Ex8027: Brownian motion of a diatomic particle

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The problem:

Consider the 1D motion of two beads of mass m, attached by a very flexible spring with constant k (the length of the spring at rest is much smaller than the fluctuations caused by random forces).The beads are immersed in viscous liquid with friction coefficients γ_1, γ_2 and temperature T. Disregard the hydrodynamic interactions between the beads and the direct collisions of the beads.

(1) Write down Langevin equations for the beads. Neglect accelerations.

(2) For $\gamma_1 = \gamma_2 \equiv \gamma$, Define $R = \frac{x_1+x_2}{2}$, $r = x_1 - x_2$ and find $\langle (r(t) - r_0)^2 \rangle$ and $\langle (R(t) - R_0)^2 \rangle$ (where r_0 is half the initial distance between the "atoms" and R_0 is the initial location of the "molecule").

(3) Solve the equations for $\gamma_1 \neq \gamma_2$ and show that the same solution as in (2) is obtained by setting $\gamma_1 = \gamma_2 \equiv \gamma$.

(4) Generalize the results to 3D.

The solution:

(1) The equations of motion:

$$\begin{cases} m\ddot{x}_1 = -k(x_1 - x_2) - \gamma_1 \dot{x}_1 + F_1(t) \\ m\ddot{x}_2 = k(x_1 - x_2) - \gamma_2 \dot{x}_2 + F_2(t) \end{cases} \tag{1}$$

Where x_i is the displacement of the ith bead, and $F_i(t)$ is the random force acting on the ith bead at time t. The correlation of the random forces is:

$$\langle F_i(t) F_j(t') \rangle = 2\gamma_i T \delta_{ij} \delta(t - t') \tag{2}$$

Neglecting the acceleration term and defining $f_i = \frac{1}{\gamma_i} F_i$, $\alpha_i = \frac{k}{\gamma_i}$ we get:

$$\begin{cases} \dot{x}_1 = -\alpha_1 (x_1 - x_2) + f_1(t) \\ \dot{x}_2 = \alpha_2 (x_1 - x_2) + f_2(t) \end{cases} \tag{3}$$

(2) The Langevin eqs. are coupled so we move to the coordinates of the center of mass $r_{c.m} \equiv R$ and relative motion $r_{rel} \equiv r$:

$$\begin{cases} R = \frac{x_1+x_2}{2} \\ r = x_1 - x_2 \end{cases} \Rightarrow \begin{cases} x_1 = R + \frac{1}{2} r \\ x_2 = R - \frac{1}{2} r \end{cases} \tag{4}$$

Substituting (4) into eqs. (3) gives:

$$\dot{R} + \frac{1}{2}\dot{r} = -\alpha r + f_1(t) \tag{5}$$

$$\dot{R} - \frac{1}{2}\dot{r} = \alpha r + f_2(t) \tag{6}$$

Adding (5) and (6) gives a Langevin type eq. for the center of mass:

$$\dot{R} = \frac{1}{2}\left[f_1(t) + f_2(t) \right] \tag{7}$$

which is the same as the Langevin eq. for a Brownian particle.
Taking the same step as done in class, we get:

$$\langle \Delta R^2(t) \rangle = \frac{T}{\gamma} \cdot t = 2(\frac{D}{2})t \tag{8}$$

Where D is the diffusion coefficient for Brownian particle. We see that the center of mass diffuses half as quickly as one free bead, which makes sense, since effectively the drag is twice as big.
Now for the relative motion. Subtracting (6) from (5) we get:

$$\dot{r} = -2\alpha r + \Big[f_1(t) - f_2(t)\Big] \equiv -2\alpha r + \phi(t) \tag{9}$$

To solve the differential eqn., lets make the substitution $\{r = ye^{-2\alpha t} \Rightarrow \dot{r} = \dot{y}e^{-2\alpha t} - 2\alpha y e^{-2\alpha t}\}$ to get:

$$\dot{y}e^{-2\alpha t} - 2\alpha y e^{-2\alpha t} = -2\alpha y e^{-2\alpha t} + \phi(t) \Rightarrow \dot{y} = \phi(t)e^{2\alpha t}$$

$$\dot{y}(t) = \dot{y}(0) + \int_0^t dt'\phi(t')e^{2\alpha t'}$$

Going back to r:

$$r(t) = r_0 e^{-2\alpha(t)} + \int_0^t dt'\phi(t')e^{-2\alpha(t-t')} \tag{10}$$

So:

$$\langle \Delta r^2(t) \rangle = \langle (r - r_0)^2 \rangle = \langle \Big[r_0(e^{-2\alpha t} - 1) + \int_0^t dt'\phi(t')e^{-2\alpha(t-t')}\Big]^2 \rangle$$

$$\langle \Delta r^2(t) \rangle = r_0^2(e^{-2\alpha t}-1)^2 + 2(e^{-2\alpha t}-1)\int_0^t dt'\langle r_0\phi(t')\rangle e^{-2\alpha(t-t')} + \int_0^t\int_0^t dt'dt''\langle \phi(t')\phi(t'')\rangle e^{-2\alpha(2t-t'-t'')}$$

The initial relative displacement and the random forces on the beads at some future time $t' > 0$ are obviously uncorrelated, so the middle term vanishes. Substituting ϕ and α back into the eqn. we get:

$$\langle \Delta r^2(t) \rangle = r_0^2(e^{-2\alpha t} - 1)^2 + \frac{1}{\gamma^2}\int_0^t\int_0^t dt'dt''\langle \big[F_1(t') - F_2(t')\big]\big[F_1(t'') - F_2(t'')\big]\rangle e^{-2\alpha(2t-t'-t'')}$$

$$\langle \Delta r^2(t) \rangle = r_0^2(e^{-2\alpha t}-1)^2 + \frac{4T}{\gamma}\int_0^t\int_0^t dt'dt''\delta(t'-t'')e^{-2\alpha(2t-t'-t'')} = r_0^2(e^{-2\alpha t}-1)^2 + \frac{4T}{\gamma}\int_0^t dt'e^{-2\alpha(2t-2t')}$$

$$\langle \Delta r^2(t) \rangle = r_0^2(e^{-2\alpha t} - 1)^2 + \frac{T}{\alpha\gamma}e^{-4\alpha t}(e^{4\alpha t} - 1) = r_0^2(e^{-\frac{2kt}{\gamma}} - 1)^2 + \frac{T}{k}(1 - e^{-\frac{4kt}{\gamma}}) \tag{11}$$

Looking at Eq(10) we see that it is the sum of noise-free solution that depends on r_0 and a second "random walk" stochastic component (integrating the noise over duration t). Therefore the expression for the spreading in Eq(11) is the sum of two terms: a noise-free solution that depends on r_0, and a second term which is the same as for "random walk", namely $2[C(0) - C(t)]$, where C is the correlation function of r (formally identical to C_{vv} whose calculation has been worked out in the lecture).

(3) Again the Langevin eqs. are:

$$\begin{cases} \dot{x}_1 = -\alpha_1(x_1 - x_2) + f_1(t) \\ \dot{x}_2 = \alpha_2(x_1 - x_2) + f_2(t) \end{cases} \tag{12}$$

Or in matrix notation:

$$\frac{d}{dt}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = M \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} + \begin{pmatrix} f_1 \\ f_2 \end{pmatrix} \tag{13}$$

Where

$$M = \begin{pmatrix} -\alpha_1 & \alpha_1 \\ \alpha_2 & -\alpha_2 \end{pmatrix} \tag{14}$$

To de-couple the eqs., we must move to the basis of the modes of motion - $\begin{pmatrix} \xi_1 \\ \xi_2 \end{pmatrix}$. We diagonalize M so $M = UDU^{-1}$:

$$D = \begin{pmatrix} 0 & 0 \\ 0 & -(\alpha_1+\alpha_2) \end{pmatrix} \quad U = \begin{pmatrix} 1 & 1 \\ 1 & -\frac{\gamma_1}{\gamma_2} \end{pmatrix} \quad U^{-1} = \begin{pmatrix} \frac{\gamma_1}{\gamma_1+\gamma_2} & \frac{\gamma_2}{\gamma_1+\gamma_2} \\ \frac{\gamma_2}{\gamma_1+\gamma_2} & \frac{-\gamma_2}{\gamma_1+\gamma_2} \end{pmatrix}$$

The transformation matrix U takes us to the new basis: $\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = U \begin{pmatrix} \xi_1 \\ \xi_2 \end{pmatrix}$. We can see that ξ_1 is the coordinate of the center of mass up to a factor, and ξ_2 plays the part of the *effective* relative motion.
So now eq. (13) becomes:

$$\frac{d}{dt}U\begin{pmatrix} \xi_1 \\ \xi_2 \end{pmatrix} = MU\begin{pmatrix} \xi_1 \\ \xi_2 \end{pmatrix} + \begin{pmatrix} f_1 \\ f_2 \end{pmatrix} \Rightarrow U^{-1}U\frac{d}{dt}\begin{pmatrix} \xi_1 \\ \xi_2 \end{pmatrix} = U^{-1}MU\begin{pmatrix} \xi_1 \\ \xi_2 \end{pmatrix} + U^{-1}\begin{pmatrix} f_1 \\ f_2 \end{pmatrix}$$

$$\frac{d}{dt}\begin{pmatrix} \xi_1 \\ \xi_2 \end{pmatrix} = D\begin{pmatrix} \xi_1 \\ \xi_2 \end{pmatrix} + U^{-1}\begin{pmatrix} f_1 \\ f_2 \end{pmatrix} \tag{15}$$

So with plugging $\alpha_{1,2}$ back in, we arrive at the eqs:

$$\begin{cases} \dot{\xi}_1 = \frac{1}{\gamma_1+\gamma_2}(F_1+F_2) \\ \dot{\xi}_2 = -k\left(\frac{1}{\gamma_1}+\frac{1}{\gamma_2}\right)\xi_2 + \frac{1}{\gamma_1+\gamma_2}\left(\frac{\gamma_2}{\gamma_1}F_1 - F_2\right) \end{cases} \tag{16}$$

Indeed we see that for $\gamma_1 = \gamma_2 = \gamma$ we get eqs. (7) and (9) from the previous section up to a factor of $\frac{1}{2}$, which can be mended with multiplying one of the eigenvectors by 2.
The solution for the center of mass is exactly the same as before (with the appropriate factor change):

$$\langle \Delta\xi_1^2(t)\rangle = \frac{2T}{\gamma_1+\gamma_2}\cdot t \tag{17}$$

With the relative motion we need to be a bit more careful because of the factor in front of F_1. We can apply the same method of solution to finally get:

$$\langle \Delta\xi_2^2(t)\rangle = \xi_2^2(0)\left(e^{-k\left(\frac{1}{\gamma_1}+\frac{1}{\gamma_2}\right)t} - 1\right)^2 + \frac{2T}{k\left(\frac{\gamma_1}{\gamma_2}+1\right)^3}\left(1 - e^{-2k\left(\frac{1}{\gamma_1}+\frac{1}{\gamma_2}\right)t}\right) \tag{18}$$

Again we see that for $\gamma_1 = \gamma_2 = \gamma$ we get the same results as in the previous section up to a factor of $\frac{1}{4}$ which can be fixed as explained before.

(4) Generalizing this result to 3D is simple enough- Since the forces in different directions are independent of each other, we would simply get the same answer as in section (3) for each direction separately. So:

$$\langle \Delta\vec{\xi}_1^2(t)\rangle = \langle \Delta\xi_{1_x}^2(t)\rangle + \langle \Delta\xi_{1_y}^2(t)\rangle + \langle \Delta\xi_{1_z}^2(t)\rangle = \frac{6T}{\gamma_1+\gamma_2}\cdot t \tag{19}$$

$$\langle \Delta\vec{\xi}_2^2(t)\rangle = \vec{\xi}_2^2(0)\left(e^{-k\left(\frac{1}{\gamma_1}+\frac{1}{\gamma_2}\right)t} - 1\right)^2 + \frac{6T}{k\left(\frac{\gamma_1}{\gamma_2}+1\right)^3}\left(1 - e^{-2k\left(\frac{1}{\gamma_1}+\frac{1}{\gamma_2}\right)t}\right) \tag{20}$$