CHM1485: Molecular Dynamics and Chemical Dynamics in Liquids

PROBLEM SET 1

Notes:

- This set contains 5 problems.
- Please start each problem on a new page and write your name on top of that page.
- This first set is special and meant to refresh your memory. The due date is therefore *in one week*, i.e. Tuesday October 4, 2005.

1 Properties of the Liouville Operator

Consider a general N particle system in a periodic cubic box of size $L \times L \times L$, with a Hamiltonian which does not depend on time explicitly:

$$H(\mathbf{x}^{(N)}) = \frac{\mathbf{p}^{(N)} \cdot \mathbf{p}^{(N)}}{2m} + U(\mathbf{r}^{(N)})$$

where

$$U(\mathbf{r}^{(N)}) = \frac{1}{2} \sum_{i \neq j} U(|\mathbf{r}_i - \mathbf{r}_j|).$$

a. Give the equations of motion in terms of the Hamiltonian. Show that they can be rewritten in the form

$$\begin{aligned} \frac{d\mathbf{x}^{(N)}}{dt} &= \{\mathbf{x}^{(N)}, H\} \\ &= \mathcal{L}\,\mathbf{x}^{(N)}. \end{aligned}$$

where $\{,\}$ are Poisson brackets and $\mathcal{L}$ is the Liouville operator.

b. Show that $\mathbf{P} = \sum_{i=1}^{N} \mathbf{p}_i$ is a constant of the motion.

c. Given functions of phase space $A(\mathbf{x}^{(N)})$, $B(\mathbf{x}^{(N)})$, $C(\mathbf{x}^{(N)})$, prove the following properties of the Poisson brackets:

$$\begin{aligned} \{AB, C\} &= A\{B, C\} + B\{A, C\} \\ \{A, F(B)\} &= \frac{dF}{dB}\{A, B\}, \end{aligned}$$

where $F(B)$ is a function of B that only depends on the phase coordinate $\mathbf{x}^{(N)}$ through B.

d. Prove that

$$\mathcal{L}\,(AB) = A\,\mathcal{L}\,B + B\,\mathcal{L}\,A.$$

e. Show that

$$e^{t\mathcal{L}}(AB) = \left(e^{t\mathcal{L}}A\right)\left(e^{t\mathcal{L}}B\right).$$

f. Show that

$$\langle A(t+\tau)B(\tau)\rangle = \langle A(t)B(0)\rangle$$

where $\langle\cdots\rangle$ is the canonical ensemble average.

g. Show that the Fourier transform of the density $A(\mathbf{r}) = \sum_{i=1}^{N} a_i\delta(\mathbf{r}-\mathbf{r}_i)$, where a_i is some microscopic function of $\mathbf{x}_i$, is equal to

$$A_{\mathbf{k}} = \sum_{i=1}^{N} a_i\, e^{i\mathbf{k}\cdot\mathbf{r}_i}.$$

What are the restrictions on the wave vectors $\mathbf{k}$ for the periodic system?

h. Prove that given two wave vectors $\mathbf{k}$ and $\mathbf{q}$, one has

$$\begin{aligned}\langle A_{\mathbf{k}}(t)A_{\mathbf{q}}\rangle &= \delta_{\mathbf{k},-\mathbf{q}}\langle A_{\mathbf{k}}(t)A_{-\mathbf{k}}\rangle \\ &= \delta_{\mathbf{k},-\mathbf{q}}\langle A_{\mathbf{k}}(t)A^*_{\mathbf{k}}\rangle,\end{aligned}$$

where $\delta_{\mathbf{k},\mathbf{q}}$ is the Kronecker delta symbol.

2 Isotropy

For an infinite isotropic system, show that given an arbitrary scalar function $A(\mathbf{r})$ which is a function of $|\mathbf{r}|$ only, the following statements are true:

a. $\displaystyle\int_V d\mathbf{r}\; A(\mathbf{r})\,\mathbf{r} \;=\; 0,$

b. $\displaystyle\int_V d\mathbf{r}\; A(\mathbf{r})\,\mathbf{r}\,\mathbf{r} \;=\; \tfrac{1}{3}\int_V d\mathbf{r}\,A(\mathbf{r})\,|\mathbf{r}|^2\,\mathbb{1},$
where $\mathbb{1}$ is the identity matrix.

3 Ergodicity

For a single one-dimensional harmonic oscillator with mass m and frequency ω, the Hamiltonian is given by

$$H(x,p) = \frac{p^2}{2m} + \frac{m\omega^2x^2}{2}.$$

a. Derive the equations of motion.

b. Give the general solution for $x(t)$ and $p(t)$ and show that they are periodic. What is the period τ?

Consider this system in the micro-canonical ensemble, giving equal weight to all configurations with $E < H(x,p) < E + \delta E$, so that the probability distribution in phase space is

$$f(x,p) = \begin{cases} \dfrac{1}{\Omega} & \text{if } E < H(x,p) < E + \delta E \\ \\ 0 & \text{otherwise.} \end{cases}$$

c. How does the fact that $f(x,p)$ is a probability distribution determine the value of Ω? Show that its value is given by $\Omega = \tau \delta E$.
Hint: change variables to $\xi = r\sqrt{m\omega^2/2}$ *and* $\eta = p/\sqrt{2m}$.

d. Using the solution of the equations of motion, show that in the limit $\delta E \to 0$, this system is ergodic, i.e. that

$$\langle G \rangle = \overline{G}$$

where

$$\langle G \rangle = \int dx\, dp\, f(x,p) G(x,p)$$

and

$$\overline{G} = \frac{1}{\tau} \int_0^\tau d\sigma\, G(x(t+\sigma), p(t+\sigma)).$$

Hint: use ξ *and* η *in the integral for* $\langle G \rangle$ *and go over to polar coordinates.*

Consider this system now in the canonical ensemble, i.e.

$$f(x,p) = \frac{e^{-\beta[H(x,p)-A]}}{h}.$$

e. Calculate the partition function and the Helmholtz free energy A.

f. Calculate $\langle H \rangle$ in the canonical ensemble. For what choice of β is its value equivalent to that of the micro-canonical ensemble?

While averages are usually, in the large system size limit, independent of the ensemble in which they are calculated, fluctuations may differ between ensembles. To illustrate this, consider the fluctuations in the kinetic energy, i.e,

$$\sigma_K^2 = \left\langle \left(\frac{p^2}{2m} \right)^2 \right\rangle - \left\langle \left(\frac{p^2}{2m} \right) \right\rangle^2 = \frac{\langle p^4 \rangle - \langle p^2 \rangle^2}{4m^4}.$$

g. Taking the above choice for β, show that the value of $\langle p^2 \rangle$ is the same in the canonical and in the micro-canonical ensemble.

h. Calculate the values of $\langle p^4 \rangle$ in the canonical and the micro-canonical ensemble, respectively. Are these values equal? What is the consequence for σ_K^2 in the two ensembles? Explain this result.
Hint for g and h: for the micro-canonical value, use ξ *and* η*, go over to polar coordinates and use that* $\int_0^{2\pi} d\phi\, \cos^2\phi = \pi$ *and* $\int_0^{2\pi} d\phi\, \cos^4\phi = 3\pi/4$.

4 Sub-Ensembles

Consider a collection of N identical three dimensional non-interacting harmonic oscillators, whose Hamiltonian is:

$$\begin{aligned} H_N(\mathbf{x}^{(N)}) &= \frac{\mathbf{p}^{(N)}\cdot\mathbf{p}^{(N)}}{2m} + \frac{m\omega^2\,\mathbf{r}^{(N)}\cdot\mathbf{r}^{(N)}}{2} \\ &= \sum_{n=1}^{N}\left(\frac{\mathbf{p}_n\cdot\mathbf{p}_n}{2m} + \frac{m\omega^2\,\mathbf{r}_n\cdot\mathbf{r}_n}{2}\right) \end{aligned}$$

We start by considering the micro-canonical ensemble for this large system.

a. Write down the micro-canonical probability distribution $f(\mathbf{x}^{(N)})$ for given energy E. Show that the normalization constant Ω as a function of the number of particles N and the energy per particle $\varepsilon = E/N$ is to linear order in δE given by

$$\Omega(N,\varepsilon) = \frac{3}{\varepsilon(3N)!}\left(\frac{2\pi N\varepsilon}{\omega}\right)^{3N}\delta E.$$

Hint: use the ξ,η *variables of the previous problem and that the volume of a* $6N$*-dimensional sphere with radius* r *is* $\pi^{3N}r^{6N}/(3N)!$.

We will single out a subsystem of the whole, namely, the first oscillator. The remaining $N-1$ oscillators are interpreted as a kind of "thermal bath". For properties $G(\mathbf{x}_1)$ that only depend on the phase space coordinate $\mathbf{x}_1$ of the single oscillator, we may write

$$\langle G\rangle = \int d\mathbf{x}_1\, f_1(\mathbf{x}_1)G(\mathbf{x}_1)$$

where $f_1(\mathbf{x}_1)$ is the reduced probability distribution for the phase space of oscillator 1:

$$f_1(\mathbf{x}_1) = \int d\mathbf{x}_2 d\mathbf{x}_3\cdots d\mathbf{x}_N\, f(\mathbf{x}^{(N)}).$$

b. Show that, to good approximation, the phase space distribution of the subsystem is given by

$$f_1(\mathbf{x}_1) = \frac{\Omega\left(N-1, \varepsilon + \frac{\varepsilon - H_1(\mathbf{x}_1)}{N-1}\right)}{\Omega(N,\varepsilon)}$$

c. Compute the limit $N \to \infty$ (i.e. the limit a of large thermal bath) of $f_1(\mathbf{x}_1)$.
Hint: use that $\lim_{N\to\infty} \left(1 + \frac{a}{N}\right)^N = e^a$.

d. Show that in this limit, the subsystem is described by the canonical ensemble.

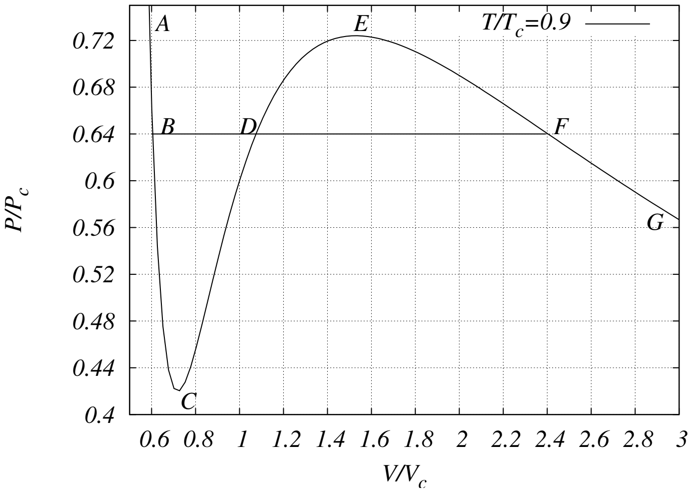
Note: we may conclude that the canonical ensemble is not only a convenient tool to calculate averages, it is also the appropriate ensemble for subsystems of larger systems. In a similar fashion one can show that the grand canonical ensemble is the appropriate ensemble for sub-volumes of larger volumes.

5 Equal-Areas Construction for Van der Waals Liquids

Consider a liquid whose equation of state is given by the Van der Waals equation:

$$P = \frac{kT\rho}{1 - b\rho} - a\rho^2.$$

where $\rho = N/V$. Below T_c the isotherms in the P-V diagram have an unphysical part, and the real isotherm is given by the equal areas construction due to Maxwell, as sketched in the figure below, where the Van der Waals isotherm $ABCDEFG$ is replaced by the physical $ABDFG$.



a. Write the equation of state in terms of the molar volume $\tilde{V}$.

b. Show how the conditions on the critical point, $\partial P/\partial \tilde{V} = 0$ and $\partial^2 P/\partial \tilde{V}^2 = 0$, lead to

$$\tilde{V}_c = 3N_A b; \quad kT_c = \frac{8a}{27b}; \quad P_c = \frac{a}{27b^2}.$$

For molar volumes for which the real isotherm is horizontal, a gas and a liquid phase coexist. The liquid phase in the system has a molar volume of $\tilde{V}_B$, i.e., the start of the plateau, and the gas phase has a molar volume of $\tilde{V}_F$, i.e., the end of the plateau.

d. Show that the Helmholtz free energy difference for one mole follows from

$$A(\tilde{V}_F, T) - A(\tilde{V}_B, T) = -\int_{\tilde{V}_B}^{\tilde{V}_F} d\tilde{V}\, P(\tilde{V}, T).$$

e. Show that the chemical potential difference (per mole) μ can be deduced from

$$\mu(\tilde{V}_F, T) - \mu(\tilde{V}_B, T) = P(\tilde{V}_F)\tilde{V}_F - P(\tilde{V}_B)\tilde{V}_B - \int_{\tilde{V}_B}^{\tilde{V}_F} d\tilde{V}\, P(\tilde{V}, T).$$

f. Given the result of e., demonstrate how the fact that the liquid and the gas are in equilibrium with one another leads to the equal-areas construction.