

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

Home Works 12 and 13

Solutions

1. You studied Rouse model of a polymer chain dynamics in one of the home works. To remind you, we can consider one “labelled” monomer in a Rouse chain, and find out its mean squared displacement as a function of time; the result is that labelled monomer undergoes a subdiffusion, with  $r \sim t^{1/4}$ . This can be derived formally, from Langevin equation for the Rouse modes, and it is also supported by the following scaling argument. One labeled monomer can move more or less independently of neighbors only a very small distance, of the order of  $a$ , the length of connection to the neighboring monomers. Beyond that distance, the farther our monomer moves, the longer chain section must move with it. Then we proceed as follows:
  - (a) Imagine that the labeled monomer undergoes a diffusion with self-consistently determined time-dependent effective diffusion coefficient  $D_{\text{eff}}(t)$ . So, the first step is to write down the displacement  $r$  as a function of time  $t$  using this  $D_{\text{eff}}(t)$ :  $r^2(t) \sim D_{\text{eff}}(t)t$ .
  - (b) To find  $D_{\text{eff}}(t)$ , let us assume that the motion of our labelled monomer had to involve some  $g(t)$  other monomers, such that the entire coil of  $g(t)$  monomers was moving. Since in Rouse model all monomers experience independent friction against immobile solvent (no hydrodynamic interactions), you should be able to use Einstein relation and write  $D_{\text{eff}}(t)$  in terms of  $g(t)$  and friction coefficient of a single monomer,  $\zeta$ :  $D_{\text{eff}}(t) \sim T/\zeta g(t)$ .
  - (c) To find  $g(t)$ , you should realize that to move our monomer distance  $r$ , we have to move a coil whose size is of the order of the same  $r$ :  $r(t) \sim r_g \sim ag^{1/2}(t) \sim r^2(t)$ .

Your task is now to repeat the consideration of the previous problem for the polymer with hydrodynamic interactions between monomers (so-called Zimm model). Your consideration (as well as the above argument for the Rouse chain) is valid only as long as the displacement of the labelled monomer is not too large. What exactly is this condition?

**Hint:** In the Rouse model, every monomer experiences friction against the solvent independently of any other monomer, accordingly, group of some  $g$  monomers moving together have friction coefficient  $g\zeta$ ; In the Zimm model, instead, chain section of  $g$  monomers moves through the liquid as a ball of radius  $r_g \sim ag^{1/2}$ , i.e., with friction coefficient  $\sim \eta r_g \sim \eta ag^{1/2} \sim \zeta g^{1/2}$ .

### Solution

The only difference from the above solution is that coil of  $g$  monomers experiences weaker friction, because its interior is screened by hydrodynamic interactions. As a result,  $D_{\text{eff}}(t) \sim \frac{T}{\zeta \sqrt{g(t)}}$ . Repeating algebra, we arrive at  $r \sim t^{1/3}$ : it is still a sub-diffusion, just a bit faster one.

This consideration is valid only as long as the displacement of labelled monomer is (much) smaller than the overall coil size.

In a bit more details, and keeping all coefficients with units, we write

$$\begin{aligned}
 r^2 &\sim D_{\text{eff}}(t)t ; \\
 r^2(t) &\sim a^2 g(t) ; \\
 D_{\text{eff}}(t) &\sim \frac{T}{\zeta g(t)} \text{ Rouse} \quad D_{\text{eff}}(t) \sim \frac{T}{\zeta g^{1/2}(t)} \text{ Zimm}
 \end{aligned} \tag{1}$$

We can say  $D_{\text{eff}}(t) \sim \frac{T}{\zeta g^\alpha(t)}$ , with  $\alpha = 1$  for Rouse and  $\alpha = 1/2$  for Zimm. Going through algebra,  $r \sim t^{1/(2+2\alpha)} (Ta^{2\alpha}/\zeta)^{1/(2+2\alpha)}$ . The condition  $r \ll R \sim aN^{1/2}$  translates to  $t \ll (\zeta a^2/T)N^{1+\alpha}$ . Note that  $\zeta a^2/T$  is the monomer diffusion time over its own size,  $\tau_0$ , so  $t \ll \tau_0 N^{1+\alpha}$ .

2. One experimental method to observe biological macromolecules is called fluorescence correlation spectroscopy. The idea of the method is as follows. Imagine a dilute solution of some biological macromolecules, each of which has a fluorescent group. Imagine that you focus a laser on a little spot of some width  $w$ . Each fluorescent group which happens to be in the illuminated spot can absorb a photon of incoming light, and then emit (after a very short delay of a couple of nanoseconds) another photon of somewhat smaller energy. For instance, one can use

a blue laser beam and observe the outgoing red fluorescent light. What is directly measured in this method is the intensity of fluorescent light. What is this good for?

At any given moment, the observed intensity is simply proportional to the number of fluorescent molecules,  $N(t)$ , which happen to be inside the illuminated spot at that moment. Every time a fluorescent molecule diffuses out of the spot, the intensity drops; every time a fluorescent molecule diffuses in, the intensity increases a bit. On average, intensity is proportional to the averaged number of molecules in the spot,  $\langle N \rangle$ . Knowing this, we can study the correlation between intensity now and intensity some time  $\tau$  later,  $\langle I(t)I(t+\tau) \rangle$ , which is proportional to  $\langle N(t)N(t+\tau) \rangle$ . In turn, the correlation  $\langle N(t)N(t+\tau) \rangle$  is related to the probability that a molecule which was inside the spot at time  $t$  still remains inside the spot at time  $t+\tau$ .

Assuming fluorescent molecules' motion is simple diffusion, find  $\langle N(t)N(t+\tau) \rangle$  as a function of  $\tau$ . Looking at your result, decide which properties of the molecules can be investigated based on this experimental method?

**Hint 1:** For the purposes of fitting, it is convenient to replace the sharply defined illuminated spot with the Gaussian distribution of intensity:

$$\text{Incoming intensity} \propto \frac{4}{\pi w^2} e^{-4x^2/w^2}, \quad (2)$$

which might in fact be an even better approximation to the reality. Here,  $w$  is the diameter of the illuminated spot.

**Hint 2:** Do not forget to examine two limits, small  $\tau$  and large  $\tau$ ; to do so, you must determine the time scale  $\tau_D$  compared to which  $\tau$  can be large or small.

**Hint 3:** To bring your analysis closer to the real experimental situation, you should realize that what is important is only the diffusion in the plane perpendicular to the incoming light beam.

### Solution

First of all, let us denote by  $N$  the average number of molecules in the illuminated spot:  $N = \langle N(t) \rangle$ . Then, at every moment  $t$  we have  $N(t) = N + \delta N(t)$ , where  $\delta N(t)$  can be positive or negative and represents physically the particles which diffuse in and out. Since average value of  $\delta N(t)$  is zero, we can use the correlation of  $\delta N(t)$ :

$$\langle N(t)N(t+\tau) \rangle = \langle (N + \delta N(t))(N + \delta N(t+\tau)) \rangle = N^2 + \langle \delta N(t)\delta N(t+\tau) \rangle. \quad (3)$$

But the latter correlation is simply  $N$  times the probability that the particle that was inside the spot at  $t$  remains inside at  $t+\tau$ . Knowing  $G$ , the Green's function of the diffusion equation, and assuming illuminated spot is sharply defined, this reads

$$\langle \delta N(t)\delta N(t+\tau) \rangle = \frac{N}{v} \int_v \int_v G(\tau, \vec{x}, \vec{x}') d\vec{x} d\vec{x}', \quad (4)$$

where  $v$  is the volume of illuminated spot (or its surface area if you want to think of a plane perpendicular to the beam), and both integrals are taken over the illuminated spot (either in three or in two dimensions).

Knowing the expression for  $G$ , or just knowing the fact that in time  $\tau$  particles diffuse by the distance about  $\sqrt{D\tau}$ , we realize that the relevant time scale  $\tau_D$  must be determined from the condition  $\sqrt{D\tau} = w$ , where  $w$  was defined as the size of illuminated spot; thus,  $\tau_D = w^2/D$ .

When  $\tau \ll \tau_D$ , particles diffuse in time  $\tau$  by the distance much smaller than  $w$ , most likely they don't move in or out of the spot, and correlation function remains almost constant. Indeed, when  $\tau$  is so small our Gaussian exponent in  $G$  is a very sharp narrow function of  $\vec{x} - \vec{x}'$ ; replacing it with  $\delta(\vec{x} - \vec{x}')$ , we get

$$\langle N(t)N(t+\tau) \rangle|_{\tau \ll \tau_D} \simeq N^2 + N. \quad (5)$$

This is the reflection of our familiar “square root of  $N$  rule”: although averaged number of particles is  $N$ , its fluctuations are typically in the range  $\pm\sqrt{N} \ll N$ , so that  $\langle \delta N(t)^2 \rangle \simeq N$ .

When  $\tau \gg \tau_D$ , particles diffuse over the distances much larger than the illuminated spot size. Mathematically, the expression in the exponent gets very small (because both  $\vec{x}$  and  $\vec{x}'$  are within the spot), so we can simply replace the exponent by unity, thus getting

$$\langle N(t)N(t+\tau) \rangle|_{\tau \gg \tau_D} \simeq N^2 + N \frac{v}{(4\pi D\tau)^{3/2}} \quad (6)$$

if we consider 3D diffusion, or

$$\langle N(t)N(t+\tau) \rangle|_{\tau \gg \tau_D} \simeq N^2 + N \frac{v}{4\pi D\tau} \quad (7)$$

if we look at planar diffusion only.

This has to be slightly modified if intensity around illuminated spot is Gauss distributed:

$$\langle \delta N(t) \delta N(t+\tau) \rangle = n \iint G(\tau, \vec{x}, \vec{x}') \left[ \frac{4}{\pi w^2} e^{-4\vec{x}^2/w^2} \right] \left[ \frac{4}{\pi w^2} e^{-4\vec{x}'^2/w^2} \right] d^2\vec{x} d^2\vec{x}' , \quad (8)$$

where  $n$  is the average number of particles per unit area. Exercising a little in the art of computing Gauss integrals, you obtain a formula which is convenient for fitting the data:

$$\langle \delta I(t) \delta I(t+\tau) \rangle \propto \langle \delta N(t) \delta N(t+\tau) \rangle = \frac{2n/(\pi w^2)}{1 + 8D\tau/w^2} . \quad (9)$$

On the other hand, averaged intensity is proportional to  $n$ , such that

$$\langle I \rangle^2 \propto n^2 . \quad (10)$$

You should be able to convince yourself that the coefficients of proportionality in equations 9 and 10 are the same (they involve cross-sections and other similar stuff). From here, you can find the theoretical formula to fit to the data.

Thus, looking the correlation of fluorescence intensity, one thing we can measure the diffusion coefficient of the particles.

3. Suppose a particle diffuses between two concentric spheres, with radii  $R_1 < R_2$ . It starts at some radius  $r_0$ ,  $R_1 < r_0 < R_2$ . What is the probability  $p_1$  that the particle arrives to the inner sphere before ever touching the outer one? Analyze the dependence of this probability  $p_1$  on the initial radius  $r_0$ .

#### Solution

To render the problem symmetric, we can smear the initial position of the particle around the sphere of radius  $r_0$ , then arriving to the diffusion equation

$$\partial_t P = D \nabla^2 P + \delta(t) \frac{\delta(|\mathbf{r}| - r_0)}{4\pi} . \quad (11)$$

Consider an auxiliary steady state problem in which we feed constant current  $J$  into sphere of radius  $r_0$  and collect out going currents  $J_1$  and  $J_2$  from spheres  $R_1$  and  $R_2$ , respectively. The current has only radial component with current density  $D\partial_r P$ . Thus, we have  $4\pi r^2 D\partial_r P = J_1$  at  $r < r_0$  and  $-4\pi r^2 D\partial_r P = J_2$  at  $r > r_0$ . The solutions read  $P = -\frac{J_1}{4\pi r} + A_1$  at  $r < r_0$  and  $P = -\frac{J_2}{4\pi r} + A_2$  at  $r > r_0$ , where  $A_1$  and  $A_2$  are integration constants, to be determined from the boundary conditions. The boundary conditions in the problem are absorbing  $P = 0$  at both inner and outer spheres,  $r = R_1$  and  $r = R_2$ ; in addition,  $P$  must be continuous at  $r = r_0$ :

$$-\frac{J_1}{4\pi R_1} + A_1 = 0 , \quad \frac{J_2}{4\pi R_2} + A_2 = 0 , \quad -\frac{J_1}{4\pi r_0} + A_1 = \frac{J_2}{4\pi r_0} + A_2 . \quad (12)$$

Finally,  $J_1 + J_2 = J$  and the probability  $p_1$  is given by  $p_1 = \frac{J_1}{J_1 + J_2}$ . From here, simple algebra gives the answer:

$$p_1 = \frac{\frac{1}{r_0} - \frac{1}{R_2}}{\frac{1}{R_1} - \frac{1}{R_2}} \quad \text{and similarly} \quad p_2 = \frac{\frac{1}{R_1} - \frac{1}{r_0}}{\frac{1}{R_1} - \frac{1}{R_2}} . \quad (13)$$

Probability  $p_1$  to arrive to the inner sphere before ever touching the outer one vanishes if you start very close to the outer sphere and monotonically increases to unity as the starting point approaches inner sphere.

This can be understood by analogy with electrical resistance. Indeed,  $p_1$  and  $p_2$  are related to electrical resistances of spherical layers between  $R_1$  and  $r$  or between  $r$  and  $R_2$ . Resistance of the spherical layer is calculated as follows. Remember that resistance of a regular wire is proportional to the length of a conductor and inversely proportional to its cross section. Apply this rule to a spherical peel. Its “length” (along the current) is  $dr$  while its “cross section” (perpendicular to the current) is  $4\pi r^2$ . Such peels are connected in series, making their resistances add:  $\int \frac{dr}{r^2}$ , yielding the answer above.

4. Imagine a narrow channel in which many particles are diffusing such that they do not swap: the channel width is sufficient for one particle to diffuse along the channel, but not sufficient for two particles to go past one another. This situation is called single file diffusion. What is the mean squared displacement of one labeled particle in a single file? Are there experimental studies of such system?

**Solution**

This is a sub-diffusion,  $r \sim t^{1/4}$ . Quite popular subject of experimental studies, e.g., [1].

5. Consider a random walker in 1D, with space-dependent diffusion coefficient  $D(x)$ , but no external field,  $U(x) = 0$ . How does Fokker-Planck (or diffusion) equation look like in this case:

$$\partial_t P_t(x) = D(x) \partial_x^2 P_t(x) , \quad \text{or} \quad \partial_t P_t(x) = \partial_x (D(x) \partial_x P_t(x)) , \quad \text{or} \quad \partial_t P_t(x) = \partial_x^2 (D(x) P_t(x)) ? \quad (14)$$

Based on the right equation, find mean first passage time to  $x = L > 0$  for the walker which starts at  $t = 0$  in some point  $x_0$  ( $0 < x_0 < L$ ) and faces reflecting boundary at  $x = 0$ . In the final answer, perform your calculation assuming  $D(x) = D_1 = \text{const}$  at  $x > x_0$  and  $D(x) = D_2 = \text{const}$  at  $x < x_0$ . Explain why your answer depends differently on  $D_1$  and  $D_2$ .

**Solution**

If the system comes to equilibrium, the equilibrium state can not depend on the transport coefficient such as  $D(x)$ . Therefore, Fokker Planck equation reads

$$\partial_t P + \partial_x J = 0 , \quad J = -D(x) \partial_x P . \quad (15)$$

To find mean first passage time, we set up an auxiliary steady process: we feed constant current  $J$  into point  $x = x_0$ , and collect it from the absorbing boundary at  $x = L$ . Then current must be a constant, equal to  $J$ , in the interval  $x_0 < x < L$ , leading to

$$P(x) = J \int_x^L \frac{1}{D(x')} dx' \quad \text{at} \quad x_0 < x < L . \quad (16)$$

At  $x < x_0$ , current must be zero, so

$$P(x) = J \int_{x_0}^L \frac{1}{D(x')} dx' \quad \text{at} \quad x < x_0 < L ; \quad (17)$$

I took into account that  $P(x)$  is continuous at  $x = x_0$ . And now we have to implement the idea that there is just one particle in the system,  $\int_0^L P(x) dx = 1$ . This gives

$$\langle \tau \rangle = \frac{1}{J} = x_0 \int_{x_0}^L \frac{1}{D(x')} dx' + \int_{x_0}^L \left[ \int_x^L \frac{1}{D(x')} dx' \right] dx . \quad (18)$$

This is the final answer for the general case  $D(x)$ . For piece-wise constant  $D(x)$ , the answer does not depend at all on  $D_2$ ; it is only the transient time of establishing the steady state that depends on  $D(x)$  in the dead end part of the system, it does not affect the mean first passage time. In this case

$$\langle \tau \rangle = \frac{1}{J} = \frac{L^2 - x_0^2}{2D_1} . \quad (19)$$

6. <sup>1</sup>Imagine a shear flow of a viscous liquid, with shear rate  $\dot{\gamma}$ , and a rod-like particle, a macromolecule or a colloid, submerged in that flow. To be specific, let fluid velocity be along  $x$ , and velocity gradient along  $z$ :  $v_x = \dot{\gamma}z$ ,  $v_y = v_z = 0$ . <sup>2</sup>Assume that the middle of the rod is fixed on a pivot at  $z = 0$ , and the rod can rotate around that point in  $(x, z)$  plane. Describe steady state probability distribution of the rod directions. Does rod motion satisfy detailed balance?

<sup>1</sup> In this form, the problem was first solved in 2017 by one of the students in this department, Watee Srinin (PhD 2018, Presently Assistant Professor in Naresuan University, Thailand); he prepared the figures for this problem. Right now, another student in the Department works on a generalization of this problem.

<sup>2</sup> Shear flow of this type can be created if the liquid is confined between two parallel plates,  $z = d/2$  and  $z = -d/2$ , moving parallel to one another with some relative velocity  $V$  along  $x$ , with  $\dot{\gamma} = V/d$ .

For simplicity, you can think of a rod as a dumbbell, with two balls connected by a negligibly thin stick. Stick length is  $\ell$  and each ball friction coefficient is  $\zeta$ .

**Hint:** Rod motion in a shear flow (see cartoon in Fig. 1) can be described as *tumbling*. Suppose initially the rod is oriented perpendicular to the flow. It is then subject to a large torque which rapidly brings rod orientation close to the alignment with velocity. In this situation, the value of torque becomes very small, rotation slows down, and eventually becomes (angular) diffusion-dominated. The rod will spend some time diffusing within a small angle  $\phi_p$ . However, sooner or later, a thermal fluctuation will tip the rod at a small negative angle, exposing its end to the flow. The rod then picks up a large torque causing a rapid advection-dominated turn over almost an angle of  $\pi$ , after which the process repeats itself. Thus, the tumbling motion consists of tours of forced rotation and diffusional rotation. You should find the torque, set up diffusion equation, and find its steady state solution. Find also how tumbling time depends on the shear rate  $\dot{\gamma}$ .

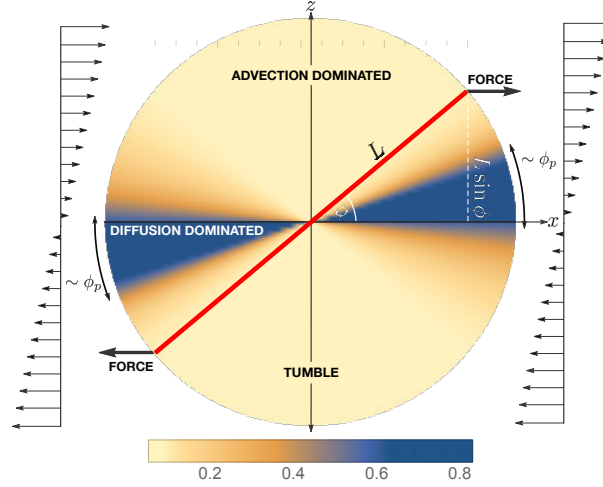


FIG. 1. Schematic depiction of the orientation dynamics of rod in shear flow. The intensity of the color corresponds to the probability of finding the rod. In the blue area the dynamics of the rod is dominated by diffusion while in the bright area the dynamics is dominated by advection. The diffusion dominated area becomes smaller as the shear rate increases. Figure courtesy of W.Srinin.

### Solution

If the rod turns with angular speed  $\omega$ , each ball moves with velocity  $\omega\ell/2$ , experiences frictional force  $\zeta\omega\ell/2$ , and the rod experiences frictional torque  $2\zeta\omega(\ell/2)^2$ ; we will write it as  $\zeta_r\omega$ , with rotational friction coefficient<sup>3</sup>  $\zeta_r = \zeta\ell^2/2$ . Clearly, along with rotational friction coefficient, there is rotational diffusion coefficient  $D_r = k_B T/\zeta_r$ . But apart from diffusion, the rod also experiences forcing from the flow.

When rod is positioned at an angle  $\phi$  to the flow (we count angle counterclockwise, see Fig. 1), each of the rod ends (balls) is exposed to the flow at velocity  $\dot{\gamma}(\ell/2)\sin\phi$ , it generates pair of oppositely pointing friction forces, and the torque on the rod  $M = -\dot{\gamma}\zeta_r\sin^2\phi$ ; minus sign means that the torque is clockwise. This torque can be formally thought of as the “gradient” of a “potential”:  $-\sin^2\phi = -\frac{du}{d\phi}$ , with  $u(\phi) = \frac{\phi}{2} - \frac{\sin 2\phi}{4}$ .

We can now set up diffusion (Fokker-Planck) equation for the probability distribution density of rod angle  $P(\phi, t)$ :

$$\frac{\partial P(\phi, t)}{\partial t} + \frac{\partial j(\phi, t)}{\partial \phi} = 0, \quad j(\phi, t) = -\dot{\gamma}\sin^2\phi P(\phi, t) - D_r \frac{\partial P(\phi, t)}{\partial \phi}. \quad (20)$$

In this form, the equation is seen to describe the slow descent of a particle into a “bottomless pit” via a bumpy incline  $u(\phi)$ , as shown in the inset in Figure 2. It is clear that motion consists of tours of drift-dominated sliding down the steep parts followed by diffusion dominated motion over the shallow parts etc. In steady state, probability current  $j$  is constant in both angle  $\phi$  and time. This, together with the obvious boundary condition

<sup>3</sup> For a continuous rod of length  $\ell$ , rotational friction coefficient is  $\zeta_r = \pi\eta\ell^3/4$ , with  $\eta$  solvent viscosity, see [? , Chapter 8]

$P(0) = P(\pi)$ , leads to the following formal expression for the steady state probability distribution:

$$P(\phi) = \frac{1}{z} \left[ \int_0^\pi \frac{d\phi'}{f(\phi')} \frac{f(\pi)}{1-f(\pi)} + \int_0^\phi \frac{d\phi'}{f(\phi')} \right] f(\phi), \quad (21)$$

with  $f(\phi) = \exp\left(-\frac{\dot{\gamma}}{D_r} u(\phi)\right)$ ,  $u(\phi) = \frac{\phi}{2} - \frac{\sin 2\phi}{4}$ , and  $z$  the normalization factor ensuring  $\int_0^\pi P(\phi) d\phi = 1$ . This expression has only one unitless parameter  $\dot{\gamma}/D_r$  and can be easily evaluated numerically (see plot in Fig. 2). As expected, when  $\dot{\gamma}/D_r \gg 1$  the probability distribution is sharply peaked at small angles – but the maximum is not at zero. Most probable state is not when the rod is aligned with the flow, it is at a small angle  $\phi_p$  or  $\pi + \phi_p$ .

One important outcome of the detailed solution is the demonstration that the time spent by the rod in the advection-dominated regime

$$\tau_{\text{adv}} \sim \int_{\phi_p}^{\pi-\phi_p} d\phi \frac{1}{\dot{\gamma} \sin^2 \phi} \simeq \frac{2}{\dot{\gamma} \phi_p} \quad (22)$$

is dominated by the small angles: the rod rapidly turns when torque is large and very slowly moves when the torque gets small.

Based on that, it is interesting to estimate angle  $\phi_p$  and the tumbling period  $\tau_t$  from simple scaling arguments, using the physically appealing assumption (supported by the solution above) that the rod spends comparable time in diffusion-dominated and in advection-dominated regimes,  $\tau_{\text{dif}} \sim \tau_{\text{adv}}$ . To turn angle  $\sim \phi_p$  by (angular) diffusion over time  $\tau_{\text{dif}}$  means  $D_r \tau_{\text{dif}} \sim \phi_p^2$ . On the other hand, in the advection dominated regime angular velocity of the rod is proportional to the torque  $\dot{\gamma} \sin^2 \phi$ ; the dominant advection time is to turn the last angle  $\sim \phi_p$  (roughly from  $2\phi_p$  to  $\phi_p$ ), in this range angular velocity is reduced to  $\phi_p/\tau_{\text{adv}} \sim \dot{\gamma} \phi_p^2$ . Multiplying both sides of this equation by two respective sides of  $D_r \tau_{\text{dif}} \sim \phi_p^2$  yields  $D_r \tau_{\text{dif}}/\tau_{\text{adv}} \sim \dot{\gamma} \phi_p^3$ . Recalling that  $\tau_{\text{adv}} \sim \tau_{\text{dif}} \sim \tau_{\text{adv}} + \tau_{\text{dif}} = \tau_t$ , we arrive at:

$$\phi_p \sim D_r^{1/3} \dot{\gamma}^{-1/3}, \quad \tau_t \sim D_r^{-1/3} \dot{\gamma}^{-2/3}. \quad (23)$$

Of course, tumbling rod does not obey detailed balance, it tumbles steadily, but almost exclusively in one direction, clockwise.

7. Smoluchowski “coagulation” theory deals with particles at concentration  $c$  diffusing in space and “searching” for a target of radius  $b$ . Mean first passage time for this system is  $\tau = 1/J$ , where rate is  $J = 4\pi b c D$ . This result is valid in 3D. It is based on the steady (time independent) solution of diffusion equation  $c(r) = c \left[1 - \frac{b}{r}\right]$ , consistent with boundary conditions  $c(r)|_{r=b} = 0$  and  $c(r)|_{r \rightarrow \infty} = c$ .

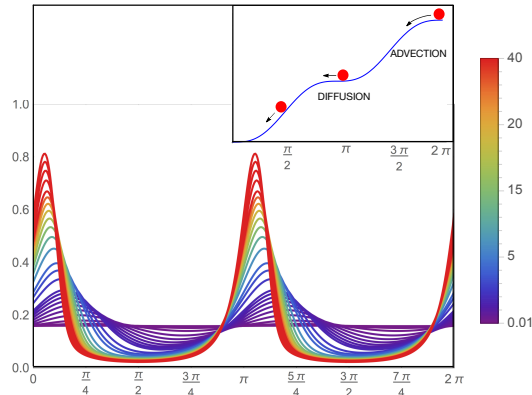


FIG. 2. **Main figure:** The steady state probability distribution for the rod direction angle  $\phi$  obtained by numerically evaluating integrals in Eq. 21. Different colors correspond to different values of the parameter  $\dot{\gamma}/D_r$ , the ratio of shear rate to angular diffusivity of the rod. It is seen how increasing value of this parameter leads to the distribution increasingly sharply peaked at small angle  $\phi_p$ . **Inset:** Potential “landscape”  $u(\phi)$ . Steady diffusion and sliding down this potential describes tumbling of the rod. The figure is courtesy of W.Srinin.

Similar solution for 2D does not exist. Indeed, steady state solution with boundary condition  $c(r)|_{r=b} = 0$  will look like  $c(r) = A \ln \frac{r}{b}$ ; whatever the coefficient  $A$ , we cannot impose boundary condition in infinity  $c(r)|_{r \rightarrow \infty}$ .

Even worse situation is in 1D, where corresponding solution would look like  $c(x) = A(x - b)$  which diverges linearly in infinity.

To circumvent this problem, in previous HW you considered a similar problem, assuming the searching particle was confined within a distance  $R$  from the target. This led to the answer in 2D like  $J = \frac{4D}{2R^2 \ln(R/b) - R^2 + b^2} \simeq \frac{2D}{R^2 \ln(R/b)}$ ; you could make it look somewhat more similar to the answer in 3D by saying  $c = 1/\pi R^2$ , yielding  $J \simeq 4\pi cD / \ln(1/\pi cb^2)$ . This may be OK in terms of the estimate, but still it looks strange, with non-linear dependence on concentration. Perform similar analysis in 1D and show that is non-linear there as well. This is surprising. Indeed, linear dependence on  $c$  in classical Smoluchowski result in 3D indicates that different particles perform search independent from one another, such that total flux into target is just proportional to  $c$ . In 2D, or in 1D for that matter, we also assume particle not interacting – but somehow arrive at the non-linear dependence of flux on  $c$ .

Why? You have to explain it.

**Hint:** Think about compactness or non-compactness of exploration. Imagine searching particles initially, at  $t = 0$ , uniformly spread at concentration  $c$  in 3D, or 2D, or 1D. How far from the target are the particles that hit the target first in these various dimensions?

### Solution

First of all, for 1D similar estimate reads  $J = 2D/R^2 = 8c^2D$ . In 1d, most likely to hit the target first is the particle that is closest to the target at the beginning. It is distance of order  $1/c$  away, the time is then distance<sup>2</sup>/ $D$ , which is indeed  $\sim c^2D$ . Thus, particles are not equivalent, those who are initially closest to the target have best chances to hit the target

By contrast, in 3D, during time  $1/J \sim 1/bcD$ , particle travels distance of the order of  $\sqrt{D/J} \sim (bc)^{-1/2}$  which is much larger than the distance to the closest particle:  $(bc)^{-1/2} \gg c^{-1/3}$ . In this sense, first hitter is recruited from a very large group of particles having roughly similar chances to hit the target first.

This of course is yet another manifestation of the difference between compact exploration in 1D and non-compact in 3D. In this sense, 2D is a border line.

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

- The diffusion controlled “annihilation” of particles according to  $A + B \rightarrow C$  assuming that in the initial state at  $t = 0$ , there is equal amount of  $A$  and  $B$ , such that average concentrations are the same,  $\bar{A} = \bar{B}$ , but concentrations of  $A$  and  $B$  have some Poisson distributed randomness. At long times, this randomness of the initial distribution results in a peculiar “patchy” distribution of (almost) purely  $A$  regions and (almost) purely  $B$  ones. In this regime, concentration decays as  $t^{-3/4}$ , much slower than  $t^{-1}$  at the earlier stages. We did it in 3D space. Repeat the analysis for other space dimensions.

### Solution

After time  $t$ , diffusion smears concentrations over distances of the order  $(Dt)^{1/2}$  which corresponds to volume  $(Dt)^{d/2}$  in  $d$  dimensions. In this volume, due to Poisson distribution, typical excess of one concentration over the other is about  $Z \sim \sqrt{\bar{A}/V}$  yielding  $Z \sim \bar{A}^{1/2}(Dt)^{-d/4}$ . This answer is valid if it decays slower than the mean field  $t^{-1}$ , which means at  $d < 4$ .

- We considered the diffusion controlled “annihilation” of particles according to  $A + B \rightarrow C$  assuming that in the initial state at  $t = 0$ , there is equal amount of  $A$  and  $B$ . Consider the opposite case, when one of the components strongly dominates,  $A \gg B$ . In this case, concentration of  $A$  changes insignificantly, but concentration of  $B$  decays. How does it decay in the smeared “mean field” picture? How do fluctuations of the initial distribution affect this decay?

**Hint:** The longest surviving  $B$  particles may be the ones which, by the lucky chance, happened to be located in the middle of some region with low concentration of  $A$ . Find (estimate!) the probability  $P(R)$  that a  $B$  particle finds itself within a “void” of size  $R$  free of  $A$  particles. Find then the survival probability of a  $B$  particle as a function of time if it starts in a “void” of size  $R$ ,  $S_t(R)$ . The product  $P(R)S_t(R)$  will tell you the survival probability for all particles starting in “voids” of size  $R$ ;  $\int P(R)S_t(R)dR$  is the total survival probability. Do you know a method to evaluate such integral?

### Solution

Neglecting the fluctuations of concentration of  $A$  (i.e., assuming that diffusion mixes them very rapidly, which is the mean field assumption), concentration of  $B$  satisfies  $\partial_t B = -kB$ . Smoluchowski theory tells us that  $k = 4\pi bcD$ , where  $c = A$  is the concentration of  $A$ . Thus, mean field prediction for  $B$  is exponential decay:  $B(t) = B_0 e^{-kt}$ .

With probability  $e^{-AR^3}$ , particle  $B$  may find itself in the beginning with the volume  $R^3$  free of  $A$ -particles. This particle will need typically the time  $\sim R^2/D$  to find a possible  $A$  partner; more specifically, it will have the survival probability  $e^{-tD/R^2}$ . Therefore, the probability to survive until time  $t$  in a “cavity” of size  $R$  will be  $\exp[-AR^3 - tD/R^2]$  (attention: I am notoriously inaccurate here, I am dropping all numerical coefficients everywhere – even in the exponentials; you need to restore all  $4\pi/3$  etc. if you need to use these results quantitatively). The point is the expression in the exponential has a maximum as a function of  $R$ : this  $R$  gives best survival chance to the  $B$  particle at time  $t$ . More formally, survival probability is an integral over all possible  $R$  of the above exponential, and this integral must be evaluated by the saddle point (steepest descent). Thus, the survival probability of  $B$  is proportional to  $\exp[-\text{const} A^{2/5} (Dt)^{3/5}]$ . This answer is valid at long times, when  $t \gg AD^{3/2}/k^{5/2}$ .

10. A certain type of sub-diffusive random walk can be described by a peculiar generalization of the Fokker-Planck equation which involves special mathematical tool called “fractional derivatives” (or, more generally, fractional calculus). This and next problems are designed to give you a glimpse of this useful tool (see more details in the paper [2]). While the usual Fokker-Planck equation reads

$$\frac{\partial P(x,t)}{\partial t} = D \hat{L}_{\text{FP}} P \quad , \quad \hat{L}_{\text{FP}} = \frac{\partial}{\partial x} e^{-U(x)} \frac{\partial}{\partial x} e^{U(x)} \quad , \quad (24)$$

where  $D$  is diffusion coefficient, the generalized (fractional) Fokker-Planck equation can be written in terms of a peculiar operator (so called Riemann-Liouville fractional operator)  ${}_0\hat{D}_t^{1-\gamma}$  as

$$\frac{\partial P(x,t)}{\partial t} = D_\gamma {}_0\hat{D}_t^{1-\gamma} \hat{L}_{\text{FP}} P \quad . \quad (25)$$

Here  $\gamma$  is a unitless parameter, related to the power  $\nu$  is  $R \sim t^\nu$ , see below;  $0 < \gamma < 1$ . At the same time,  $D_\gamma$  is a generalized diffusion coefficient (akin to  $D_{\text{app}}$  in the paper [3]), it has peculiar units, and the Riemann-Liouville fractional operator is defined through

$${}_0\hat{D}_t^{1-\gamma} W = \frac{1}{\Gamma(\gamma)} \frac{\partial}{\partial t} \int_0^t \frac{W(x,t')}{(t-t')^{1-\gamma}} dt' \quad . \quad (26)$$

As usual,  $U(x)$  is an external potential; for simplicity, we have also set  $k_B T = 1$  and the Einstein relation is implicit.

- Check that the fractional Fokker-Planck equation reduces to the regular Fokker-Planck equation (or diffusion equation) for  $\gamma = 1$ .
- Show that probability is conserved, in the sense that  $\int P(x,t) dx$  does not depend on time  $t$ ; probability can only flow in and out through the boundaries, just like in a regular Fokker-Planck equation.
- Consider  $U(x) = 0$  case, i.e., sub-diffusion in a free unbounded space, and find  $\langle x^2 \rangle$  as a function of time, thus determining the relation between  $\gamma$  and  $\nu$  (in  $x \sim t^\nu$ ).  
**Hint:** multiply fractional Fokker-Planck equation (25) by  $x^2$  and integrate over  $x$ .
- Suppose potential  $U(x)$  is such that  $U(x) \rightarrow \infty$  at  $x \rightarrow \pm\infty$ , such that diffusing particle cannot escape. Find steady state solution of fractional Fokker-Planck equation and explain its nature.
- Show that fractional Fokker-Planck equation (25) can be equivalently re-written as

$${}_0\hat{D}_t^\gamma P(x,t) - \frac{t^{-\gamma} P(x,0)}{\Gamma(1-\gamma)} = D_\gamma \hat{L}_{\text{FP}} P \quad (27)$$

**Hint:** You may want to follow these steps. Step 1. Use integration by parts to show that

$${}_0\hat{D}_t^\gamma P(x,t) - \frac{t^{-\gamma} P(x,0)}{\Gamma(1-\gamma)} = -\frac{1}{\Gamma(1-\gamma)} \int_0^t \frac{\partial P / \partial t'}{(t-t')^\gamma} dt' \quad . \quad (28)$$

Step 2. Act with the operator  ${}_0\hat{D}_t^{1-\gamma}$  on the expression you just obtained and show that it is equal  $\partial P / \partial t$ .



- (f) Fractional Fokker-Planck equation is a linear equation. Unfortunately, Fokker-Planck operator  $\hat{L}_{FP}$  is not symmetric (not Hermitian). Show that the problem can be made symmetric by the same transformation which we used for this purpose in the case of regular Fokker-Planck equation.
- (g) Given the initial ( $t = 0$ ) distribution  $P(x, 0) = \delta(x - x_0)$ , the solution to equation (25),  $P(x, t; x_0, 0)$  is given by the bilinear expansion over eigenfunctions. For simplicity assume  $U(x) \rightarrow \infty$  at  $x \rightarrow \pm\infty$ , such that spectrum is discrete. Derive bilinear expansion. Show that spatial dependence involves the same eigenfunctions independently of  $\gamma$ .

**Hint:** Equation

$$\frac{dT_n(t)}{dt} = -\lambda_n {}_0\hat{D}_t^\gamma T_n(t) \quad (29)$$

is satisfied by the function which is called Mittag-Leffler function  $E_\gamma(z)$  (MittagLefflerE[z,γ] in the notations of *Mathematica*) which is the generalization of exponential function (and becomes exponential at  $\gamma = 1$ ) and which can be defined as a series

$$E_\gamma(z) = \sum_{m=0}^{\infty} \frac{z^m}{\Gamma(1 + \gamma m)} . \quad (30)$$

### Solution

In the free space case, let us multiply fractional Fokker-Planck equation (25) by  $x^2$  and integrate over  $x$ . In the left side, we get  $\partial_t \langle x^2 \rangle$ . In the right hand side, integration over  $x$  commutes with Rieman-Liouville operator, and we have  $\int x^2 \hat{L}_{FP} dx = \int x^2 \partial_x^2 P dx = 2$ , where we used integration by parts. When Rieman-Liouville operator acts on the time-independent quantity 2, it is easy to compute:

$${}_0\hat{D}_t^{1-\gamma} 2 = \frac{1}{\Gamma(\gamma)} \frac{\partial}{\partial t} \int_0^t \frac{2}{(t-t')^{1-\gamma}} dt' = 2 \frac{\gamma t^{\gamma-1}}{\Gamma(\gamma)} , \quad (31)$$

which gives  $\partial_t \langle x^2 \rangle = \frac{2D_\gamma t^{\gamma-1}}{\Gamma(\gamma)}$  or

$$\langle x^2 \rangle = \frac{2D_\gamma t^\gamma}{\Gamma(1 + \gamma)} , \quad (32)$$

which means  $\nu = \gamma/2$ .

Steady state solution reads  $\exp(-U(x))$ , it is just the usual Boltzmann distribution. This is because equilibrium distribution does not depend on the transport mechanism which leads to equilibrium.

Consider now bilinear expansion. Equation can be made symmetric by introducing

$$\hat{L}_{FP}^{\text{Hermitian}} = e^{U(x)/2} \hat{L}_{FP} e^{-U(x)/2} . \quad (33)$$

Then eigenfunctions are related as  $\phi_n(x) = e^{-U(x)/2} \psi_n(x)$ , with

$$\hat{L}_{FP} \phi_n(x) = -\lambda_n \phi_n(x) , \quad \hat{L}_{FP}^{\text{Hermitian}} \psi_n(x) = -\lambda_n \psi_n(x) . \quad (34)$$

And then the bilinear expansion reads

$$P(x, t; x_0, 0) = e^{U(x_0)/2 - U(x)/2} \sum_{n=0}^{\infty} \psi_n(x) \psi_n(x_0) E_\gamma(-\lambda_n t^\gamma) . \quad (35)$$

Note that the coordinate dependence comes through the eigenfunctions  $\psi_n(x)$  or  $\phi_n(x)$ , which are the same as for regular diffusion. However, as to the time dependence, which for classical diffusion is described by exponentials ( $e^{-\lambda_n t}$ ), for sub-diffusion it is a more sophisticated Mittag-Leffler function.

11. Consider sub-diffusion in 1D interval of length  $2L$  described by the fractional Fokker-Planck equation and derive differential equation satisfied by the mean first passage time (MFPT) as a function of starting point  $x_0$ .

**Hint:** Show first that the MFPT can be calculated from the Green's function  $P(x, t; x_0, 0)$  as

$$\tau(x_0) = \int_0^\infty \int_{-L}^L P(x, t; x_0, 0) dx dt \quad (36)$$

and then apply the operator  $e^{U(x_0)}L_{\text{FP},x_0}e^{-U(x_0)}$  to both sides of the equation (36).

### Solution

To derive an ordinary differential equation satisfied by  $\tau(x_0)$ , apply the operator  $e^{U(x_0)}L_{\text{FP},x_0}e^{-U(x_0)}$  to equation (36) and use the eigenfunction expansion solution (35) for  $P(x, t; x_0, 0)$ ,

$$\begin{aligned} e^{U(x_0)}L_{\text{FP},x_0}e^{-U(x_0)}\tau(x_0) &= \int_0^\infty \int_{-L}^L e^{U(x_0)/2-U(x)/2} \sum_{n=0}^\infty (-\lambda_n)\psi_n(x)\psi_n(x_0)E_\gamma(-\lambda_n t^\gamma) dx dt \\ &= \int_0^\infty \int_{-L}^L \hat{L}_{\text{FP}}P(x, t) dx dt = \int_0^\infty \int_{-L}^L \left[ {}_0\hat{D}_t^\gamma P(x, t) - \frac{t^{-\gamma}P(x, 0)}{\Gamma(1-\gamma)} \right] dx dt \end{aligned}$$

In the last two steps, the eigenvalue equations and the second version of the FFPE (equation (27)) was used. Using the initial condition  $P(x, 0) = \delta(x - x_0)$  and the definition of the fractional operator, after some algebra one obtains

$$\begin{aligned} e^{U(x_0)}L_{\text{FP},x_0}e^{-U(x_0)}\tau(x_0) &= \\ &= -\lim_{t \rightarrow \infty} \left[ \frac{t^{1-\gamma}}{\Gamma(2-\gamma)} - \frac{1}{\Gamma(1-\gamma)} \int_0^t \frac{S(t')}{(t-t')^\gamma} dt' \right] \end{aligned} \quad (37)$$

or

$$\begin{aligned} D_\gamma e^{U(x_0)} \frac{\partial}{\partial x_0} e^{-U(x_0)} \frac{\partial}{\partial x_0} \tau(x_0) &= \\ &= -\lim_{t \rightarrow \infty} \left[ \frac{t^{1-\gamma}}{\Gamma(2-\gamma)} - \frac{1}{\Gamma(1-\gamma)} \int_0^t \frac{S(t')}{(t-t')^\gamma} dt' \right] \end{aligned} \quad (38)$$

For  $\gamma = 1$ , corresponding to classical diffusion, the survival probability  $S(t')$  decays exponentially and the term with the integral goes to zero, yielding the familiar result of  $-1$  for the right-hand-side. For  $\gamma < 1$ ,  $S(t')$  goes like  $(t')^{-\gamma}$  and the term with the integral goes like  $t^{1-2\gamma}$ . The right-hand-side diverges, which hints at the non-existence of the MFPT for this type of sub-diffusion.

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