New York University
Physics Department
Class GA.2061 "Non-Equilibrium Statistical Physics", Fall 2021

Home Work 09 *Solutions*

1. Find probability, $P(t)dt$, of the first passage time being between t and $t+dt$ for a random walker on a semi-infinite line $x>0$, with absorbing boundary condition at $x=0$ and starting from some given $x_0>0$, with given diffusion coefficient D and given bias velocity v. That means, consider gambler's ruin problem in a dishonest casino, in which probability to win at every step is slightly but systematically smaller (if $v<0$) or larger (if $v>0$) than the probability to loose. Is $\int_0^\infty P(t)dt = 1$? Why yes or why no? Plot $P(t)$ against t, in properly dimensionless form, for both $v>0$ and $v<0$.

Hint: To enforce absorbing boundary condition, consider introducing an image "antiparticle" at time $t=0$ in the point $-x_0$ with some weight w, and adjust w properly.

Solution

The diffusion equation in this case reads

$$\partial_t c = D\partial_x^2 c - v\partial_x c \ , \tag{1}$$

which means current $j=-D\partial_x c + vc$; $v<0$ means drift towards zero, $v>0$ drift away from zero. Its solution on an infinite line, starting from x_0 at $t=0$ reads

$$c(t,x) = \frac{1}{(4\pi Dt)^{1/2}} e^{-\frac{(x-x_0-vt)^2}{4Dt}} \ . \tag{2}$$

It has simple meaning: every particle moves with speed v and, in addition to that, also undergoes a random walk around its moving mean position $x = x_0 + vt$.

For a system with no bias, reflection method is used to find the solution with absorbing boundary condition $c(t,x)|_{x=0} = 0$. To generalize reflection method to include bias velocity v, consider an image "antiparticle" introduced in the system with some weight w. Then the Green's function reads

$$c(t,x) = \frac{1}{(4\pi Dt)^{1/2}} \left[e^{-\frac{(x-x_0-vt)^2}{4Dt}} - w e^{-\frac{(x+x_0-vt)^2}{4Dt}} \right] \ , \tag{3}$$

and we should adjust w such as to obey the boundary condition $c(t,x)|_{x=0} = 0$. Simple calculation then gives $w = e^{-vx_0/D}$ and

$$c(t,x) = \frac{1}{(4\pi Dt)^{1/2}} \left[e^{-\frac{(x-x_0-vt)^2}{4Dt}} - e^{-\frac{vx_0}{D} - \frac{(x+x_0-vt)^2}{4Dt}} \right] \ . \tag{4}$$

Clearly, it does satisfy the equation, and boundary conditions, and initial conditions; so, this is the solution. Knowing it, we find the distribution of first passage times by finding the flow through zero, which is $J(t) = (-D\partial_x c(t,x) + vc(t,x))|_{x=0}$. The answer reads

$$P(t) = \frac{x_0}{\sqrt{4\pi D} t^{3/2}} e^{-(x_0+vt)^2/4Dt} \ . \tag{5}$$

This was derived by nobody lesser than E.Schrödinger [1] and, independently in the same year of 1915, by M.Smoluchowski [2].

Let us analyze the result. $P(t)dt$ represents the probability to get absorbed at time between t and $t+dt$. If $v<0$, which means drift towards zero, then $\int_0^\infty P(t)dt = 1$; that means, with probability 1 the walker will end up absorbed. As we know, this is still true at $v=0$. It is not surprising that eventual absorption is inevitable in the presence of drift towards zero. By contrast, if there is a drift away from zero, i.e. $v>0$, then $\int_0^\infty P(t)dt = e^{-vx_0/D}$: only a fraction of walkers get absorbed, while others escape to infinity.

The plot of this probability $P(t)$ is shown in the figure 1

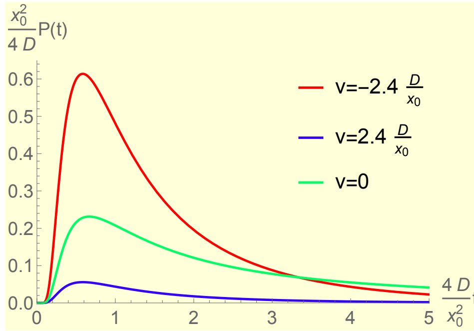

FIG. 1. Absrption probability at time t, $P(t)$, as a function of t, according to formula (5). With negative drift velocity (red curve), or even with zero (green), the distribution is normalized, meaning eventual certainty of absorption. But with positive drift (blue curve), the probability of eventual absorption is smaller than one: $\int_0^\infty P(t)dt = e^{-vx_0/D} < 1$.

2. For the 1D model of diffusion on the interval between a and b in some potential $U(x)$, find the probabilities $p_A(x_0)$ and $p_B(x_0)$ – the probability to reach one of the ends without ever touching the other, starting from x_0. This problem is a simplified version of the one arising in the fields such as protein folding and other complex reactions. Imagine a system that navigates a very complex multidimensional energy landscape that has two very stable states, represented by very deep minima, call them a and b (in case of a protein, they maybe the totally unfolded state, whereby protein is subject to degradation, and correctly folded state, in which protein may be performing its biological function). In this type of the context, you can imagine a state x_0 whereby, for instance, protein has not folded yet, but already cleared all the high barriers on the way towards folding and, therefore, *committed* to fold; for other states x_0, it may be committed to unfold, or be somewhere in between. In this context, probability that you should find, $p_A(x_0)$ (or $p_B(x_0)$) is sometimes referred to as a *commitor*; I encourage you to Google on this term, paying attention to the fact that the next to last letter is o, not e!

Solution

We should consider stationary process, impose absorbing boundary conditions at both ends, and compare current flowing out from the two ends. To find the concentration profile, let us assume that current J flows into the system at point x_0, while currents J_A and J_B flow out at the corresponding ends. Under stationary conditions $J = J_A + J_B$, and as regards current $J(x)$, it must be equal $J(x) = -J_A$ at $x < x_0$, and $J(x) = J_B$ at $x > x_0$. Then the solution of Smoluchowski equation for the concentration profile reads

$$c(x) = \begin{cases} \frac{J_A}{D} e^{-U(x)} \int_a^x e^{U(x')} dx' & \text{for} \quad x < x_0 \\ \\ \frac{J_B}{D} e^{-U(x)} \int_x^b e^{U(x')} dx' & \text{for} \quad x > x_0 \end{cases} \tag{6}$$

These two expressions should yield the same thing at $x = x_0$, which means

$$J_A \int_a^{x_0} e^{U(x')} dx' = J_B \int_{x_0}^b e^{U(x')} dx' \ , \tag{7}$$

which means that total current J is distributed between two parallel resistors inversely proportional to their resistances. Indeed, let us denote

$$R_{pq} = \int_p^q e^{U(x')} dx' \tag{8}$$

and call it resistance between points p and q. Then formula (7) reads

$$J_A R_{A0} = J_B R_{0B} \ , \tag{9}$$

which is the familiar Kirchoff law statement. Thus, we obtain for the probabilities in question

$$p_A = \frac{J_A}{J} = \frac{R_{0B}}{R_{A0} + R_{0B}} = \frac{R_{0B}}{R_{AB}} = \frac{\int_{x_0}^b e^{U(x')} dx'}{\int_a^b e^{U(x')} dx'} \tag{10a}$$

$$p_B = \frac{J_B}{J} = \frac{R_{A0}}{R_{A0} + R_{0B}} = \frac{R_{A0}}{R_{AB}} = \frac{\int_a^{x_0} e^{U(x')} dx'}{\int_a^b e^{U(x')} dx'} \tag{10b}$$

For instance, if $U = 0$, then $p_A(x_0) = \frac{b-x_0}{b-a}$ and $p_B(x_0) = \frac{x_0-a}{b-a}$. As another example, suppose there is a very high barrier between a and x_0; in this case, $p_A \ll p_B$, i.e., the system at x_0 is almost entirely committed to the side b.

3. Consider a heavy particle in a gas of light ones at a given temperature, and write down the Fokker-Planck equation describing the relaxation of momentum distribution of the heavy particle. What is the equilibrium distribution of momenta? Imagine that the initial momentum of a heavy particle is $\mathbf{p}_0$, i.e., the initial distribution of heavy particle momentum is $f(\mathbf{p}) = \delta(\mathbf{p} - \mathbf{p}_0)$; $\mathbf{p}_0 = 0$ is a possible example. How does this distribution relax to the equilibrium? What is the relaxation time? Write down the complete solution for time dependent momentum distribution $f(t, \mathbf{p})$ in terms of eigenfunctions of quantum harmonic oscillator (which you may assume known). You may want to follow the steps below.

Step 1:: Write down the Fokker-Planck equation (which is continuity equation in momentum space), with two coefficients – "drift" and "diffusion". Express the "drift" coefficient in this equation through the "diffusion" coefficient based on your knowledge of the equilibrium distribution of momenta (i.e., use the analog of Einstein relation).

Step 2:: In general, the "diffusion coefficient" in momentum space is a tensor $B_{\alpha\beta}$, but if the speeds of heavy particles are small compared to speeds of light particles, the former ones can be considered immobile in collisions and then $B_{\alpha\beta}$ does not depend on heavy particle momentum $\mathbf{p}$ – which makes it inevitable that $B_{\alpha\beta} = B\delta_{\alpha\beta}$, B being a constant (since there is no other direction apart from $\mathbf{p}$ on which $B_{\alpha\beta}$ could depend).

Step 3:: You must have obtained Fokker-Planck equation which looks like a diffusion equation for a particle in a certain potential field, U. What kind of field is it?

Step 4:: Bring your Fokker-Planck equation to the symmetric (Hermitian) form, by defining a new function $F(t, \mathbf{p}) = f(t, \mathbf{p})e^{U(\mathbf{p})/2T}$.

Step 5:: Your symmetric equation should look familiar to you from quantum mechanics, and you should be able to write the answer $F(t, \mathbf{p}) = \sum_{n=0}^{\infty} e^{\lambda_n t}\psi_n(\mathbf{p})\psi_n(\mathbf{p}_0)$ (bilinear expansion), where λ_n are the eigenvalues (related by re-naming variables to the energy levels), and ψ_n are eigenfunctions.

Solution

Fokker-Planck equation reads

$$\frac{\partial f(\mathbf{p})}{\partial t} = -\frac{\partial}{\partial p_\alpha} J_\alpha \ , \quad \text{where} \quad J_\alpha = -A_\alpha f(\mathbf{p}) - B_{\alpha\beta}\frac{\partial f(\mathbf{p})}{\partial p_\beta} \ . \tag{11}$$

The flux J must vanish when distribution is equilibrated, i.e., when it is equal to Maxwell distribution $e^{-p^2/2mT}$. Equation $J = 0$ for this distribution gives

$$mTA_\alpha = B_{\alpha\beta}p_\beta \ . \tag{12}$$

Assuming further $B_{\alpha\beta} = B\delta_{\alpha\beta}$ as suggested in the problem, we arrive at

$$\frac{\partial f}{\partial t} = B\nabla_{\mathbf{p}}\left[\nabla_{\mathbf{p}} f + \frac{\mathbf{p}}{mT} f\right] \ , \tag{13}$$

which looks like the diffusion equation for a particle in a harmonic potential, and B plays the role of diffusion coefficient and, interestingly, kinetic energy plays the role of potential:

$$\frac{\partial f}{\partial t} = B\nabla_{\mathbf{p}}\left[e^{-U/T}\nabla_{\mathbf{p}}\left(fe^{U/T}\right)\right] \ \text{, where} \ \ U = \frac{\mathbf{p}^2}{2m} \ . \tag{14}$$

In terms of $F(t, \mathbf{p}) = f(t, \mathbf{p})e^{U(\mathbf{p})/2T}$, this reads

$$\frac{\partial F}{\partial t} = B\nabla^2_{\mathbf{p}} F - B\frac{\mathbf{p}^2}{4m^2T^2}F + \frac{3B}{2mT}F \ . \tag{15}$$

This looks similar to Shroedinger equation for a harmonic oscillator:

$$i\hbar\frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2_{\mathbf{x}}\psi + \frac{k\mathbf{x}^2}{2}\psi \ . \tag{16}$$

Energy levels for the harmonic oscillator in 3D are $E_n = \hbar\omega\left(n+\frac{3}{2}\right)$ $(n = n_x + n_y + n_z)$. Comparing the two equations, we write down the answer: Eigenvalues for our problem are $\lambda_n = -nB/mT$, one of them is zero and all others are negative. And then bilinear expansion reads

$$F(t, \mathbf{p}) = \sum_{n=0}^{\infty} e^{\lambda_n t}\psi_n(\xi)\psi_n(\xi_0) \ , \tag{17}$$

where $\xi = \mathbf{p}/\sqrt{2mT}$ and $\xi_0 = \mathbf{p}_0/\sqrt{2mT}$, while ψ_n are the usual Hermit functions (I skip details). In $t \to \infty$ limit, the system relaxes to the ground state, which is Maxwell's distribution. The longest relaxation time corresponds to λ_1, and it is $\tau = -1/\lambda_1 = mT/B$.

4. We know that a particle in a viscous fluid is described by Langevin equation $\zeta\dot{x} = \xi(t)$. We can say, if the motion is driven by the white noise, with flat spectrum $\left(\xi^2\right)_\omega = 2\zeta T$, then this motion is a simple diffusion, with $\left\langle x^2(t)\right\rangle = 2(T/\zeta)t$. What happens if the motion is driven by the colored noise, $\zeta\dot{x} = \eta(t)$, with $\left(\eta^2\right)_\omega = \frac{2\zeta T}{1+(\omega\tau)^2}$? Find mean squared displacement of the particle during time t.

   Hint: Note that colored noise, unlike white one, is characterized by the parameter τ that has dimension of time. Therefore, you may expect two different types of behavior depending on time, with crossover at $\sim\tau$.

   Solution

   Displacement over time t is $x(t) = \frac{1}{\zeta}\int_0^t \eta(t')dt'$. Averaged displacement is zero, but averaged square $\left\langle x^2(t)\right\rangle = \frac{1}{\zeta^2}\int_0^t\int_0^t \left\langle \eta(t')\eta(t'')\right\rangle dt'dt''$ is expressed in terms of correlation function of the random force. This correlation function is the Fourier transform of the given power spectrum, i.e. $\left\langle \eta(t')\eta(t'')\right\rangle = \exp\left(-\left|t'-t''\right|/\tau\right)/2\tau$. Performing the double integral yields

   $$\left\langle x^2(t)\right\rangle = \frac{2T}{\zeta}\left[t - \tau + \tau e^{-t/\tau}\right] \ . \tag{18}$$

   As expected, there are two regimes. At $t \ll \tau$ (three terms of Taylor expansion are necessary for the exponential) $\left\langle x^2(t)\right\rangle \simeq \frac{T\zeta\tau}{t}^2$. As always, $\left\langle x^2\right\rangle \propto t^2$ $(x \propto t)$ means ballistic regime. This is because over time shorter than τ the driving force is correlated, does not fluctuate, and drives the particle to move in one particular direction.

   The long time limit, $t \gg \tau$, the motion is diffusive, $\left\langle x^2(t)\right\rangle = \frac{2T}{\zeta}t$; this is because at this time driving force is already uncorrelated.

5. Consider a system with some set of states labeled i, j etc, and moving from state to state with known rates $k_{i\to j}$. States of the system can be thought of as vertices of a graph (see Fig. 2 a), transition from vertex i to vertex j is possible if these two vertices are connected by a link, and in that case both rates $k_{i\to j}$ and $k_{j\to i}$ are known to you. Suppose further that the given rates are such that the system eventually arrives to the equilibrium, with population of every node P_i^{eq} which is also known to you.

   (a) Show that the system can come to the equilibrium state obeying the detailed balance IFF rates satisfy the condition $\prod_{\text{arround loop}} k_{i_1\to i_2}k_{i_2\to i_3}\ldots k_{i_{n-1}\to i_n}k_{i_n\to i_1} = \prod_{\text{arround loop}} k_{i_1\to i_n}k_{i_n\to i_{n-1}}\ldots k_{i_3\to i_2}k_{i_2\to i_1}$ around each and every of the closed loops in the graph.

   (b) Imagine transforming the given graph into a resistor network by replacing every bond with a resistor of resistance R_{ij} and connecting every node to the ground via a capacitor C_i (Fig. 2 b). You can then place some amount of electric charge in each capacitor and then watch how these charges redistribute between capacitors by flowing through resistors to establish at the end the equilibrium of equal potential level on all nodes. Show that the master equation describing the original system is equivalent to the set of Kirchoff laws describing charges and currents in the electrical system. Find the exact mapping between these two systems. What are the equivalent capacitances C_i and resistances R_i given the known $k_{i\to j}$ and P_i^{eq}?

   Solution

   (a) The detailed balance condition for any pair of connected nodes is $\frac{P_i^{\mathrm{eq}}k_{i\to j}}{P_j^{\mathrm{eq}}k_{j\to i}} = 1$. Multiplying these along any loop, we see that all P_i^{eq} cancel out, leaving $\prod_{\text{arround loop}} \frac{k_{i_1\to i_2}}{k_{i_2\to i_1}} \times \frac{k_{i_2\to i_3}}{k_{i_3\to i_2}} \times \ldots \frac{k_{i_{n-1}\to i_n}}{k_{i_n\to i_{n-1}}} \times \frac{k_{i_n\to i_1}}{k_{i_1\to i_n}} = 1$, which is the requisite condition.

   The meaning of this condition is that equilibration is only possible in a *potential* field, where work along a closed contour is zero. Indeed, if you identify the logarithm of every equilibrium constant between two

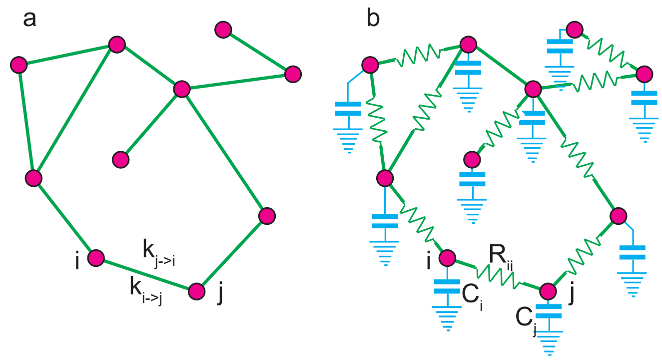

FIG. 2. For problem 5.

states as the difference of their (free) energies between these two states, $\ln \frac{k_{i\to j}}{k_{j\to i}} = f_i - f_j$, then the above condition becomes $(f_1 - f_2) + (f_2 - f_3) + \ldots + (f_{n-1} - f_n) + (f_n - f_1) = 0$ – which is the condition of the potential field.

(b) The mapping is as follows:

$$\begin{aligned} \text{time dependent charge on a node } Q_i(t) &\leftrightarrow P_i(t) \\ \text{capacitance of a node } C_i &\leftrightarrow P_i^{\mathrm{eq}} \\ \text{resistance of a bond } \frac{1}{R_{ij}} &\leftrightarrow P_i^{\mathrm{eq}} k_{i\to j} \equiv P_j^{\mathrm{eq}} k_{j\to i} \end{aligned} \tag{19}$$

With this mapping, time-dependent voltage on the node i is $V_i(t) = Q_i(t)/C_i$, while current through the bond ij becomes, according to Ohm's law, $\frac{V_i(t)-V_j(t)}{R_{ij}} = \frac{Q_i(t)}{C_i R_{ij}} - \frac{Q_j(t)}{C_j R_{ij}} \leftrightarrow P_j(t)k_{j\to i} - P_i(t)k_{j\to i}$, as it should be in the master equation.

The problems below are not required and will not be graded, but recommended to those students who want to improve their knowledge and performance.

6. Active Brownian particle is a hugely popular model of the so-called active systems. In the simplest case, this is a particle that moves in 3D (or on a surface in 2D) in the following way: this particle has position $\mathbf{r}$ and orientation (a unit vector) $\mathbf{n}$ (like, e.g., a rod), and at every moment it moves (using its internal energy depot) with some fixed speed v in the direction pointed by $\mathbf{n}$, while the direction itself undergoes free rotational diffusion with rotational diffusion coefficient D_{rot}:

$$\begin{aligned} \dot{\mathbf{r}} &= v\mathbf{n} \\ \dot{\mathbf{n}} &= \sqrt{2D_{\mathrm{rot}}}\xi(t) \ , \end{aligned} \tag{20}$$

with $\xi(t)$ the usual delta-correlated white noise. Find mean-squared displacement of an active Brownian particle over time t. Find the general expression for any t as well as short and long time asymptotics; interpret both asymptotic laws.

Hint:

(a) Use the results of the other HW regarding $\langle \mathbf{n}(t) \cdot \mathbf{n}(t') \rangle$.

(b) When you obtain the result for any t, look at it and remember when you saw that same mathematical expression in this very class.

Solution

Knowing particle velocity at any time $\dot{\mathbf{r}}(t) = v\mathbf{n}(t)$, its displacement over time t is given as $\mathbf{r}(t) - \mathbf{r}(0) = v\int_0^t \mathbf{n}(t')dt'$. Average displacement is, of course, zero, but we can consider average squared displacement (in exactly the same way as we did for a regular Brownian particle if we did not neglect inertia):

$$\left\langle (\Delta \mathbf{r}(t))^2 \right\rangle = \int_0^t dt' \int_0^t dt'' \left\langle \mathbf{n}(t') \cdot \mathbf{n}(t'') \right\rangle \ . \tag{21}$$

We know that for rotational diffusion

$$\langle \mathbf{u}(t') \cdot \mathbf{u}(t'') \rangle = e^{-2D_{\mathrm{rot}}\left|t'-t''\right|} \ . \tag{22}$$

Performing the integral (which is done in exactly the same way as we did before), we end up with

$$\left\langle (\Delta \mathbf{r}(t))^2 \right\rangle = \frac{v^2}{2D_{\mathrm{rot}}^2} \left[2D_{\mathrm{rot}} t + e^{-2D_{\mathrm{rot}} t} - 1 \right] \ . \tag{23}$$

As discussed before, $1/2D_{\mathrm{rot}}$ is the "direction forgetting time". At $t \ll 1/2D_{\mathrm{rot}}$, we get (by Taylor expanding exponential to the third order) $\left\langle (\Delta \mathbf{r}(t))^2 \right\rangle = v^2 t^2$ – which is the ballistic motion with speed v in a practically unchanged direction. In the opposite limit, at $t \gg 1/2D$, we get $\left\langle (\Delta \mathbf{r}(t))^2 \right\rangle = \frac{v^2}{D_{\mathrm{rot}}} t$: linear dependence on time is a signature of a random walk behavior, with effective diffision coefficient $D_{\mathrm{eff}} = v^2/2D_{\mathrm{rot}}$.

[1] E. Schrödinger, Zur theorie der fall-und steigversuche an teilchen mit brownscher bewegung, Physikalische Zeitschrift **16**, 289 (1915).
[2] M. V. Smoluchowski, Uber die zeitliche veranderlichkeit der gruppierung von emulsionsteilchen und die reversibilitat der diffusionserscheinungen, Physikalische Zeitschrift **16**, 321 (1915).