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Exam in TFY4275 CLASSICAL TRANSPORT THEORY
Thursday May 22, 2008
09:00–13:00

Allowed help: Alternativ **D**
Authorized calculator and mathematical formula book

This problem set consists of 4 pages, plus an Appendix of one page.

Problem 1. Anomalous diffusion

a) Consider a particle undergoing (symmetric) diffusion in one-dimension (for simplicity). How will the mean square displacement, $\langle x^2 \rangle$, scale with time, t, for this process (no derivation is needed), and how will it depend on the diffusion constant D?

b) Define what is meant by the term *anomalous diffusion*. Anomalous diffusion can be classified into *sub*- and *super*-diffusion. Define them, and specify if they are Markovian or non-Markovian. What may the physical origin in the two cases be for the deviation from ordinary diffusion?

c) Consider a (symmetric) Lévy distribution $\mathcal{L}_\alpha(x)$ of tail exponent $0 < \alpha < 2$ that asymptotically scales like (when $x \to \infty$)

$$\mathcal{L}_\alpha(x) \sim x^{-(\alpha+1)}.$$

What is the condition α has to satisfy in order to ensure that the moment $\left\langle |x|^\delta \right\rangle$ is finite. How would your answer change if $p(x)$ was not a (symmetric) Lévy distribution, but, however, still asymptotically scaled like $p(x) \sim x^{-(\alpha+1)}$? In this latter case, what will happen if $\alpha \geq 2$?

d) Assume that a particle's movement is well described by the *continuous time random walk model*, where the joint probability $\psi(x,t)$ for jump sizes (x) and waiting times (t) is separable, $\psi(x,t) = \lambda(x)w(t)$, with $\lambda(x)$ and $w(t)$ being the marginal jump size and waiting time distributions, respectively.

Assume that these marginal distributions asymptotically scale like power laws, *i.e.*

$$\lambda(x) \sim |x|^{-(\mu+1)}$$

and

$$w(t) \sim t^{-(\gamma+1)}$$

where $\mu > 0$ and $\gamma > 0$.

In each of the following cases specify if the resulting continuous time random walk process corresponds to *i*) normal (ordinary) diffusion; *ii*) sub-diffusion; and/or *iii*) super-diffusion (justify your answer in each case):

1) $\mu = 4$; $\gamma = 2$

2) $\mu = 5/2$; $\gamma = 1$

3) $\mu = 1$; $\gamma = 1/2$

4) $\mu = 7/3$; $\gamma = 3/2$

5) $\mu = 3/2$; $\gamma = 3/2$

6) $\mu = 2$; $\gamma = 3/2$

Problem 2. Non-isotropic Random Walk

We will now study a random walk model somewhat different from the one presented in the lectures. Let p_+ be the probability for making a step to the *right*; p_- the probability for a step to the *left*; and $1 - p_- - p_+$ for not moving at all. Moreover, let Δx denote the constant jump size. When $p_+ \neq p_-$ the walker is non-isotropic (or asymmetric). Such an asymmetry can be physically realized due to *e.g.* an external force, like a diffusing particle on an inclined plane.

Note that the random walk model presented in the lectures corresponds to the special case of $p_+ = p_- = 1/2$.

a) Write down an expression for the jump size probability distribution function (PDF), $p_1(\xi)$, assuming the length of each non-vanishing jump to have a constant length $\Delta x > 0$. Calculate the corresponding characteristic function $\hat{p}_1(k) = \langle \exp(ik\xi) \rangle$.

b) Obtain the average jump size $\langle \xi \rangle$ as well as the average drift velocity of the walker when the time interval between consecutive jumps is Δt. What is the maximum possible drift velocity? Make a sketch of one realization of the random walker for the cases *i)* $p_+ = p_-$; *ii)* $p_+ > p_-$; and *iii)* $p_+ < p_-$.

[Comment: The distribution of the walker's position after N time steps can be obtained as the inverse Fourier transform of $[\hat{p}_1(k)]^N$. We will not follow this route here since the expressions become cumbersome in general. Instead an alternative approach will be followed below.]

c) Let $P(x,t)$ denote the probability for the walker being at (discrete) position $x = i\Delta x$ ($i = 0, \pm 1, \pm 2, \ldots$) at (discrete) time $t = j\Delta t$ ($j = 0, 1, 2, \ldots$). Make a sketch of the in/out-flow of probability into position x, during the transition from t to $t + \Delta t$. Use this to show that the conservation of probability implies

$$P(x, t + \Delta t) = P(x,t) + p_+ \left[P(x - \Delta x, t) - P(x,t) \right] + p_- \left[P(x + \Delta x, t) - P(x,t) \right]. \tag{1}$$

d) Introduce the (jump) rates (probability per unit time) defined by $r_\pm = p_\pm / \Delta t$ where Δt is the constant time-interval between two consecutive jumps. Take the *continuous time limit*, $\Delta t \to 0^+$, of Eq. (1). What is this equation called?

e) We will now continue by taking the *continuous space limit* of the equation from the previous sub-problem. In this case $P(x,t)$ may be understood as the probability for finding the particle in an interval of length Δx about x. Introducing the probability density function (PDF) $f(x,t)$, so that $P(x,t) = f(x,t)\Delta x$ and show that it satisfies the equation

$$\partial_t f(x,t) = -\nu \partial_x f(x,t) + D\partial_x^2 f(x,t). \tag{2}$$

What is this equation called? Obtain the expressions for the constants ν and D, and express them in terms of $p_\pm$, Δx and Δt. Obtain the limiting expressions for ν and D in the special case that $p_+ = p_- = 1/2$. Is the result reasonable?

[Comment: Even if we use a continuous representation of space and time, the physical nature of the problem implies that Δx and Δt are finite, of the order of the mean free path and mean free time, respectively]

f) What is the implication of the ν-term in Eq. (2) when $\nu \neq 0$? Use this to argue why the solution of Eq. (2) is

$$f(x,t) = \frac{1}{\sqrt{4\pi D t}} \exp\left(-\frac{(x - x_0 - \nu t)^2}{4Dt} \right), \tag{3}$$

given the initial condition $f(x, t = 0) = \delta(x - x_0)$.

g) Derive expressions for $\langle x(t) \rangle$ and $\langle x^2(t) \rangle$ as well as the standard deviation, $\sigma_x(t)$, of the spacial coordinate. Assume that the walker starts off from $x = x_0$ at $t = 0$. How is this latter result influenced by potential asymmetries, *i.e.* of $p_+ \neq p_-$?

Problem 3. Ion diffusion; Electro-chemistry

Consider an electrolyte consisting of positive and negative ions, *i.e.* charged particles in solution. They have charges $q_\pm = \pm e$, concentrations $c_\pm(x)$, and diffusion constants $D_\pm$, respectively. Einsteins relation connects $D_\pm$ to the mobility of the ions, $\mu_\pm$, via the relation $\mu_\pm = D_\pm / k_B T$ where k_B is Boltzmann's constant and T the absolute temperature of the solvent.

To treat the electrical forces acting on a given ion from all the surrounding ions is demanding. We will instead work within the mean field approximation where each ion only "feels" an *average* electric force,

$$F_\pm(x) = -q_\pm \frac{d\phi(x)}{dx} = \mp e \frac{d\phi(x)}{dx},$$

where $\phi(x)$ is the (time independent) electrostatic potential at position x (due to the surrounding ions). Note that within this approximation each ion moves *independently*! Hence, the concentrations, $c_\pm(x)$, will satisfy the Fokker-Planck equation (recall that $\mu_\pm F_\pm(x)$ is the drift velocity term)

$$\partial_t c_\pm(x) = -\partial_x \left[\mu_\pm F_\pm(x) c_\pm(x) \right] + D_\pm \partial_x^2 c_\pm(x). \tag{4}$$

In electro-chemistry this equation is also known as the Nernst-Planck equation.

The electrostatic potential satisfies the Poisson's equation

$$-\varepsilon \frac{d^2\phi(x)}{dx^2} = \rho(x) = e\left[c_+(x) - c_-(x)\right]$$

where ε is the dielectric function of the solvent (*e.g.* water), and $\rho(x)$ denotes the charge density at position x.

An (uncharged) wall is placed at $x = 0$ and the solvent fills the region $x > 0$. The two ion concentrations are initially equal and independent of position, *i.e.* $c_\pm(x) = c_0$.

a) Now at $t = 0$, the electrical potential of the wall is reduced (from zero) and kept at the constant negative level $\phi(0) = -\phi_0$ where $\phi_0 > 0$ is a constant. Describe in words what will happen to the ions close to the wall shortly after the potential is "turned" on at $t = 0$? What will happen for long times? What is the boundary condition for $c_\pm(x = \infty)$?

b) We will now address the equilibrium (stationary) concentration $c_\pm(x)$. What is the equation satisfied by $c_\pm(x)$ in this case, and show that its solution is

$$c_\pm(x) = c_0 \exp\left(\mp \frac{e\phi(x)}{k_B T}\right).$$

c) Show that the electrical potential satisfies the following non-linear equation (know as the Poisson-Boltzmann equation)

$$\varepsilon \frac{d^2\phi(x)}{dx^2} = 2c_0 e \sinh\left(\frac{e\phi(x)}{k_B T}\right). \tag{5}$$

This equation can be solved analytically, but we will not do so here.

d) Linearize Eq. (5) and show that the (linearized) electrical potential can be written as (when you impose the appropriate boundary conditions):

$$\phi(x) = -\phi_0 e^{-x/\lambda}.$$

What is the expression for λ?

e) Obtain an expression for the equivalent (linearized) charge density $\rho(x)$ and make a sketch of this function. Explain why λ is called the (Debye) "screening length"?

Mathematics:

- The Fourier Transform:

$$\hat{f}(k) = \int_{-\infty}^{\infty} dx\, f(x) e^{-ikx}$$

$$f(x) = \int_{-\infty}^{\infty} \frac{dk}{2\pi}\, \hat{f}(k) e^{ikx}$$

- The Lévy distribution

$$\hat{\mathcal{L}}_\alpha(k) = \exp(-a|k|^\alpha)$$

- Sin hyperbolicus

$$\sinh(x) = \frac{e^x - e^{-x}}{2}$$

- Taylor expansion

$$f(x+\delta) \simeq f(x) + \delta f'(x) + \frac{\delta^2}{2!} f''(x) + \ldots$$

$$\sinh(x) \simeq x + \frac{x^3}{3!} + O(x^5)$$

- Gaussin integrals

$$\int_{-\infty}^{\infty} dx\, e^{-\left(ax^2+2bx+c\right)} = \sqrt{\frac{\pi}{a}} \exp\left(\frac{b^2 - ac}{a}\right), \qquad a > 0$$

$$\int_{-\infty}^{\infty} dx\, x\, e^{-\left(ax^2+2bx+c\right)} = \frac{-b}{a} \sqrt{\frac{\pi}{a}} \exp\left(\frac{b^2 - ac}{a}\right), \qquad a > 0$$

$$\int_{-\infty}^{\infty} dx\, x^2\, e^{-\left(ax^2+2bx+c\right)} = \frac{a + 2b^2}{2a^2} \sqrt{\frac{\pi}{a}} \exp\left(\frac{b^2 - ac}{a}\right), \qquad a > 0$$