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

Home Work 11 *Solutions*

1. In class, we derived the sub-diffusive behavior of an arbitrary middle monomer (or the end) of a Rouse polymer: $\langle r^2 \rangle \sim \left(D_1 a^2 t\right)^{1/2}$, or $r \sim t^{1/4}$, on the time scale shorter than full relaxation time of the coil, $t \ll \tau_1 = 2\zeta a^2 N^2/\pi^2 T$. This was done using physical scaling arguments. Re-derive this result more formally, based on Langevin equations for modes of Rouse polymer derived and discussed in one of the previous HWs.

Solution

We know that position vector of a particular monomer i is expressed in term of modes as

$$\mathbf{r}(t,i) = \mathbf{y}_0(t) + 2\sum_{p=1}^{\infty} \mathbf{y}_p(t) \cos\frac{\pi p i}{N} \ . \tag{1}$$

Therefore, we can write down the expression for the displacement of the monomer during time from 0 to t

$$\mathbf{r}(t,i) - \mathbf{r}(0,i) = \mathbf{y}_0(t) - \mathbf{y}_0(0) + 2\sum_{p=1}^{\infty} \left(\mathbf{y}_p(t) - \mathbf{y}_p(0)\right) \cos\frac{\pi p i}{N} \ . \tag{2}$$

Of course, averaged displacement vanishes. Thus, we square the above relation and note that different modes are independent, which means all cross-terms disappear upon averaging:

$$\left\langle \left(\mathbf{r}(t,i) - \mathbf{r}(0,i)\right)^2 \right\rangle = \left\langle \left(\mathbf{y}_0(t) - \mathbf{y}_0(0)\right)^2 \right\rangle + 2\sum_{p=1}^{\infty} \left\langle \left(\mathbf{y}_p(t) - \mathbf{y}_p(0)\right)^2 \right\rangle \cos^2\frac{\pi p i}{N} \ . \tag{3}$$

As a reminder, we found before

$$\begin{aligned} \zeta N \frac{\partial \mathbf{y}_0}{\partial t} &= \vec{\Xi}_0(t) \ , \qquad\qquad q = 0 \\ 2\zeta N \frac{\partial \mathbf{y}_q}{\partial t} &= -\frac{\pi^2 k q^2}{N} \mathbf{y}_q + \vec{\Xi}_q(t) \ , \quad q \neq 0 \end{aligned} \tag{4}$$

All modes $\mathbf{y}_p(t)$ are decoupled, and each is driven its own noise. Each noise has zero mean, $\left\langle \vec{\Xi}_q(t) \right\rangle = 0$, they are independent, and their variance

$$\begin{aligned} \langle \Xi_{\alpha,0}(t) \Xi_{\beta,0}(t') \rangle &= 2\zeta N T \delta_{\alpha\beta} \delta(t - t') \\ \langle \Xi_{\alpha,p}(t) \Xi_{\beta,q}(t') \rangle &= 4\zeta N T \delta_{\alpha\beta} \delta(t - t') \delta_{pq} \end{aligned} \tag{5}$$

Thus, every mode satisfies regular Langevin equation (with fluctuation-dissipation balanced friction and noise). In the standard way, we find

$$\left\langle \left(\mathbf{y}_p(t) - \mathbf{y}_p(0)\right)^2 \right\rangle = \frac{2Na^2}{\pi^2 p^2} \left[1 - e^{-t/\tau_p}\right] \tag{6}$$

with $\tau_p = 2\zeta N^2/\pi^2 k p^2$ for any $q \neq 0$, and

$$\left\langle \left(\mathbf{y}_0(t) - \mathbf{y}_0(0)\right)^2 \right\rangle = \frac{6}{\zeta N} t \tag{7}$$

Thus,

$$\left\langle \left(\mathbf{r}(t,i) - \mathbf{r}(0,i)\right)^2 \right\rangle = \frac{6}{\zeta N} t + \frac{4Na^2}{\pi^2} \sum_{p=1}^{\infty} \frac{1}{p^2} \left[1 - e^{-tp^2/\tau_1}\right] \cos^2\frac{\pi p i}{N} \ . \tag{8}$$

At the time scales of our interest, $t \ll \tau_1$, many modes contribute to the sum, and the sum can be replaced by the integral. Furthermore, rapidly oscillating cosine-squared term can be replaced by its average value (which is 1/2), yielding very simple integral, and the result :

$$\left\langle \left(\mathbf{r}(t,i) - \mathbf{r}(0,i)\right)^2 \right\rangle \simeq \left(\frac{12}{\pi} \frac{Ta^2}{\zeta} t \right)^{1/2} \quad , \tag{9}$$

exactly as expected.

2. Consider random walk on a lattice in space, and assume there is a potential well of random depth $-u_i$ on every lattice site i, while barriers between sites are all on the potential energy level zero. What should be the distribution of random depths to generate a continuous time random walk – a sub-diffusion $r \sim t^{\nu}$ with index $\nu < 1/2$?

Solution

According to Kramers, waiting time for a particle in the well of depth u goes as $\tau(u) \sim \tau_0 e^{u/T}$, given that surrounding barriers are all at the level zero. To generate sub-diffusion, we need waiting times to have a fat tail distribution $w(\tau) \sim 1/\tau^{1+\mu}$, with $0 < \mu = 2\nu < 1$. Knowing the distribution of τ, we find distribution of u from $w(\tau)d\tau = P(u)du$ which means $P(u) = w(\tau)d\tau/du$ which leads to $P(u) \sim \exp(-\mu u/T)$. So, it should be an exponential distribution of potential well depths, somewhat mathematically similar to Boltzmnann distribution – except with an increased temperature, T/μ.

3. Consider paper [1], where authors observe a subdiffusive motion, with $\langle r^2 \rangle \approx 4D_{\mathrm{app}} t^{2\nu}$.

   (a) Does ATP activity affect the power ν?

   (b) What is the observed power ν? Is it consistent with observations of the paper [2] on a different biological system?

   (c) What is the dimension of the "apparent diffusion coefficient" D_{app}?

   (d) What is its temperature dependence, and why?

   (e) What is the fractional Langevin memory kernel?

Solution

   (a) ATP activity does not appear to have any effect on the power ν, as figure 1 suggests. It means, power ν is controlled by some physical factors not related to active energy consumption.

   (b) The observed power ν is close to 0.4, which is why this is called a subdiffusion. It is qualitatively consistent with observations of the paper [2] on a different biological system, but quantitative comparison is impossible because different quantities are measured.

   (c) The dimension of the "apparent diffusion coefficient" D_{app} depends on the power ν! Authors measure it in $\mu m^2/s^{\nu}$.

   (d) Apparent diffusion coefficient D_{app} is not linearly proportional to absolute temperature, as Einstein relation for the regular diffusion coefficient would suggest ($D = T/\zeta$). Instead, it seems to follow the Arrhenius law ($\sim e^{-E/T}$), with activation energy close to T at room temperature.

   (e) Fractional Langevin memory kernel comes into play if you view the process as a continuous time random walk. See problem 9 below for further details.

4. Consider paper [3]. Can you reproduce the main result (second term of their formula 1b) by thinking that two ends of the chain in question undergo a subdiffusion, finding the right index ν, and establishing if fractal dimension $d_f = 1/\nu$ is larger (compact exploration) or smaller (non-compact exploration) than the surrounding space dimension.

Solution

Authors consider Rouse dynamics (with no hydrodynamic interactions), that means chain ends undergo subdiffusion $r \sim t^{1/4}$, their trajectories are fractal of fractal dimension $d_f = 1/\nu = 4$. It is larger than the embedding space dimension, so ends explore space compactly. Therefore, to meet the other end, each of them has to move only once the distance of the order of coil size, or $t^{1/4}(Ta^2/\zeta)^{1/4} \sim aN^{1/2}$, or $t \sim N^2(\zeta/Ta^2)$ which is the main answer of the paper in question (second term of their formula 1b; their D is our T/ζ, and their b is our a).

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

5. Consider a particle diffusing in the space between two spheres with radii $R_1 < R_2$. Find probability p_2 that this particle hits outer sphere for the first time before ever touching the inner sphere, and also similar probability p_1, assuming particle starts at some radius r inside the gap between the speheres: $R_1 < r < R_2$.

   Solution

   $p_1 = \frac{\frac{1}{r} - \frac{1}{R_2}}{\frac{1}{R_1} - \frac{1}{R_2}}$ and $p_2 = \frac{\frac{1}{R_1} - \frac{1}{r}}{\frac{1}{R_1} - \frac{1}{R_2}}$.

   This can be understood by analogy with electrical resistance. we can smear initial place of the particle around the sphere of radius r thus rendering the problem spherically symmetric. After that, 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 is proportional to the length of a conductor and inversely proportional toits 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.

6. 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., [4].

7. The diffusion controlled "annihilation" of particles according to $A + B \rightharpoonup C$ assuming that in the initial state at $t = 0$, there is equal amount of A and B, such that average concentrations are the same, $\overline{A} = \overline{B}$, 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 that 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 $Z \sim \sqrt{\overline{A}/V}$ yielding $Z \sim \overline{A}^{1/2}(Dt)^{-d/4}$. This answer is valid if it decays slower than the mean field t^{-1}, which means at $d < 4$.

8. We considered the diffusion controlled "annihilation" of particles according to $A + B \rightharpoonup C$ 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 $\exp\left[-AR^3 - tD/R^2\right]$ (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 $\exp\left[-\mathrm{const} A^{2/5}(Dt)^{3/5}\right]$. This answer is valid at long times, when $t \gg AD^{3/2}/k^{5/2}$.

9. 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 [5]). While the usual Fokker-Planck equation reads

$$\frac{\partial P(x,t)}{\partial t} = D\hat{L}_{\mathrm{FP}}P \quad , \; \hat{L}_{\mathrm{FP}} = \frac{\partial}{\partial x}e^{-U(x)}\frac{\partial}{\partial x}e^{U(x)} \; , \tag{10}$$

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

$$\frac{\partial P(x,t)}{\partial t} = D_\gamma \; {}_0\hat{D}_t^{1-\gamma}\hat{L}_{\mathrm{FP}}P \; . \tag{11}$$

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

$${}_0\hat{D}_t^{1-\gamma}W = \frac{1}{\Gamma(\gamma)}\frac{\partial}{\partial t}\int_0^t \frac{W(x,t')}{(t-t')^{1-\gamma}}dt' \; . \tag{12}$$

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

(a) Check that the fractional Fokker-Planck equation reduces to the regular Fokker-Planck equation (or diffusion equation) for $\gamma = 1$.

(b) 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.

(c) 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 γ and nu (in $x \sim t^\nu$).
Hint: multiply fractional Fokker-Planck equation (11) by x^2 and integrate over x.

(d) Suppose potential $U(x)$ is such that $U(x) \to \infty$ at $x \to \pm\infty$, such that diffusing particle cannot escape. Find steady state solution of fractional Fokker-Planck equation and explain its nature.

(e) Show that fractional Fokker-Planck equation (11) can be equivalently re-written as

$${}_0\hat{D}_t^{\gamma}P(x,t) - \frac{t^{-\gamma}P(x,0)}{\Gamma(1-\gamma)} = D_\gamma \hat{L}_{\mathrm{FP}}P \tag{13}$$

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

$${}_0\hat{D}_t^{\gamma}P(x,t) - \frac{t^{-\gamma}P(x,0)}{\Gamma(1-\gamma)} = -\frac{1}{\Gamma(1-\gamma)}\int_0^t \frac{\partial P/\partial t'}{(t-t')^{\gamma}}dt' \; . \tag{14}$$

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 $\hat{L}_{\mathrm{FP}}$ 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 (11), $P(x,t;x_0,0)$ is given by the bilinear expansion over eigenfunctions. For simplicity assume $U(x) \to \infty$ at $x \to \pm\infty$, such that spectrum is discrete. Derive bilinear expansion. Show that spatial dependence involves the same eigenfunctions independently of γ.
Hint: Equation

$$\frac{dT_n(t)}{dt} = -\lambda_n \; {}_0\hat{D}_t^{\gamma}T_n(t) \tag{15}$$

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

$$E_\gamma(z) = \sum_{m=0}^{\infty} \frac{z^m}{\Gamma(1+\gamma m)} \ . \tag{16}$$

Solution

In the free space case, let us multiply fractional Fokker-Planck equation (11) 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 $\int x^2 \hat{L}_{\mathrm{FP}} dx = \int x^2 \partial_x^2 P dx = 2$, where we used integration by parts. When Rieman-Liouville operator acts on the time-independent quantity 2, it is easy to compute:

$${}_0\hat{D}_t^{1-\gamma} 2 = \frac{1}{\Gamma(\gamma)} \frac{\partial}{\partial t} \int_0^t \frac{2}{(t-t')^{1-\gamma}} dt' = 2\frac{\gamma t^{\gamma-1}}{\Gamma(\gamma)} \ , \tag{17}$$

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

$$\langle x^2 \rangle = \frac{2D_\gamma t^\gamma}{\Gamma(1+\gamma)} \ , \tag{18}$$

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

$$\hat{L}_{\mathrm{FP}}^{\mathrm{Hermitian}} = e^{U(x)/2} \hat{L}_{\mathrm{FP}} e^{-U(x)/2} \ . \tag{19}$$

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

$$\hat{L}_{\mathrm{FP}} \phi_n(x) = -\lambda_n \phi_n(x) \ , \ \hat{L}_{\mathrm{FP}}^{\mathrm{Hermitian}} \psi_n(x) = -\lambda_n \psi_n(x) \ . \tag{20}$$

And then the bilinear expansion reads

$$P(x,t;x_0,0) = e^{U(x_0)/2 - U(x)/2} \sum_{n=0}^{\infty} \psi_n(x)\psi_n(x_0) E_\gamma(-\lambda_n t^\gamma) \ . \tag{21}$$

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.

10. 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

$$\tau(x_0) = \int_0^\infty \int_{-L}^{L} P(x,t;x_0,0) dx dt \tag{22}$$

and then apply the operator $e^{U(x_0)} L_{\mathrm{FP},x_0} e^{-U(x_0)}$ to both sides of the equation (22).

Solution

To derive an ordinary differential equation satisfied by $\tau(x_0)$, apply the operator $e^{U(x_0)} L_{\mathrm{FP},x_0} e^{-U(x_0)}$ to equation (22) and use the eigenfunction expansion solution (21) for $P(x,t;x_0,0)$,

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

In the last two steps, the eigenvalue equations and the second version of the FFPE (equation (13)) 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

$$e^{U(x_0)} L_{\mathrm{FP},x_0} e^{-U(x_0)} \tau(x_0) = \\ -\lim_{t\to\infty} \left[\frac{t^{1-\gamma}}{\Gamma(2-\gamma)} - \frac{1}{\Gamma(1-\gamma)} \int_0^t \frac{S(t')}{(t-t')^\gamma} dt' \right] \tag{23}$$

or

$$D_\gamma e^{U(x_0)} \frac{\partial}{\partial x_0} e^{-U(x_0)} \frac{\partial}{\partial x_0} \tau(x_0) = \\ -\lim_{t\to\infty} \left[\frac{t^{1-\gamma}}{\Gamma(2-\gamma)} - \frac{1}{\Gamma(1-\gamma)} \int_0^t \frac{S(t')}{(t-t')^\gamma} dt' \right] \tag{24}$$

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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