Chemistry 276 - AUTUMN 2009-10 - Advanced Physical Chemistry

Problem Set 2 (due 10/8/09 in class)

Langevin equation for a harmonically bound particle (*part 1*)

The Langevin equation was originally developed to describe the dynamics of a large heavy particle suspended in a fluid of much smaller lighter molecules. In fact, it has been used not only for this purpose but also to describe the dynamics of molecules (or even of individual degrees of freedom of one molecule) that are not much larger or heavier than their surroundings.

This problem set is concerned with the simple problem of a Brownian particle in a harmonic potential. Essentially this is a classical harmonic oscillator that is subject to a combination of systematic and random forces from the environment. This type of models and its generalizations are widely used in physics and chemistry.

A. Harmonically bound particle with no other applied field. Consider a one dimensional oscillator of mass m whose coordinate is x and whose velocity is v. Thus $v = \dot{x}$. Suppose it is subject to a harmonic potential energy of the form $V(x) = kx^2/2$, where k is the force constant of the oscillator. (We will later need Boltzmann's constant. Let's use the symbol k_B for Boltzmann's constant. Don't confuse these two uses of the symbol k.)

If there were no solvent or other environment of the oscillator, its equation of motion would be

$$m\dot{v}(t) = -kx(t)$$

However, because of the solvent or environment, there is an additional systematic frictional force and a random force $R(t)$.

$$m\dot{v}(t) = -kx(t) - \zeta v(t) + R(t)$$

As in the case discussed in class, we make the following assumptions about the random force.

$$\langle R(t) \rangle = 0$$

$$\langle R(t)v(0) \rangle = 0$$

$$\langle R(t)R(t') \rangle = R_0 \delta(t - t')$$

In the present problem, there is a natural origin for the coordinate system, unlike the situation discussed in class. Thus, we should make some assumptions about how, if at all, the random force is correlated with the position of the particle. Let's assume that $\mathbf{R}(t)$ is uncorrelated with the initial position and that hence

$$\langle R(t)x(0)\rangle = 0.$$

Assume that $\zeta << (k/m)^{1/2}$. This corresponds to assuming that the oscillator is weakly damped rather than overdamped.

In class we derived a relationship between ζ and R_0. That relationship was obtained for a free particle, not a harmonically bound particle. Let us assume that the same relationship holds in the present case. That will guarantee that the theory we are constructing is valid for $k = 0$. (In fact, this assumption also gives us a consistent theory for the case of $k \neq 0$.)

This system is in thermodynamic equilibrium. The probability distribution function of the x and v at time 0 is proportional to

$$P(x, v; 0) \propto \exp\left(-\left(\frac{1}{2}mv^2 + \frac{1}{2}kx^2\right)/k_BT\right)$$

1. Calculate the normalization constant for this distribution function and obtain a complete expression for the distribution function.

2. Calculate the following static correlation functions for the initial time ($t = 0$):

   (a) $\langle x(0)\rangle$

   (b) $\langle x(0)^2\rangle$

   (c) $\langle v(0)\rangle$

   (d) $\langle v^2(0)\rangle$

   (e) $\langle x(0)v(0)\rangle$.

   If we have a consistent theory of the dynamics, we would expect that $\langle x(t)\rangle$, $\langle x(t)^2\rangle$, $\langle v(t)\rangle$, $\langle v^2(t)\rangle$, and $\langle x(t)v(t)\rangle$ for $t > 0$ are all equal to their $t = 0$ values.

3. $x(0)$ and $v(0)$ are random variables. Are they statistically independent?

4. Calculate the following time correlation functions. In each case, give a physical reason for the sign of the answer.[1]

   (a) $\langle x(t)x(0)\rangle$

   (b) $\langle x(t)v(0)\rangle$

[1] The most straightforward way to obtain the first correlation function is to obtain a differential equation for the correlation function and then solve the differential equation. The relevant differential equation is that for a damped harmonic oscillator, and it is second order in time. One way to solve the equation is first to find solutions that are exponentially dependent on time. The most general solution of the second order equation is a sum of two such exponentials. Find the linear combination of exponential solutions that matches the initial values of the position and velocity and that satisfies the differential equation. That will be the unique solution of the differential equation that satisfies the initial conditions.