Brownian Motion

Presenting methods of statistical physics, we have discussed characteristics of physical systems averaged over intervals of time which are so long that effects of fluctuations occurring at a shorter time scale can be ignored.

Let us consider, as an example, a pressure which results from collisions of gas particles with a container wall of unit area. If on average one particle hits the wall in time interval τ, we observe the smooth pressure if averaged over the time interval $\Delta t \gg \tau$. The pressure fluctuations show up if Δt becomes comparable to τ.

Pressure fluctuations are not of particular interest but there are phenomena, known as stochastic, which fully depend on random events. The Brownian motion is the first discovered stochastic process and historically the most important. Its understanding led to the establishment of molecular structure of matter.

In 1827, Robert Brown (1773-1858) – a Scottish botanist – observed under a microscope the chaotic continuous motion of small particles suspended in a liquid. It was only in the years 1905-1906 that Albert Einstein (1879-1955) and Marian Smoluchowski (1872-1917) – a Polish physicist and mountaineer, gave a satisfactory explanation of the phenomenon as a result of collisions of the observed particles with liquid molecules. The predicted regularities of Brownian motion were soon observed by the French physicist Jean Baptiste Perrin (1870-1942), the Nobel Prize winner in 1926.

I start the presentation of the Brownian motion theory with the Einstein approach formulated in his 1905 paper. I will pay some attention to a diffusion equation here. Further on the approach formulated by Paul Langevin will be presented.

Einstein approach

- A Brownian motion typically takes place on the surface of the liquid that is it occurs in two dimensions. A three dimensional motion is also possible but at the beginning we consider a one-dimensional motion along axis x of N particles.

- Let $n(t, x)$ be the time dependent density of particles – *Brownian* or *random walkers*. The normalization condition reads
$$\int_{-\infty}^{\infty} dx \, n(t, x) = N. \tag{1}$$

- There is a permanent thermal motion of molecules of liquid which hit a Brownian walker and cause its motion left or right. Let us assume that in the time interval τ the walker moves at a distance Δ with the probability $\phi(\Delta)$.

- The probability $\phi(\Delta)$ obeys the normalization condition
$$\int_{-\infty}^{\infty} d\Delta \, \phi(\Delta) = 1, \tag{2}$$
and the left-right symmetry requires that
$$\phi(\Delta) = \phi(-\Delta). \tag{3}$$

- If at the time $t + \tau$ the walker is in the position x, then it was at t in $x - \Delta$ with the probability $\phi(\Delta)$. So, we write
$$n(t + \tau, x) = \int_{-\infty}^{\infty} d\Delta \, n(t, x + \Delta) \, \phi(\Delta), \tag{4}$$
where the condition (3) is taken into account.

- If τ is much shorter than the characteristic time interval Δt when $n(t,x)$ changes substantially that is $|n(t,x) - n(t+\Delta t, x)|$ is of the order of $n(t,x)$, then we expand $n(t+\tau, x)$ around t as
$$n(t+\tau, x) = n(t,x) + \frac{\partial n(t,x)}{\partial t}\tau. \tag{5}$$

- Now, we assume $\phi(\Delta)$ is small for such Δ that $n(t,x)$ changes substantially and we expand
$$n(t, x+\Delta) = n(t,x) + \frac{\partial n(t,x)}{\partial x}\Delta + \frac{1}{2}\frac{\partial^2 n(t,x)}{\partial x^2}\Delta^2. \tag{6}$$

- Substituting the expansions (5, 6) into Eq. (4) we get
$$\begin{aligned} n(t,x) + \frac{\partial n(t,x)}{\partial t}\tau &= n(t,x)\int_{-\infty}^{\infty} d\Delta\, \phi(\Delta) \\ &+ \frac{\partial n(t,x)}{\partial x}\int_{-\infty}^{\infty} d\Delta\, \Delta\, \phi(\Delta) + \frac{1}{2}\frac{\partial^2 n(t,x)}{\partial x^2}\int_{-\infty}^{\infty} d\Delta\, \Delta^2 \phi(\Delta). \end{aligned} \tag{7}$$

- Taking into account the conditions (2, 3), we get the well known diffusion equation
$$\frac{\partial n(t,x)}{\partial t} = D\frac{\partial^2 n(t,x)}{\partial x^2}, \tag{8}$$
where
$$D \equiv \frac{1}{2\tau}\int_{-\infty}^{\infty} d\Delta\, \Delta^2 \phi(\Delta), \tag{9}$$
is the diffusion constant.

- Let us note that a specific form of the probability distribution $\phi(\Delta)$ merely influences the diffusion constant (9) but not the diffusion equation (8) provided the distribution is normalized (2), symmetric (3) and its second moment (9) exists.

- It should be noted that a process of diffusion – a spontaneous propagation of one substance relative to another and the diffusion equation were known long before Einstein and Smoluchowski studied the Brownian motion. The method of derivation of the equation and its application to describe random walkers were innovative.

Diffusion equation

- We are going to briefly discuss the diffusion equation (8), or rather its three-dimensional generalization
$$\frac{\partial n(t,\mathbf{r})}{\partial t} = D\nabla^2 n(t,\mathbf{r}). \tag{10}$$

- First of all we note that the presented derivation of the diffusion equation is far not the only possible. One immediately gets the equation starting with the experimentally established Fick's law
$$\mathbf{j} = -D\nabla n \tag{11}$$
which states that the flux of diffusing substance $\mathbf{j}$ is proportional to the concentration gradient. The sign minus in Eq. (11) tell us that the flux flows in the direction of the concentration decrease as $D \geqslant 0$.

- Substituting the flux (11) into the continuity equation

$$\frac{\partial n}{\partial t} + \nabla \cdot \mathbf{j} = 0, \tag{12}$$

which expresses the conservation of particle number of diffusing substance, we find the diffusion equation (10).

- The Fick's law and the diffusion equation can be derived within the kinetic theory as the identical in form the equation of heat conductivity which is discussed in Lecture X.

- We are going to solve the equation (10) with the initial condition

$$n(0, \mathbf{r}) = n_0(\mathbf{r}). \tag{13}$$

- Substituting into Eq. (10) the density $n(t, \mathbf{r})$ expressed through its Fourier transform as

$$n(t, \mathbf{r}) = \int \frac{d^3k}{(2\pi)^3}\, e^{-i\mathbf{k}\cdot\mathbf{r}} n(t, \mathbf{k}), \tag{14}$$

one finds the equation

$$\frac{\partial n(t, \mathbf{k})}{\partial t} = -D\mathbf{k}^2 n(t, \mathbf{k}), \tag{15}$$

solved as

$$n(t, \mathbf{k}) = C(\mathbf{k})\, e^{-D\mathbf{k}^2 t}, \tag{16}$$

where $C(\mathbf{k})$ is an arbitrary function to be found from the initial condition.

- Computing the Fourier transform we have

$$n(t, \mathbf{r}) = \int \frac{d^3k}{(2\pi)^3}\, e^{-i\mathbf{k}\cdot\mathbf{r}} C(\mathbf{k})\, e^{-D\mathbf{k}^2 t}. \tag{17}$$

- Since for $t = 0$ Eq. (17) gives the initial condition

$$n_0(\mathbf{r}) = \int \frac{d^3k}{(2\pi)^3}\, e^{-i\mathbf{k}\cdot\mathbf{r}} C(\mathbf{k}), \tag{18}$$

we see that the function $C(\mathbf{k})$ is the Fourier transform of $n_0(\mathbf{r})$ that is

$$C(\mathbf{k}) = \int d^3r\, e^{i\mathbf{k}\cdot\mathbf{r}} n_0(\mathbf{r}). \tag{19}$$

- Substituting the expression (19) into Eq. (17), we obtain the general solution of the diffusion equation

$$n(t, \mathbf{r}) = \frac{1}{(4\pi D t)^{3/2}} \int d^3r' n_0(\mathbf{r}')\, e^{-\frac{(\mathbf{r}-\mathbf{r}')^2}{4Dt}}, \tag{20}$$

where we have computed the integral

$$\int \frac{d^3k}{(2\pi)^3}\, e^{-i\mathbf{k}\cdot\mathbf{r}}\, e^{-a\mathbf{k}^2} = \frac{e^{-\frac{\mathbf{r}^2}{4a}}}{(4\pi a)^{3/2}}. \tag{21}$$

- We note that the solution (20) satisfies the expected normalization condition

$$\int d^3r\, n(t, \mathbf{r}) = \int d^3r\, n_0(\mathbf{r}). \tag{22}$$

- If the diffusing particles originate from $\mathbf{r} = 0$ and
$$n_0(\mathbf{r}) = N\delta^{(3)}(\mathbf{r}), \tag{23}$$
then
$$n(t, \mathbf{r}) = \frac{N}{(4\pi Dt)^{3/2}}\, e^{-\frac{\mathbf{r}^2}{4Dt}}. \tag{24}$$

- Defining $\langle \mathbf{r}^k \rangle$ as
$$\langle \mathbf{r}^k \rangle \equiv \frac{1}{N} \int d^3r\, \mathbf{r}^k n(t, \mathbf{r}), \tag{25}$$
the solution (24) provides the desired relation
$$\langle \mathbf{r}^2 \rangle = 6Dt. \tag{26}$$
We note that $\langle \mathbf{r} \rangle = 0$.

- Eq. (26) tell us that the average of a displacement square of the Brownian walker linearly grows with time which was the main prediction of the Einstein-Smoluchowski theory which was soon later confirmed experimentally by Jean Perrin.

Langevin approach

Paul Langevin developed an alternative approach to the Brownian motion. The approach is dynamically well motivated and applicable to various stochastic problems. We will present its three-dimensional version.

- The starting point for the approach is the Newtonian equation of motion
$$m\frac{d\mathbf{v}(t)}{dt} = -\lambda \mathbf{v}(t) + \mathbf{F}(t), \tag{27}$$
where m is the mass of the Brownian walker and $\mathbf{v}(t)$ its velocity. There are two forces acting of the walker: the friction equal to $-\lambda \mathbf{v}(t)$ and the stochastic force $\mathbf{F}(t)$ which occur due to the thermal motion of liquid molecules. One usually writes down the equation divided by m
$$\frac{d\mathbf{v}(t)}{dt} = -\gamma \mathbf{v}(t) + \mathbf{L}(t), \tag{28}$$
where $\gamma \equiv \lambda/m$ is the friction coefficient and $\mathbf{L} \equiv \mathbf{F}/m$ is called the Langevin force, which, as we will see soon, plays a key role in the approach.

- We will solve Eq. (28) with the initial condition
$$\mathbf{v}(0) = \mathbf{v}_0, \tag{29}$$
using the technique of Laplace transform

- The Laplace transform of a function $f(t)$ is defined as
$$\tilde{f}(s) \equiv \int_0^\infty dt\, e^{-st} f(t). \tag{30}$$
It obviously assumed that the above integral exists. The inverse transform can be found as
$$f(t) = \int_{-i\infty+c}^{i\infty+c} \frac{ds}{2\pi i}\, e^{st} \tilde{f}(s), \tag{31}$$
where the real number c is chosen in such a way that singularities of $\tilde{f}(s)$ are on the left side of the straight line $s = c$.

- Except the definition (30) and Eq. (31) we will refer to two simple formulas. The first is the Laplace transform of the derivative of a function

$$\int_0^\infty dt\, e^{-st}\,\frac{df(t)}{dt} = f(t)e^{-st}\Big|_0^\infty + s\int_0^\infty dt\, e^{-st} f(t) = -f(0) + s\,\tilde{f}(s), \tag{32}$$

where the partial integration has been performed. The second needed formula is the transform of the exponential function

$$\int_0^\infty dt\, e^{-st} e^{-at} = \frac{1}{s+a}. \tag{33}$$

- Let us now perform the Laplace transformation of the Langevin equation (28). After the transformation the differential equation (28) becomes algebraic

$$s\tilde{\mathbf{v}}(s) - \mathbf{v}_0 = -\gamma\tilde{\mathbf{v}}(s) + \tilde{\mathbf{L}}(s), \tag{34}$$

which is solved by

$$\tilde{\mathbf{v}}(s) = \frac{\mathbf{v}_0 + \tilde{\mathbf{L}}(s)}{s+\gamma}. \tag{35}$$

- To get $\mathbf{v}(t)$, the inverse transformation of the function (35) should be performed. According to the formula (31) the first term of the solution (35) gives

$$\mathbf{v}_0 \int_{-i\infty+c}^{i\infty+c} \frac{ds}{2\pi i}\,\frac{e^{st}}{s+\gamma} = \mathbf{v}_0 e^{-\gamma t}, \tag{36}$$

which is obtained either using the integral Cauchy's formula or the equation (33).

- The transformation of the second term of the function (35) is performed as follows

$$\begin{aligned}\int_{-i\infty+c}^{i\infty+c} \frac{ds}{2\pi i}\, e^{st}\,\frac{\tilde{\mathbf{L}}(s)}{s+\gamma} &= \int_0^\infty dt'\,\mathbf{L}(t') \int_{-i\infty+c}^{i\infty+c} \frac{ds}{2\pi i}\,\frac{e^{s(t-t')}}{s+\gamma} \\ &= \int_0^\infty dt'\,\mathbf{L}(t')\,\Theta(t-t')\,e^{-\gamma(t-t')} = e^{-\gamma t}\int_0^t dt'\, e^{\gamma t'}\mathbf{L}(t'),\end{aligned} \tag{37}$$

where $\Theta(t)$ is the step function which equals unity for $t \geqslant 0$ and vanishes otherwise.

- The solution of the Langevin equation (28) finally equals

$$\mathbf{v}(t) = \mathbf{v}_0 e^{-\gamma t} + e^{-\gamma t}\int_0^t dt'\, e^{\gamma t'}\mathbf{L}(t'). \tag{38}$$

- An important element of the Lagevin formalism is the averaging over statistical ensemble. So, we consider not one but a whole ensemble of random walkers and we assume that the averages over the ensemble satisfy the following equalities

$$\langle \mathbf{L}(t)\rangle = 0, \tag{39}$$

$$\langle v_0^i L^j(t)\rangle = 0, \tag{40}$$

$$\langle L^i(t_1)\, L^j(t_2)\rangle = \Gamma\delta^{ij}\delta(t_1 - t_2). \tag{41}$$

The relation (39) tells us the average value of the Langevin force vanishes. According to the second one (40) the initial velocity is independent of the Langevin force and consequently the average of their product vanishes. The third relation (41) states that the Langevin forces at different moments of time are independent from each other. The correlation, which is characterized by the parameter Γ, occurs only when the forces are simultaneous.

- Using the relations (39, 40, 41), we find that

$$\langle \mathbf{v}(t)\rangle = \mathbf{v}_0 e^{-\gamma t}. \tag{42}$$

- Let us now compute the velocity correlation function that is $\langle v^i(t_1)\, v^j(t_2)\rangle$. Using the relations (39, 40, 41), one obtains

$$\langle v^i(t_1)\, v^j(t_2)\rangle = v_0^i v_0^j\, e^{-\gamma(t_1+t_2)} + e^{-\gamma(t_1+t_2)} \int_0^{t_1} dt' \int_0^{t_2} dt'' e^{\gamma(t'+t'')} \Gamma \delta^{ij} \delta(t'-t''). \tag{43}$$

- To take the integral over t' and t'' we must decide which time t_1 or t_2 is later. If $t_2 \geqslant t_1$, we first integrate over t'' and get rid of the delta function. Thus, we find

$$\langle v^i(t_1)\, v^j(t_2)\rangle = \left(v_0^i v_0^j - \delta^{ij} \frac{\Gamma}{2\gamma}\right) e^{-\gamma(t_1+t_2)} + \delta^{ij} \frac{\Gamma}{2\gamma} e^{-\gamma(t_2-t_1)}. \tag{44}$$

For $t_1 \geqslant t_2$, we have

$$\langle v^i(t_1)\, v^j(t_2)\rangle = \left(v_0^i v_0^j - \delta^{ij} \frac{\Gamma}{2\gamma}\right) e^{-\gamma(t_1+t_2)} + \delta^{ij} \frac{\Gamma}{2\gamma} e^{-\gamma(t_1-t_2)}. \tag{45}$$

- For any t_1 and t_2 the correlation function can be written as

$$\langle v^i(t_1)\, v^j(t_2)\rangle = \left(v_0^i v_0^j - \delta^{ij} \frac{\Gamma}{2\gamma}\right) e^{-\gamma(t_1+t_2)} + \delta^{ij} \frac{\Gamma}{2\gamma} e^{-\gamma|t_1-t_2|}. \tag{46}$$

- The formula (46) tells us, in particular, that

$$\langle \mathbf{v}^2(t)\rangle = \left(\mathbf{v}_0^2 - \frac{3\Gamma}{2\gamma}\right) e^{-2\gamma t} + \frac{3\Gamma}{2\gamma}. \tag{47}$$

Therefore, after the time $t \gg \gamma^{-1}$ the average value of the velocity square reaches its equilibrium value equal

$$\lim_{t\to\infty} \langle \mathbf{v}^2(t)\rangle = \frac{3\Gamma}{2\gamma}. \tag{48}$$

- If the liquid, where the Brownian walker is immersed, has the temperature T, the equilibrium energy equals

$$\frac{m\langle \mathbf{v}^2(t)\rangle}{2} = \frac{3}{2} k_B T. \tag{49}$$

- Comparing the formulas (48) and (49) we find the relation among Γ and γ as

$$\Gamma = \frac{2k_B T\gamma}{m}. \tag{50}$$

This is a special case of the fluctuation-dissipation relations which connect the quantities which control a rate of dissipation and equilibration of the system under study, in our case this is the friction coefficient, and the quantities which characterize fluctuations in the system which is Γ in case of the Brownian motion.

- Let us note that when $\mathbf{v}_0^2 = 3k_B T/m$, the correlation becomes particularly simple

$$\langle v^i(t_1)\, v^j(t_2)\rangle = \delta^{ij} \frac{k_B T}{m} e^{-\gamma|t_1-t_2|}. \tag{51}$$

- If the velocity of the Brownian walker is known, its trajectory is

$$\mathbf{r}(t) = \int_0^t dt'\, \mathbf{v}(t'), \tag{52}$$

where we have chosen $\mathbf{r}(0) = 0$.

- The average square of the walker's displacement equals

$$\langle \mathbf{r}^2(t) \rangle = \int_0^t dt' \int_0^t dt''\, \langle \mathbf{v}(t') \cdot \mathbf{v}(t'') \rangle. \tag{53}$$

Using the correlation function (51), Eq. (53) gives

$$\begin{aligned} \langle \mathbf{r}^2(t) \rangle &= \frac{3k_BT}{m} \int_0^t dt' \int_0^t dt''\, e^{-\gamma|t'-t''|} \qquad (54) \\ &= \frac{3k_BT}{m} \int_0^t dt' \Big(\int_0^{t'} dt''\, e^{-\gamma(t'-t'')} + \int_{t'}^t dt''\, e^{-\gamma(t''-t')} \Big) = \frac{6k_BT}{m\gamma} \Big(t + \frac{e^{-\gamma t} - 1}{\gamma} \Big). \end{aligned}$$

- For times which are so long that $t \gg \gamma^{-1}$, we find

$$\langle \mathbf{r}^2(t) \rangle = \frac{6k_BT}{m\gamma}\, t. \tag{55}$$

- Comparing the results (26) and (55), one expresses the diffusion constant D through the friction coefficient γ as

$$D = \frac{k_BT}{m\gamma}, \tag{56}$$

which is another fluctuation-dissipation relation known as the Einstein relation.

T H E E N D