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Advanced Statistical Physics II – Problem Sheet 10

Problem 1 – **Stationary solution of the Fokker-Planck equation** (2P)
Show that the Boltzmann distribution $\rho_{\text{eq}}(x,p) \propto e^{-H(x,p)/k_B T}$ with $H(x,p) = p^2/2m + U(x)$ is a stationary solution of the Fokker-Planck equation for a massive particle in one dimension:

$$\frac{\partial}{\partial t}\rho(x,p,t) = \left[-\frac{p}{m}\frac{\partial}{\partial x} + U'(x)\frac{\partial}{\partial p} + \frac{\gamma}{m}\frac{\partial}{\partial p}p + \gamma k_B T\frac{\partial^2}{\partial p^2}\right]\rho(x,p,t) \tag{1}$$

Problem 2 – **Mapping of the diffusion equation onto the Schrödinger equation** (2P)
Make the ansatz $\rho(x,t) = \sqrt{\rho_{\text{eq}}(x)}\psi(x,t)$, where $\rho_{\text{eq}}(x) = e^{-U(x)/k_B T}/Z$ is the equilibrium distribution, and show that the diffusion or Smoluchowski equation

$$\frac{\partial \rho(x,t)}{\partial t} = D\frac{\partial}{\partial x}e^{-U(x)/k_B T}\frac{\partial}{\partial x}e^{U(x)/k_B T}\rho(x,t) \tag{2}$$

can be cast into a Schrödinger-like equation

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

with an effective "potential" $U_{\text{eff}}(x)$.

Problem 3 – **Dissociation of a diatomic molecule**
Consider the following potential:

$$U(x) = 3\Delta U\left(\frac{x}{x_0}\right)^2 - 2\Delta U\left(\frac{x}{x_0}\right)^3 \tag{4}$$

a) (3P) Using Kramer's formula derived in the lecture, calculate the reaction *time* for the potential (4) and friction constant γ.

b) (1P) Is (4) a realistic pair-potential for the atoms in a diatomic molecule? Think about why it (still) may be used to calculate/estimate the dissociation time of a diatomic molecule using Kramer's formula.

c) (3P) As an application, we want to use our model to calculate the dissociation time of a Cl_2 molecule in water at 300 K: The dissociation energy of Cl_2 is 242 kJ/mol which we choose as the barrier height. We estimate the friction constant γ from the diffusion constant $D = 2\ \text{nm}^2\text{ns}^{-1}$ of a single chloride ion at 300 K in water. For the location of the maximum x_0, we choose the bond length which is roughly 0.1 nm.

Problem 4 – **Diffusion in a potential well**
Solve the Smoluchowski equation for the potential

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

where it is assumed that the flux $J(x,t)$ defined via

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

vanishes at the boundaries $x = 0$ and $x = L$.

a) (6P) Make the separation ansatz $\rho(x,t) = A(t)B(x)$ for the region $0 < x < L$ and show that this leads to

$$\frac{d^2}{dx^2} B(x) = -\lambda B(x) \tag{7}$$

for some real constant λ. Show that $\lambda = \frac{n^2\pi^2}{L^2}$ is the only non-trivial choice which yields a solution that fulfils the boundary conditions. Derive the final result

$$\rho(x,t) = \sum_{n=0}^{\infty} c_n e^{-\frac{n^2\pi^2}{L^2} Dt} \cos\left(\frac{n\pi}{L} x\right) \tag{8}$$

b) (3P) Assume an initial distribution $\rho(x, t = 0) = \delta(x - x_0)$ with $0 < x_0 < L$ and determine the coefficients c_n. *Hint:* Recall that $\int_0^\pi dx \cos(mx)\cos(nx) = \frac{\pi}{2}\delta_{n,m}$.