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Hand in on January 30th 2017 before the lecture

Advanced Statistical Physics II – Problem Sheet 12

Problem 1 – **Schrödinger equation**

a) (2P) Show that the Smoluchowski-equation

$$\frac{\partial \rho(x,t)}{\partial t} = \frac{\partial}{\partial x}\frac{U'(x)}{\gamma}\rho(x,t) + \frac{\partial^2}{\partial x^2}\frac{k_B T}{\gamma}\rho(x,t)\,, \tag{1}$$

where $\rho(x,t)$ denotes the particle density distribution, $U(x)$ a position-dependent external potential, γ the friction coefficient, is solved by the equilibrium distribution

$$\rho_{\text{eq}}(x) = \frac{1}{Z}\mathrm{e}^{-U(x)/k_B T}\,, \tag{2}$$

with normalization constant Z.

b) (3P) Show that the Smoluchowski-equation can be transformed into a Schrödinger-like equation of the form

$$\frac{\partial \Psi(x,t)}{\partial t} = -D\left[-\frac{\partial^2}{\partial x^2} + U_{\text{eff}}(x)\right]\Psi(x,t)\,, \tag{3}$$

where D is the diffusion coefficient. As an ansatz use

$$\rho(x,t) = \sqrt{\rho_{\text{eq}}(x)}\,\Psi(x,t)\,, \tag{4}$$

with equilibrium distribution $\rho_{\text{eq}}(x)$ from a). Derive the effective potential $U_{\text{eff}}(x)$.

Problem 2 – **Diffusion in a potential well**

Consider the Smoluchowski-equation from problem 1 with the potential

$$U(x) = \begin{cases} 0 & \text{if } 0 < x < a \\ \infty & \text{else} \end{cases}\,. \tag{5}$$

a) (5P) In the lecture we defined the particle flux $J(x,t)$ by the equation

$$\frac{\partial \rho(x,t)}{\partial t} = -\frac{\partial}{\partial x}J(x,t)\,, \tag{6}$$

Use a separation ansatz similar to problem 1 e) on sheet 5 and the fact that the particle flux vanishes at the potential walls at 0 and a to solve the Smoluchowski equation for this potential. The result should be

$$\rho(x,t) = \sum_0^\infty A_n \cos\left(\frac{n\pi}{a}x\right)\exp\left(-\frac{n^2\pi^2}{a^2}Dt\right)\,, \tag{7}$$

with the diffusion constant D.

b) (3P) Now assume that at time $t=0$ the distribution is $\rho(x,t=0) = N\delta(x-x_0)$ with $0 < x_0 < a$, where N denotes the total number of particles. Determine the coefficients A_n and write down the full solution of $\rho(x,t)$.

Problem 3 – **Mean first passage time**

The mean first passage time is the average time a particle needs to cross position x_B for the first time when starting at position x_0 at $t = 0$. It the lecture we derived the formula

$$\tau^{FP} = \frac{1}{D} \int_{x_0}^{x_B} \mathrm{d}x' \mathrm{e}^{U(x')/k_B T} \int_{x_L}^{x'} \mathrm{d}x'' \mathrm{e}^{-U(x'')/k_B T} \tag{8}$$

with $x_L < x_0 < x_B$.

a) (3P) We assume that $U(x < x_L) = \infty$. Calculate the mean first passage time as a function of x_0, x_A and x_B for the potential function

$$U(x) = \begin{cases} \infty & \text{if } x < x_L \\ U_0 & \text{if } x_L \leq x \leq x_A \\ U_1 & \text{if } x_A \leq x \leq x_B \end{cases} . \tag{9}$$

b) (4P) From mean-first passage times to reaction rates

Now assume the potential is analytic and $U(x_B) >> k_B T$ so that $\mathrm{e}^{U(x')/k_B T}$ is sharply peaked around x_B. In this case we only have to consider the outer integral around $x' \approx x_B$.

1. Expand the outer integral around $x = x_B$ and the inner around $x = x_A$ both up to second order. Note that $U(x)$ has a maximum at $x = x_B$ and a minimum at $x = x_A$
2. Calculate the mean-first passage time by saddle point approximation. What is the resulting reaction rate?
   Note: The limits need to be changed to $-\infty$ and $+\infty$.