"Many particle systems out of equilibrium" Problems, Series 10, 2006-07.

Problem 22. Brownian motion

a) Two variables x and y are distributed according to the bivariate gaussian distribution

$$P(x,y) = \frac{1}{N}\exp -\frac{1}{2}\left[\alpha(x-\langle x\rangle)^2 + 2\beta(x-\langle x\rangle)(y-\langle y\rangle) + \gamma(y-\langle y\rangle)^2\right]. \quad (1)$$

Find expressions for the averages $\langle x^2\rangle$, $\langle y^2\rangle$ and $\langle xy\rangle$.

b) A Brownian particle is described by the Langevin equation. If it starts at position $\boldsymbol{r}_0$ with velocity $\boldsymbol{u}_0$, show that its position $\boldsymbol{r}$ and velocity $\boldsymbol{u}$ at time t satisfy the fluctuation equations

$$\langle(\boldsymbol{u}-\boldsymbol{u}_0)(\boldsymbol{u}-\boldsymbol{u}_0)\rangle - \langle(\boldsymbol{u}-\boldsymbol{u}_0)\rangle\langle(\boldsymbol{u}-\boldsymbol{u}_0)\rangle = \frac{k_B T}{M}\mathbf{1}[1-\exp(-2\zeta t)] \quad (2)$$

$$\langle(\boldsymbol{r}-\boldsymbol{r}_0)(\boldsymbol{r}-\boldsymbol{r}_0)\rangle - \langle(\boldsymbol{r}-\boldsymbol{r}_0)\rangle\langle(\boldsymbol{r}-\boldsymbol{r}_0)\rangle = \frac{2k_B T}{M\zeta}\mathbf{1}\left[t-t_0-\frac{2}{\zeta}(1-\exp(-\zeta(t-t_0))+ \frac{1}{2\zeta}(1-\exp -2\zeta(t-t_0)\right] \quad (3)$$

$$\langle(\boldsymbol{u}-\boldsymbol{u}_0)(\boldsymbol{r}-\boldsymbol{r}_0)\rangle - \langle(\boldsymbol{u}-\boldsymbol{u}_0)\rangle\langle(\boldsymbol{r}-\boldsymbol{r}_0)\rangle = \frac{k_B T}{M\zeta}\mathbf{1}\left[1-\exp -\zeta(t-t_0)\right]^2 \quad (4)$$

c) Find the joint distribution for the variables $\boldsymbol{r}$ and $\boldsymbol{u}$, at time t, for given $\boldsymbol{r}_0$ and $\boldsymbol{u}_0$.

d) Under what condition are also the distributions of $\boldsymbol{r}-\boldsymbol{r}_0$ and $\boldsymbol{u}$, averaged over the initial velocity, gaussian? How does the mean square displacement including this average differ from the mean square displacement with fixed initial velocity?

e) How does the mean square displacement behave for very short times? What is the persistence time, i.e. the characteristic time for the decay of the initial velocity? The persistence length $l_p(|\boldsymbol{u}_0|)$ is defined as the total average displacement from the initial position at fixed initial velocity. How does it depend on the initial speed u_0? Show that the diffusion coefficient may be expressed as

$$D = \frac{1}{d}\langle u l_p(u)\rangle. \quad (5)$$

Make an estimate how the persistence length of a colloidal particle in water at room temperature (shear viscosity $\sim 1\, mPa$) depends on its radius. How long is it about for a typical radius of 1 micron?

Problem 23. Diffusion equation with time dependent diffusion coefficient

When the displacement $\boldsymbol{r}$ of a tagged particle from its initial position satisfies a Gaussian distribution, with zero mean and second moment $\langle \boldsymbol{r}^2(t)\rangle$, show that its distribution satisfies the generalized diffusion equation

$$\frac{\partial P(\boldsymbol{r},t)}{\partial t} = D(t)\nabla^2 P(\boldsymbol{r},t), \tag{6}$$

with

$$D(t) = \frac{1}{2d}\frac{\partial\langle \boldsymbol{r}^2(t)\rangle}{\partial t}. \tag{7}$$

This may be turned around: suppose the Fourier transform of the distribution $P(\boldsymbol{r},t)$ satisfies the equation

$$\frac{\partial P(\boldsymbol{k},t)}{\partial t} = -D(t)k^2 P(\boldsymbol{k},t), \tag{8}$$

with $D(t)$ independent of k. It then follows that $P(\boldsymbol{r},t)$ is gaussian (so the Fourier transform of a gaussian is a gaussian!, as is well-known from wave packets in quantum mechanics). Going back to the definition of the frequency and wave number dependent diffusion coefficient, one may identify some plausible conditions under which this is satified for small k and large t. Remember that $C(\boldsymbol{k},t)$ is defined as

$$C(\boldsymbol{k},t) = \frac{1}{d}\langle \boldsymbol{v}\cdot\boldsymbol{v}(t)\exp(-i\boldsymbol{k}\cdot[\boldsymbol{r}(t)-\boldsymbol{r}(0)])\rangle. \tag{9}$$

Now assume that the velocity correlation is independent for large t of the displacement $\boldsymbol{r}(t)-\boldsymbol{r}(0)$. Assume also (to be confirmed a posteriori) that the distribution for this diplacement is a gaussian. Then we have

$$C(\boldsymbol{k},t) = C(t)\exp(-\frac{1}{2d}k^2\langle|\boldsymbol{r}(t)-\boldsymbol{r}(0)|^2\rangle), \tag{10}$$

with $C(t)$ $1/d$ times the velocity autocorrelation function. Assume that for long times

$$C(t) \approx ct^{\alpha-2}, \tag{11}$$

hence

$$\langle|\boldsymbol{r}(t)-\boldsymbol{r}(0)|^2\rangle \approx \frac{2dc}{\alpha(\alpha-1)}t^{\alpha}. \tag{12}$$

Next consider the Laplace transform of C, which satisfies

$$C(\boldsymbol{k}, z) = \int_0^\infty d\,t\, \exp(-zt) C(t) \exp(-\frac{1}{2d} k^2 \langle |\boldsymbol{r}(t) - \boldsymbol{r}(0)|^2 \rangle). \tag{13}$$

One may distinguish two basic ranges for the variables $\boldsymbol{k}, z$, namely $k^2\langle|\boldsymbol{r}(1/z) - \boldsymbol{r}(0)|^2\rangle \ll 1$ and $k^2\langle|\boldsymbol{r}(1/z) - \boldsymbol{r}(0)|^2\rangle \gg 1$.
Show that in the former range $C(\boldsymbol{k}, z) \approx C(z)$ and in the latter $C(\boldsymbol{k}, z) \approx C(\boldsymbol{k}, 0)$. Next show, with the aid of (11) and (12), that as a consequence of this, in the former range $U(\boldsymbol{k}, z) \approx C(z)$ and in the latter $U(\boldsymbol{k}, z) \approx 0$. Hence $U(\boldsymbol{k}, z)$, and consequently $D(\boldsymbol{k}, t)$, is basically independent of $\boldsymbol{k}$.

A specific case for which the factorization property (10) can be shown explicitly, is the model of single file diffusion treated in problem (16). See for example: H. van Beijeren, K. W. Kehr and R. Kutner, *Diffusion in concentrated lattice gases III, Tracer diffusion on a one-dimensional lattice*, Physical Review **B28** (1983) 5711-5723.