Homework 7: Time-dependent processes

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1. *Dynamics of Chemical Reactions*. In class, we had these equations for the equilibrium dynamics of the deviation from equilibrium:

$$\frac{dC}{dt} = -(k_f + k_b)C + \delta F(t) \tag{1}$$

$$\langle \delta F(t) \delta F(t') \rangle = 2B\delta(t - t') \tag{2}$$

   Follow the procedure used to find B for the velocity-velocity correlation functions to show that in this case, $B = (k_f + k_b)\langle C^2 \rangle_{eq}$.

2. The optical absorption coefficient in spectroscopy is related to the dipole-dipole correlation coefficient. Using Fermi's Golden Rule, the following formula can be obtained, for the absorption coefficient α at frequency ω:

$$\alpha(\omega) = \frac{2\pi\omega^2\beta}{3nc} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle. \tag{3}$$

   Here, c is the speed of light, n is the index of refraction, and $\mathbf{M}$ is the total electric dipole moment.

   In the case where our molecule is a rigid dipole, then $\mathbf{M}$ is its permanent dipole moment of magnitude μ, and

$$\langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle = \mu^2 \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle. \tag{4}$$

   Here, $\mathbf{u}$ is the molecular orientation vector.

   Suppose we consider the molecule to be restricted in 2-d for simplicity. Then $\mathbf{u}(t) = (\cos(\theta(t)), \sin(\theta(t))) = e^{i\theta}$. This means

$$\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle = \langle e^{-i\theta(0)} e^{i\theta(t)} \rangle \tag{5}$$

We can write a set of Langevin equations for the angle, which look like the following, where I is the moment of inertia of the molecule:

$$\frac{d\Delta\theta}{dt} = \Omega \tag{6}$$

$$\frac{Id\Omega}{dt} = -\zeta\Omega + \delta F(t) \tag{7}$$

$$\langle \delta F(t)\delta F(t')\rangle = 2\zeta k_B T\delta(t-t') \tag{8}$$

(a) Show that (analogous to mean squared displacement of a Brownian particle)

$$\langle \Delta\theta(t)^2\rangle_{eq} = 2\frac{k_B T}{\zeta}\left(t - \frac{I}{\zeta} + \frac{I}{\zeta}e^{-\zeta t/I}\right) \tag{9}$$

(b) The orientational time correlation function is

$$C(t) = \langle e^{-i\theta(0)}e^{i\theta(t)}\rangle_{eq} = \langle e^{i\Delta\theta(t)}\rangle_{eq} \tag{10}$$

$\Delta\theta(t)$ should be sampled from a Gaussian with mean $\mu = 0$ zero. Use the following useful result for Gaussian distributions with $\langle x\rangle = \mu$:

$$\langle e^{iax}\rangle = e^{(ia\mu - \frac{a^2}{2}\langle (x-\mu)^2\rangle)}, \tag{11}$$

to show that:

$$C(t) = e^{-\frac{1}{2}\langle \Delta\theta(t)^2\rangle_{eq}} \tag{12}$$

And use a preceding result to show that at long times

$$C(t) \to e^{-\frac{k_B T}{\zeta}t} \tag{13}$$