22.903 Home Work Set No. 1 (Professor Sow-Hsin Chen) Spring Term 2005. Due March 7, 2005

1. This problem concerns calculations of analytical expressions for the self-intermediate scattering function (ISF) of the test particle in a liquid which captures both the short-time and the long-time behavior of the function correctly.

   In the classical limit the self-ISF in the Gaussian approximation is given by

   $$F_s(Q,t) = \left\langle e^{iQ[X(t)-X(0)]} \right\rangle = \left\langle e^{iQ\Delta X(t)} \right\rangle = e^{-\frac{1}{2}Q^2\left\langle (\Delta X(t))^2 \right\rangle} = e^{-\frac{1}{2}Q^2 W(t)} \qquad (1)$$

   where the width function W(t) is defined by

   $$W(t) = \left\langle (\Delta X(t))^2 \right\rangle = \int_0^t dt_1 \int_0^t dt_2 \left\langle V_x(t_1)V_x(t_2) \right\rangle = 2\int_0^t dt'(t-t')\left\langle V_x(0)V_x(t') \right\rangle. \qquad (2)$$

   (a) Show that Eq.(2) is valid when the velocity auto-correlation function $\left\langle V_x(t_1)V_x(t_2) \right\rangle$ depends only on the time difference t' = t$_1$- t$_2$, such as in a steady state.

   (b) Define the normalized velocity auto-correlation function

   $$\psi(t) = \frac{\left\langle V_x(0)V_x(t) \right\rangle}{\left\langle V_x^2 \right\rangle}, \quad \text{where} \quad \left\langle V_x^2 \right\rangle = V_0^2 = \frac{k_B T}{M} \qquad (3)$$

   and its Fourier transform (the density of states function)

   $$\psi(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} \psi(t) = \frac{1}{\pi} \int_0^{\infty} dt \cos \omega t \, \psi(t). \qquad (4)$$

   Show that (by using Eq.(2) and Eq.(4)) the width function can be written as

   $$W(t) = 4V_0^2 \int_0^{\infty} d\omega \frac{1-\cos\omega t}{\omega^2} \psi(\omega). \qquad (5)$$

   (c) Show that if the velocity of the test particle satisfies the Langevin equation, then the normalized velocity auto-correlation function is given by

   $$\psi(t) = e^{-\frac{t}{\tau}}. \qquad (6)$$

Calculate the width function W(t) and give its short-time and long-time limits. Relate the relaxation time τ to the friction constant of the test particle in the liquid. Give also the density of states function in this case.

(d) By examining long time behavior of the width function, derive the general relationships between the diffusion constant D of the test particle and the normalized velocity auto-correlation function $\psi(t)$. Give also the relation between D and the density of states function $\psi(\omega)$.

(e) The Brownian particle model given above is a one-parameter model in which the parameter is the relaxation time τ. It gives the short time and the long time limits of the self-ISF correctly. One can formulate a more advanced model, call the relaxing cage model of Desai and Yip (Physical Review **166**, 129 (1968)). This model is a two-parameter model in which the density of states function is modeled as

$$\psi(\omega) = \frac{2}{\pi} \frac{\omega_0^2 / \tau_0}{\left(\omega^2 - \omega_0^2\right)^2 + \left(\omega / \tau_0\right)^2}. \tag{7}$$

Show that the normalized velocity auto-correlation function is given by

$$\psi(t) = \int_0^\infty d\omega \cos \omega t\, \psi(\omega) = e^{-\frac{t}{2\tau_0}}\left[\cos \Omega t + \frac{1}{2\tau_0 \Omega} \sin \Omega t\right] \tag{8}$$

where $\Omega^2 = \omega_0^2 - \frac{1}{4\tau_0^2}$.

(f) Give the expression of the width-function. Check its short-time and long-time behavior. You shall find that this model describes the motion of the test particle as a vibrational one with a characteristic frequency ω_0 at short time, and a diffusional one with a frictional coefficient $\omega_0^2 \tau_0$ at long time. In terms of a typical atom in a liquid, the picture corresponds to putting the atom in an external parabolic potential well which relaxes in time so that eventually the atom diffuses away experiences only the frictional force. Thus it is appropriate to call it a relaxing cage model.

2. The objective of this problem is to calculate the total cross section of scattering of cold neutrons from hydrogen molecules in gas phase where inter-molecular correlation effect can be neglected.

(a) If we denote the neutron and nuclear spin operators respectively by $\hat{s}$ and $\hat{i}$, the scattering length operator $\hat{b}$ can be written as:

$$\hat{b} = A + B\hat{s} \cdot \hat{i} \tag{9}$$

where A and B are constants to be determined. Now denote the total spin operator (sum of the neutron and nuclear spins) by $\hat{t} = \hat{s} + \hat{i}$, and noting the operator relationship

$$\hat{s} \cdot \hat{i} = \frac{1}{2}\left(\hat{t}^2 - \hat{i}^2 - \hat{s}^2\right) \ , \tag{10}$$

which has an eigen value of

$$\frac{1}{2}[t(t+1) - i(i+1) - s(s+1)] = \frac{1}{2}\left[t(t+1) - i(i+1) - \frac{3}{4}\right].$$

By demanding that the $\hat{b}$ operator has an eigen value b_+ when $t = i + \frac{1}{2}$, and an eigen value b_- when $t = i - \frac{1}{2}$, obtain the following values for the two constants:

$$A = \frac{i+1}{2i+1}b_+ + \frac{i}{2i+1}b_- = b_{coh} \quad \text{and} \quad B = \frac{2}{2i+1}\left(b_+ - b_-\right). \tag{11}$$

(b) Now turn our attention to scattering of cold neutrons of wave length 5 A (energy ~ 2 meV) which is larger than the inter-nuclear separation of 0.74 A in a hydrogen molecule. As a result, the spatial interference effect due to the two hydrogen atoms in a molecule can be neglected in the calculation of scattering cross sections. We can calculate the differential scattering cross section by the formula

$$\left(\frac{d\sigma}{d\Omega}\right)^{\lambda}_{\lambda'} = \frac{k'}{k}\left|\left\langle\lambda'\left|\sum_{\xi}\hat{b}_{\xi}\exp(i\vec{Q}\cdot\vec{R}_{\xi})\right|\lambda\right\rangle\right|^2 \tag{12}$$

where λ and λ' denote the initial and the final states of the molecule in the scattering process, and the index ξ runs over 1 and 2 hydrogen atoms in the molecule. Since we can neglect the special correlation due to the finite separation of the two protons in a molecule, the exponential factor in the matrix element can be put equal to unity. In order to get the measured differential scattering cross section, we further sum over the final states λ' in Eq.(12) to obtain

$$\left(\frac{d\sigma}{d\Omega}\right)^{\lambda} = \frac{k'}{k}\langle\lambda|(\hat{b}_1 + \hat{b}_2)^+(\hat{b}_1 + \hat{b}_2)|\lambda\rangle \tag{13}$$

The relevant initial state of the molecule and the neutron is $|\lambda\rangle = |I, m_I\rangle|s, m_s\rangle$, where the first factor represents the total spin state of the molecule, $\hat{I} = \hat{i}_1 + \hat{i}_2$. By using the scattering length operator given in Eq.(9) for the 1 and 2 protons, you can calculate the matrix element in Eq.(13). Show that

$$(\hat{b}_1 + \hat{b}_2)^+(\hat{b}_1 + \hat{b}_2) = (2A + B\hat{s}\cdot I)^2 = 4A^2 + (4AB - \frac{1}{2}B^2)\hat{s}\cdot\hat{I} + \frac{1}{4}B^2\hat{I}^2 \tag{14}$$

(d) In order to obtain the result of Eq.(14), you need to show the operator relation:

$$(\hat{I}\cdot\hat{s})^2 = \frac{1}{4}\hat{I}^2 - \frac{1}{2}\hat{s}\cdot\hat{I} \tag{15}$$

(e) Substitute the result of Eq.(14) into Eq.(13) and calculate the matrix element by assuming an unpolarized incident neutron beam, show that

$$\left(\frac{d\sigma}{d\Omega}\right)_{unpol} = \frac{k'}{k}\left[4A^2 + \frac{1}{4}B^2 I(I+1)\right] \tag{16}$$

(f) There are two kinds of molecular hydrogen. When the two nuclear spins of the two protons are parallel, it is in the ortho-state (I = 1). On the other hand, when the two spins are anti-parallel, it is in the para-state (I = 0). Show that

$$\left(\frac{d\sigma}{d\Omega}\right)_{ortho} = \frac{k'}{k}\left[\frac{1}{4}(3b_+ + b_-)^2 + \frac{1}{2}(b_+ - b_-)^2\right] \tag{17}$$

$$\left(\frac{d\sigma}{d\Omega}\right)_{para} = \frac{k'}{k}\left[\frac{1}{4}(3b_+ + b_-)^2\right] \tag{18}$$

(g) Integrating the above expressions over the solid angle to get the free molecular cross sections, like that is done in the lecture notes, show that

$$\sigma_{ortho} = \frac{4}{9}4\pi\left[\frac{1}{4}(3b_+ + b_-)^2 + \frac{1}{2}(b_+ - b_-)^2\right]$$ (19)

$$\sigma_{para} = \frac{4}{9}4\pi\left[\frac{1}{4}(3b_+ + b_-)^2\right]$$ (20)

Explain how does the factor 4/9 in the above expressions arise.