Statistical Physics IV: Non-equilibrium statistical physics
ECOLE POLYTECHNIQUE FEDERALE DE LAUSANNE (EPFL)

Exercise No.1

1.1 Langevin equation

A Langevin equation describes the motion of a particle in the presence of friction, and is given by,

$$m\frac{dv}{dt} = F_{\text{ex}}(t) - \alpha v + F_L(t).$$

Here v is the particle's velocity, m its mass, F_{ex} is an externally applied force, and the last term is the random Langevin force[1]. We will here consider the case where the Langevin force has a vanishing mean, i.e., $\langle F_L(t)\rangle = 0$.

(a) Show that in the absence of external forces ($F_{\text{ex}} = 0$), the Langevin equation implies,

$$m\frac{d}{dt}(xv) = mv^2 - \alpha\, xv + x\, F_L.$$

(b) It is now required to take the statistical average of the above equation, with respect to all the possible realizations of the stochastic Langevin force $F_L(t)$. To do this, we need to use

$$\left\langle \frac{df}{dt} \right\rangle = \frac{d}{dt}\langle f \rangle\,.$$

Is this valid for any stochastic function f?

(c) Assuming that the position and the random Langevin force are statistically independent, i.e. $\langle F_L(t)x(t)\rangle = \langle F_L(t)\rangle \langle x(t)\rangle$, show that, for long times $t \gg m/\alpha$, we have,

$$m\frac{d}{dt}\langle xv\rangle = k_B T - \alpha \langle xv\rangle\,.$$

We assume that the system will reach thermodynamic equilibrium at long times.

(d) Show that $\langle x(t)^2\rangle = 2Dt$ for times $t \gg m/\alpha$. What is the expression for the diffusion constant D?

(e) Assume now that the particle carries a charge q, and is in a homogeneous electric field E. Calculate the particle's mean equilibrium velocity $\langle v\rangle_{eq}$ at long times. Derive from this the expression for the mobility, defined by $\mu = \langle v\rangle_{eq}/E$. Show that the diffusion constant and the mobility are related by the Einstein relation,

$$\frac{\mu}{D} = \frac{q}{k_B T}.$$

1.2 Smoluchowski equation

Consider a discrete asymmetric random walk in time and 1D space, in the presence of an external force. Let the particle perform a random walk, in time increments τ, such that the probability to take a step (of size Δ) depends on the position $x = n\Delta$. The probability to make a step to the right is $r(n\Delta) = \frac{1}{2} + \Delta\alpha(n\Delta)$, and to the left $\ell(n\Delta) = \frac{1}{2} - \Delta\alpha(n\Delta)$, such that $r + \ell = 1$. Note that the probability depends on the position of the particle x due to the spatially varying force field, described by $\alpha(x)$.

[1] Note that the Langevin equation is not a differential equation in the conventional sense owing to the non-differentiable character of the Langevin force.

Write down a recursion relation for the discrete probability $p(n\Delta, k\tau)$. Take the continuous limit of this recursion relation, keeping $D = \Delta^2/(2\tau)$ constant. This leads to the Smoluchowski equation for the continuous probability distribution $P(x,t)$,

$$\frac{\partial P}{\partial t} = -\frac{1}{m\gamma}\frac{\partial}{\partial x}[F(x)P(x,t)] + D\frac{\partial^2 P}{\partial x^2}.$$

Here, the force is identified with $F(x) = 4Dm\gamma\alpha(x)$.

1.3 Random walk in a molecular chain(*)

Random walks make an appearance in the description of the persistance length of polymers, especially long biological ones.

Consider a polymer that is composed of $N+1$ monomers, such that one end of the chain is held fixed (at the origin), while the other end terminates at the position $\mathbf{r}$. Assume that (a) the inter-monomer distance is a and constant along the chain, and (b) the orientation of the bonds is completely random, i.e., the probability density of the monomer position $\mathbf{r}_i$ given previous monomer position $\mathbf{r}_{i-1}$ is given by

$$P(\mathbf{r}_i|\mathbf{r}_{i-1}) = \frac{1}{4\pi a^2}\delta(|\mathbf{r}_i - \mathbf{r}_{i-1}| - a).$$

Show that the probability density for the end-point position $\mathbf{r}$ of the chain is given by

$$P_N(\mathbf{r}) = \left(\frac{3}{2\pi N a^2}\right)^{3/2} \exp\left(-\frac{3|\mathbf{r}|^2}{2Na^2}\right).$$