \cdot e^{-\gamma t} \sin \omega t = \frac{2kT}{I}. \end{cases} \quad (28)$$

In the absence of anisotropy energy ($A \rightarrow 0$), the two equations of system (28) coincide, as expected. Therefore, in this case, it is possible to analyse only the first equation of (28). But since such materials are not found in magnetic nanoparticles, they are less interesting for us, and therefore we consider the case when $A \neq 0$.

The system of equations (28) is significantly simplified if we take into account that the Brownian particle spends most of the time (from collision to collision) in uniform-rotational motion. In this case, in the system of equations (28), we can ignore (inertia) forces proportional to angular accelerations

$$\ddot{\xi}^2 \rightarrow 0, \quad \ddot{\zeta}^2 \rightarrow 0 \quad (29)$$

And finally we get a system of equations

$$\begin{cases} \dot{\xi}^2 = \frac{1}{\tau_B} (1 - \varepsilon \cdot \overline{\xi \sin \theta} \cdot e^{-\gamma t} \sin \omega t), \\ \dot{\zeta}^2 = \frac{1}{\tau_B} (1 - a \overline{\zeta \sin 2\zeta} - \varepsilon \cdot \overline{\zeta \sin \theta} \cdot e^{-\gamma t} \sin \omega t), \end{cases} \quad (30)$$

$\frac{1}{\tau_B} = \frac{kT}{3V\eta}$ is the Brownian relaxation rate (it is the inverse time of the diffusive rotation), $a = \frac{A}{kT}$ is the dimensionless anisotropy constant, $\varepsilon = \frac{mb}{kT}$ is the small interaction parameter.

The system of equations (30), which describes the Brownian rotational motion (diffusive rotation) of a magnetic nanoparticle in suspension, is similar to equation (13), which describes Brownian translational motion in suspension.

If we introduce the dimensionless time $\tilde{t} = \frac{t}{4\pi\tau_B}$, then equation (30) takes the form

$$\begin{cases} \frac{d\bar{\xi}^2}{d\tilde{t}} = 4\pi(1 - \varepsilon \cdot \overline{\xi \sin \theta} \cdot e^{-\bar{\gamma} \tilde{t}} \sin \bar{\omega} \tilde{t}), \\ \frac{d\bar{\zeta}^2}{d\tilde{t}} = 4\pi(1 - a\overline{\zeta \sin 2\zeta} - \varepsilon \cdot \overline{\zeta \sin \theta} \cdot e^{-\bar{\gamma} \tilde{t}} \sin \bar{\omega} \tilde{t}). \end{cases}$$

(31)

where $\bar{\omega} = 4\pi\omega\tau_B$ and $\bar{\gamma} = 4\pi\gamma\tau_B$. For the magnetic moment of a magnetite nanoparticle - $m = 10^{-19}$ J/T, for a water suspension - $\eta = 10^{-3}$ kg/m · sec, at room temperature and for a weak radio frequency field - $b = 0.4 \cdot 10^{-3}$ T, we get: $\tau_B = 0,4 \cdot 10^{-6}$, $a = 2,5$ and $\varepsilon = 10^{-2}$. Let's take the solution of system (31) in the form of the power series of ε

$$\begin{aligned} \bar{\xi}^2 &\approx [\bar{\xi}^2]^{(0)} + \varepsilon [\bar{\xi}^2]^{(1)} + \dots, \\ \bar{\zeta}^2 &\approx [\bar{\zeta}^2]^{(0)} + \varepsilon [\bar{\zeta}^2]^{(1)} + \dots, \end{aligned} \quad (32)$$

where the zero order quantities $[\bar{\xi}^2]^{(0)}$, $[\bar{\zeta}^2]^{(0)}$, are determined from the following equations

$$\begin{cases} \frac{d[\overline{\xi^2}]^{(0)}}{d\tilde{\tau}} = 4\pi, \\ \frac{d[\overline{\zeta^2}]^{(0)}}{d\tilde{\tau}} = 4\pi(1 - a\overline{\zeta \sin 2\zeta}^{(0)}), \end{cases} \quad (33)$$

And the first-order corrections $[\overline{\xi^2}]^{(1)}$ and $[\overline{\zeta^2}]^{(1)}$ - from the equations

$$\begin{cases} \frac{d[\overline{\xi^2}]^{(1)}}{d\tilde{\tau}} = -4\pi\overline{\xi \sin \theta}^{(0)} e^{-\bar{\nu}\tilde{\tau}} \sin \bar{\omega} \tilde{\tau}, \\ \frac{d[\overline{\zeta^2}]^{(1)}}{d\tilde{\tau}} = -4\pi\overline{\zeta \sin \theta}^{(0)} e^{-\bar{\nu}\tilde{\tau}} \sin \bar{\omega} \tilde{\tau}, \end{cases} \quad (34)$$

Where the line on the top of the formula and (0) denotes averaging with undisturbed condition.

The solution of the first equation of (33) is $[\overline{\xi^2}]^{(0)} = \frac{t}{\tau_B} = \frac{kT}{3V\eta} t$, which is a rotational analogue of Einstein's formula (20).

Let us study the flow of fluctuations in the zero approximation of the perturbation theory. The 2nd equation of the system (31) on the right side can be represented as a product of infinite series:

$$\overline{\zeta \sin 2\zeta}^{(0)} \approx 2[\overline{\zeta^2} - \frac{\overline{\zeta^4}}{3!} + \dots]^{(0)} [1 - \frac{\overline{\zeta^2}}{2!} + \frac{\overline{\zeta^4}}{4!} \dots]^{(0)}. \quad (35)$$

If we use N. Bogolubov's ideas about "separation of correlations":

$$\overline{\zeta^{2n}} \approx [[\overline{\zeta^2}]^{(0)}]^{(n)}$$

Then we are able to represent the left side of (35) with $[\overline{\zeta^2}]^{(0)}$:

$$2\sqrt{\overline{\zeta^2}^{(0)}} \left[\sqrt{\overline{\zeta^2}^{(0)}} - \frac{\sqrt{(\overline{\zeta^2}^{(0)})^3}}{3!} + \dots \right]^{(0)} \left[1 - \frac{\overline{\zeta^2}}{2!} + \frac{\overline{\zeta^2}^2}{4!} + \dots \right]^{(0)} = \sqrt{\overline{\zeta^2}^{(0)}} \sin 2\sqrt{\overline{\zeta^2}^{(0)}}. \quad (36)$$

Then, using formulas (35) and (36), we get from (33):

$$\frac{d[\overline{\zeta^2}]^{(0)}}{d\tilde{\tau}} = 4\pi \left(1 - a\sqrt{\overline{\zeta^2}^{(0)}} \sin 2\sqrt{\overline{\zeta^2}^{(0)}} \right). \quad (37)$$

We obtained the equation (37) closed with respect to $[\overline{\zeta^2}]^{(0)}$.

(37) is Inhomogeneous equation with respect to $\sqrt{\overline{\zeta^2}^{(0)}}$, so its solution $[\overline{\zeta^2}]^{(0)}$ can be presented as a sum:

$$[\overline{\zeta^2}]^{(0)} = \overline{\zeta^2}_h^{(0)} + \overline{\zeta^2}_{nh}^{(0)} \quad (38)$$

Where $\overline{\zeta^2}_h^{(0)}$ is a general solution of a homogeneous equation:

$$\frac{d\overline{\zeta^2}_h^{(0)}}{d\tilde{\tau}} = -4\pi a \sqrt{\overline{\zeta^2}_h^{(0)}} \sin 2\sqrt{\overline{\zeta^2}_h^{(0)}}, \quad (39)$$

And $\overline{\zeta^2}_{nh}^{(0)}$ - Inhomogeneous equation:

$$\sqrt{\overline{\zeta^2}_{nh}^{(0)}} \sin 2\sqrt{\overline{\zeta^2}_{nh}^{(0)}} = \frac{1}{a}, \quad a \neq 0 \quad (40)$$

- private solution.

Equation (40) is a transcendental equation and therefore can only be solved by numerical methods. Let us introduce the notation $\sqrt{\overline{\zeta^2}(a, \tau \rightarrow 0)} \equiv \zeta_\infty(a)$. At room temperature, for magnetite nanoparticles - ($a \approx 2.5$), the solution of the transcendental equation (40), obtained by numerical methods, is. $\zeta_\infty(2,5) \approx 0,5$ нм $\approx 28^0$.

The general solution of the homogeneous equation (39) is:

$$\sqrt{\overline{\zeta^2}_h^{(0)}} = \tan^{-1}(C e^{-4\pi a \tilde{\tau}}), \quad (41)$$

where C is the integration constant. If the initial condition of equation (38) is $[\overline{\zeta^2}]^{(0)}(0) = 0$, then $C = -\tan \zeta_\infty(a)$. So this complete solution of (38) is :

$$\sqrt{[\overline{\zeta^2}]^{(0)}} = -\tan^{-1}[\tan \zeta_\infty(a) e^{-4\pi a \tilde{\tau}}] + \zeta_\infty(a). \quad (42)$$

At large times ($\tilde{\tau} \gg 1/4\pi a$) from (42) we get:

$$\sqrt{[\overline{\zeta^2}]^{(0)}}(\tilde{\tau} \rightarrow \infty) = \zeta_\infty(a).$$

Suppose that $\overline{\xi^2}$ and $\overline{\zeta^2}$ follow the corresponding variables ξ and ζ . Since the dimensionless period of motion is π , the fluctuation period of $\overline{\xi^2}$ is also $\widetilde{T}_0 = \pi$

$$[\overline{\xi^2}]^{(0)}(\tilde{\tau} + \widetilde{T}_0) = [\overline{\xi^2}]^{(0)}(\tilde{\tau}), \quad (43)$$

\widetilde{T}_0 - fluctuation in time gets the maximum value $[\overline{\xi^2}]^{(0)}(\widetilde{T}_0) = 4\pi^2$.

Taking into account the periodicity condition (43), the solution of the first equation of the system (33) is:

$$[\overline{\xi^2}]^{(0)} = 4\pi(\tilde{\tau} - \pi|n|), \quad (44)$$

where

$$n\pi \leq \tilde{\tau} < (n+1)\pi, \quad n = 0, \pm 1, \pm 2, \dots$$

The function (44) has a "sawtooth" shape (Fig. 5)

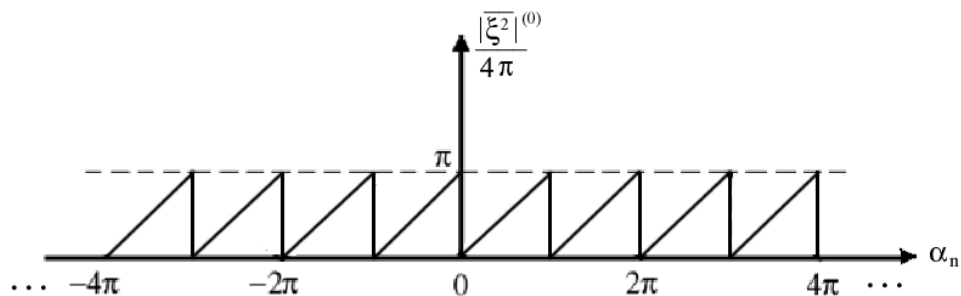


Fig. 5. Dependence of fluctuation flux on time.

By expanding the function (44) into a Fourier series, the spectral composition of the fluctuation stream is:

$$\overline{[\xi^2]}^{(0)} = 4\pi^2 \left[\frac{1}{2} - \frac{1}{\pi} \left(\frac{\sin \tilde{\tau}}{1} + \frac{\sin 2\tilde{\tau}}{2} + \dots + \frac{\sin n\tilde{\tau}}{n} + \dots \right) \right], \quad (45)$$

Its asymptotic value at long times $t \gg \tau_B$ is, $\overline{\overline{[\xi^2]}}^{(0)} = 2\pi^2$, where the double line at the top of the formula denotes averaging over longer times than what was meant by the (5) averaging formula

$$\overline{\overline{A(t)}} = \frac{1}{t} \int_0^t A(x) dx \Big|_{t \gg \tau_B} \quad (46)$$

At large times $t \gg \tau_B$ we get $\xi_\infty \equiv \sqrt{\overline{[\xi^2]}^{(0)}} \approx \sqrt{2}\pi \approx 1,4\pi$. For "old" variables - $\theta_\infty(a) = \frac{\sqrt{2}}{2}\pi + \frac{1}{2}\zeta_\infty(a)$ and $\psi_\infty(a) = \frac{\sqrt{2}}{2}\pi - \frac{1}{2}\zeta_\infty(a)$.

Now let's study the resonance effect of the radio frequency field on the periodic motion of the fluctuation, which is present in the first order corrections $\overline{[\xi^2]}^{(1)}$, $\overline{[\zeta^2]}^{(1)}$ and are determined by the system of equations (34). It follows from the same system that in order to calculate these quantities, we need to calculate the expressions $\overline{\xi \sin \theta}^{(0)}$ and $\overline{\zeta \sin \theta}^{(0)}$. We take into account that the main contribution to these terms is the resonance harmonic ($\tilde{\omega} = 2$), which is proportional to $\sin \tilde{\omega} \tilde{\tau}$ ($\omega_0 = \frac{1}{4\pi\tau_B}$). At the same time, we use the following formulas for the "separation" of average values $\overline{[\xi^{2n}]}^{(0)} \approx \left[\overline{[\xi^2]}^{(0)} \right]^n$, $\overline{[\xi^{2n+1}]}^{(0)} \approx \left[\overline{[\xi^2]}^{(0)} \right]^n \bar{\xi} \approx 0$.

Therefore, we get:

$$\overline{\xi \sin \theta}^{(0)} \approx \overline{\overline{\xi \sin \theta}}^{(0)} \approx \overline{\xi \sin \frac{\zeta_\infty}{2}} \cos \frac{\zeta_\infty}{2} + \overline{\xi \cos \frac{\zeta_\infty}{2}} \sin \frac{\zeta_\infty}{2} \approx$$

$$\approx \overline{\xi \left(\frac{\xi}{2} - \frac{\xi^3}{2^3 \cdot 3!} + \dots \right)}^{(0)} \cos \frac{\zeta_\infty}{2} + \overline{\xi \left(1 - \frac{\xi^2}{2^2 \cdot 2!} + \dots \right)}^{(0)} \sin \frac{\zeta_\infty}{2} \approx \quad (47)$$

$$\approx \left(\frac{1}{2} [\overline{\xi^2}]^{(0)} - \frac{[\overline{\xi^2}]^{(0)(2)}}{2^3 3!} + \dots \right) \cos \frac{\zeta_\infty}{2},$$

$$\overline{\zeta \sin \theta}^{(0)} = 0.$$

Let's say only one harmonic enters the resonance $\gamma \ll \omega_0$. Since we are only interested in the main ($\omega \approx \omega_0$) resonant terms, we neglect all other multiple harmonics in the right-hand side of equation (34). If in the last part of transformation (47) we leave only the first term, in which we keep only the first resonant harmonic of (45), we get:

$$\overline{\zeta \sin \theta}^{(0)} \Big|_{\omega \approx \omega_0} \approx \frac{1}{2} [\overline{\xi^2}]_{\omega_0}^{(0)} \cos \frac{\zeta_\infty(a)}{2} \approx -2\pi \cos \frac{\zeta_\infty(a)}{2} \sin \tilde{\omega} \tilde{\tau} \quad (48)$$

where $\tilde{\omega} = \frac{2\pi}{T_0} = 2$.

If we return to the dimensional quantities in equations (34) and (48), equations (34) takes the form:

$$\begin{aligned} \dot{[\overline{\xi^2}]}^{(1)} &= \frac{2\pi}{\tau_B} \cos \frac{\zeta_\infty(a)}{2} e^{-\gamma t} \sin \omega t \sin \omega_0 t \\ \dot{[\overline{\zeta^2}]}^{(1)} &= 0 \end{aligned} \quad (49)$$

where $\omega_0 = \frac{1}{4\pi\tau_B}$

Let's note that the contribution of magnetic anisotropy is included in the system of equations (49) only through the quantity $\zeta_\infty(a)$.

If we leave only the resonance terms in (49) ($\omega_0 \approx \omega$), then their solution

$$\begin{aligned} [\overline{\xi^2}]^{(1)} &= \frac{\pi}{\tau_B} \cos \frac{\zeta_\infty(a)}{2} \cdot \frac{1}{\gamma^2 + \Delta^2} [e^{-\gamma t} (\Delta \sin \Delta t - \gamma \cos \Delta t) + \gamma], \\ [\overline{\zeta^2}]^{(1)} &= \zeta_\infty(a), \end{aligned} \quad (50)$$

where $\omega - \omega_0 = \Delta$. In the limit $\tau_B \ll t \ll \frac{1}{\gamma}, \frac{1}{\Delta}$ the solutions of (50) :

$$[\overline{\xi^2}]^{(1)} \approx \frac{\pi}{\tau_B} \cos \frac{\zeta_\infty(a)}{2} \cdot \frac{\Delta^2}{\gamma^2 + \Delta^2} t. \quad (51)$$

Second equation of (49) shows that at very long times ($t \gg \tau_B$) $\zeta = \zeta_\infty(a)$ the magnitude of the angle is preserved even in the presence of a resonant field.

At longer times $t \gg 1/\gamma$, as follows from (50), the stationary resonance correction is:

$$\langle [\overline{\xi^2}]^{(1)} \rangle = \frac{\pi}{\tau_B} \cos \frac{\zeta_\infty(a)}{2} \cdot \frac{\gamma}{\gamma^2 + \Delta^2} \quad (52)$$

where $\langle \dots \rangle$ denotes the asymptotic value of the function $t \gg (1/\gamma)$. It follows from this solution that the resonant field causes the rotation of the angles θ and ψ (Fig. 6), keeping the angle between them unchanged.

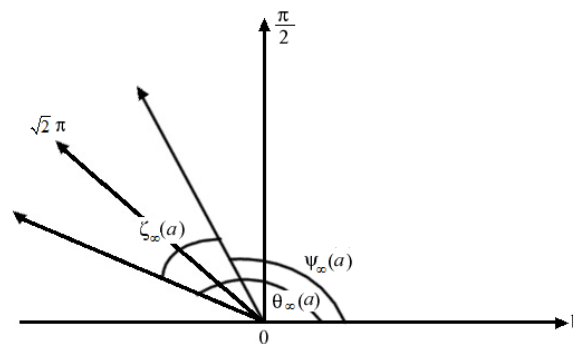


Fig. 6. Fluctuations of θ and ψ angles

For magnetite nanoparticles, at room temperature ($a \approx 2,5$), $\cos \frac{\zeta_{\infty}(2,5)}{2} \approx 0,95$. Under exact resonance conditions ($\Delta=0$) and for the value of the radio frequency field width - $\gamma = 10^3$ 1/s, the stationary value of the fluctuation:

$$\langle \bar{\xi}^2 \rangle = \overline{[\xi^2]}^{(0)} + \langle \varepsilon [\xi^2] \rangle^{(1)} \approx 2\pi^2 + \frac{\pi\varepsilon}{\gamma\tau_B} \cos \frac{\zeta_{\infty}(2,5)}{2} \approx 9\pi^2, \quad (53)$$

$$\sqrt{\langle \bar{\xi}^2 \rangle} \approx 3\pi.$$

From this, we subtract the 2π -period for ξ and get the value $\bar{\xi} \equiv \sqrt{\langle \bar{\xi}^2 \rangle} \approx \pi$, which means the reversal of the moment. It follows from the equations (52) and (53) that any orientation of the magnetic moment can be obtained by selecting b and γ parameters.

The radio frequency resonant field in the time interval $\tau_0 \ll t \ll 1/\gamma$ causes the fluctuation flow rate to increase. As can be seen from (51), the correction of the fluctuating flow rate under the considered conditions is:

$$\langle [\dot{\bar{\xi}}^2] \rangle^{(1)} = \frac{\pi}{\tau_B} \cos \frac{\zeta_{\infty}}{2} \cdot \frac{\Delta^2}{\gamma^2 + \Delta^2}. \quad (54)$$

As follows from (54), in the case of a monochromatic resonant field ($\gamma=0$), the rotational velocity of the fluctuation under the influence of the resonant field increases by $\pi\varepsilon \cos \frac{\zeta_{\infty}}{2} \approx 3 \cdot 10^{-2}$, which is equal to 3% of $1/\tau_B$

4. Resume

As we have seen, Brownian motion in suspension is characterized by different time scales that satisfy the following conditions of the time hierarchy $\tau \ll \tau_0 \ll t_0$, where

$$\tau_0 = \frac{m}{6\pi r\eta}, t_0 = \frac{3\pi r\eta}{kT} \quad (55)$$

- for transitional Brownian motion ,

$$\tau \ll \tau_S \ll \tau_B,$$

Where

$$\tau_S = \frac{I}{3V\eta}, \quad \tau_B = \frac{3V\eta}{kT} \quad (56)$$

for rotational Brownian motion.

Chaos is generated during the shortest τ -time due to the impact of collisions caused by uncompensated forces. At this stage, Cartesian coordinates become useless for describing motion. The role of the "good" variable at this stage is played by the mean square fluctuation $\overline{x^2}$. In τ_0 time, fluctuating flows of exponential braking motion, caused by fluid viscosity, coexists with chaotic motion, but after τ_0 time passes, it fades away and only chaotic motion remains. For the rate of change in time of the s-displacement of the Brownian particle under the conditions of chaotic motion, at times $t \gg \tau_0$ we get

$$s = \sqrt{\overline{x^2}} = \sqrt{t/t_0}.$$

Similarly, for rotational Brownian motion at $t \gg \tau_S$ times, we have

$$\sqrt{\overline{\varphi^2}} = \sqrt{t/\tau_B}.$$

Dependence on the time of displacement from the root "t" is the main characteristic of chaotic motion.

Brownian rotational motion becomes periodic after a longer time $t \gg \tau_B$. Frequency of this motion $\omega_0 = 1/4\pi\tau_B$ is in the radio frequency range. Under the influence of the radio-frequency electromagnetic field, a characteristic picture of the resonance process is obtained: forced rotation of the fluctuating flow and, also, an increase in the rotational speed. At this last stage, the current process depends only on the main parameters of the problem - viscosity and temperature – through ω_0 . The main characteristic of such a resonance process is: if the temperature changes, the resonance frequency will also change, and the resonance effect of the radio frequency field will disappear. This type of resonance is called stochastic resonance.

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