

## G25.2651: Advanced Statistical Mechanics

### Problem set #6

Due: April 27, 2009

1. The classical isothermal-isobaric ( $NPT$ ) ensemble is particularly useful for determining the *bulk viscosity* of a substance via Green-Kubo theory. Recall the partition function of this ensemble is

$$\Delta(N, \bar{P}, T) = \frac{1}{V_0 N! h^{3N}} \int_0^\infty dV \int d^N \mathbf{p} d^N \mathbf{r} e^{-\beta(H(\mathbf{p}, \mathbf{r}) + PV)}$$

where  $P$  is the external applied pressure.

- a. Show that the linear response formula does not change if the equilibrium distribution is chosen to be  $f_0(H(\mathbf{p}, \mathbf{r}), V)$ , i.e., the isothermal-isobaric distribution function  $\exp(-\beta(H(\mathbf{p}, \mathbf{r}) + PV))/\Delta(N, P, T)$ .
- b. Next, consider coupling a system to an external compression field described by the equations of motion

$$\begin{aligned} \dot{r}_{i,\alpha} &= \frac{p_{i,\alpha}}{m_i} + \sum_{\beta} r_{i,\beta} M_{\beta\alpha} \\ \dot{p}_{i,\alpha} &= F_{i,\alpha} - \sum_{\beta} p_{i,\beta} M_{\beta\alpha} \end{aligned}$$

where  $\alpha$  and  $\beta$  index the three spatial directions,  $x$ ,  $y$ , and  $z$ . Show that the equations of motion satisfy the incompressibility condition.

- c. Consider the specific choice:

$$M_{\alpha\beta} = \frac{1}{3} \gamma \delta_{\alpha\beta}$$

where  $\gamma$  is the compression rate. The coefficient of bulk viscosity,  $\eta_V$  is given by a generalization of Newton's law of viscosity:

$$\langle V \rangle_0 \eta_V = - \lim_{t \rightarrow \infty} \frac{\langle P(t)V(t) \rangle}{\gamma}$$

where  $\langle \dots \rangle_0$  means average over the equilibrium  $NPT$  distribution function and  $\langle \dots \rangle$  is the full nonequilibrium average. Using the linear response formula to evaluate  $\langle P(t)V(t) \rangle$ , derive the appropriate Green-Kubo expression for  $\eta_V$ .

2. The quantum time correlation function corresponding to an absorption process is

$$C_{BB}(t) = \langle B(t)B(0) \rangle = \frac{1}{Q} \text{Tr} \left[ e^{iHt/\hbar} B e^{-iHt/\hbar} B e^{-\beta H} \right]$$

where  $Q$  is the canonical partition function. Consider a more "symmetric" correlation function

$$G_{BB}(t) = \frac{1}{Q} \text{Tr} \left[ B e^{iH\tau^*/\hbar} B e^{-iH\tau/\hbar} \right]$$

where  $\tau = t - i\beta\hbar/2$  is a complex time variable.

- a. Give a relationship between the Fourier transforms  $\tilde{C}_{BB}(\omega)$  and  $\tilde{G}_{BB}(\omega)$ .

b. Assume that the operator  $B$  is a function only of the position operator. Write  $G_{BB}(t)$  as

$$G_{BB}(t) = \frac{1}{Q} \int dx dx' b(x) b(x') \langle x | e^{iH\tau/\hbar} | x' \rangle \langle x' | e^{-iH\tau/\hbar} | x \rangle$$

where  $b(x)$  is the eigenvalue of the operator  $B$ ,  $B|x\rangle = b(x)|x\rangle$ . By deriving path-integral expressions for the two coordinate-space matrix elements in the above expression, show that the correlation function can be written in the form

$$G_{BB}(t) = \lim_{P \rightarrow \infty} \frac{\int dx_1 \cdots dx_{2P} f(x_1, \dots, x_{2P}) e^{i\phi(x_1, \dots, x_{2P})} b(x_1) b(x_{P+1})}{\int dx_1 \cdots dx_{2P} f(x_1, \dots, x_{2P}) e^{i\phi(x_1, \dots, x_{2P})}}$$

where  $f(x_1, \dots, x_{2P})$  is a positive-definite function and  $\phi(x_1, \dots, x_{2P})$  is a phase function. Derive expressions for  $f(x_1, \dots, x_{2P})$  and  $\phi(x_1, \dots, x_{2P})$ .

c. Based on your expression for part b, explain why computing quantum time correlation functions via path-integrals is numerically a highly challenging problem.

3. Consider the free rotational motion of a *rigid heteronuclear* diatomic molecule of (fixed) bond length  $R$  and moment of inertia  $I = \mu R^2$ , where  $\mu$  is the reduced mass, about an axis through its center of mass perpendicular to the internuclear bond axis. The molecule is constrained to rotate in the  $x$ - $y$  plane only. One of the atoms carries a charge  $q$  and the other a charge  $-q$ .

a. Ignoring center of mass motion, write down the Hamiltonian,  $H_0$  for the molecule.

b. Find the eigenvalues and eigenvectors of  $H_0$ .

c. If the molecule is exposed to spatially homogeneous, monochromatic radiation with an electric field  $\mathbf{E}(t)$  given by

$$\mathbf{E}(t) = E_\omega e^{i\omega t} \hat{\mathbf{x}}$$

write down the perturbation Hamiltonian  $H_1$ .

d. Calculate the energy spectrum  $Q(\omega)$  for  $\omega > 0$ . Interpret your results, and in particular, explain how the allowed absorptions and emissions are manifest in your final expression. Plot the absorption part of your spectrum. Where do you expect the peak intensity to occur?

**Hint:** Consider using a convergence factor,  $\exp(-\epsilon|t|)$ , and let  $\epsilon$  to go 0 at the end of the calculation.

e. Based on your results from parts (a)-(d), plot the spectrum 3-dimensional rigid rotor, for which the energy eigenvalues are  $E_{lm} = \hbar^2 l(l+1)/2I$  and  $m = -l, \dots, l$  is the quantum number for the  $z$ -component of angular momentum. Where do you expect the peak intensity to occur in the 3-dimensional case?

4. On the course Web site, at the link

<http://www.nyu.edu/classes/tuckerman/stat.mechII/psets.html>

there is a link to a molecular dynamics trajectory of a system of 32 deuterated water molecules in a periodic box of length 9.86 Å. The trajectory is the numerical solution of Hamilton's equations of motion for 60,000 time steps, each of length 0.1 fs. From the trajectory, calculate the mean-square displacement as a function of time and, using the Einstein relation, calculate the diffusion constant. Compare your result to the experimental value 0.186 Å<sup>2</sup>/ps. You will need the following information about the trajectory:

i. Each line of the file contains the  $x$ ,  $y$ , and  $z$  coordinates of an atom in units of Bohr. Thus, you will need the conversion factor 0.529177 Å/Bohr.

- ii. The first line of the file holds the position of the oxygen atom of molecule 1, lines 2 and 3 hold the positions of the two hydrogens of molecule 1. Line 4 holds the oxygen atom of molecule 2, lines 5 and 6 hold the positions of the two hydrogens of molecule 2, etc. After the coordinates of the 32 water molecules, each configuration also contains three additional lines corresponding to the box matrix of the system.
- iii. The mean-square displacement you should compute is that of the molecular centers of mass. However, there is an overall drift of the center of mass of the entire system that is not physical and needs to be removed. To do this, compute the system center of mass at each time step and subtract it from each atomic position before you compute the mean-square displacement.
- iv. Use linear regression to fit the long-time part behavior of your mean-square displacement to a line and use the slope to obtain the diffusion constant.

In order to receive full credit, you must turn in both your plot of the mean-square displacement, your prediction of the diffusion constant, and a printout of the program you write to calculate these two quantities.