CHEM-GA 2600: Statistical Mechanics

Problem set #2

Due: Feb. 15, 2016

1. A measure of the entropy of a system associated with its phase-space distribution $f(\mathrm{x}, t)$ is the so-called Shannon entropy

$$S(t) = -k_{\mathrm{B}} \int d\mathrm{x}\ f(\mathrm{x}, t) \ln f(\mathrm{x}, t)$$

   a. Suppose $\eta(\mathrm{x}, t)$ is a divergence-free vector field $\nabla_{\mathrm{x}} \cdot \eta(\mathrm{x}, t) = 0$ and that $f(\mathrm{x}, t)$ satisfies the Liouvlle equation

$$\frac{\partial}{\partial t} f(\mathrm{x}, t) + \eta(\mathrm{x}, t) \cdot \nabla_{\mathrm{x}} f(\mathrm{x}, t) = 0$$

   Show that $dS/dt = 0$.

   Hint: Be carefuly how you handle the operation of d/dt on the integral!

   b. Now consider the (equilibrium) canonical ensemble, for which $f(\mathrm{x}) = \exp(-\beta H(\mathrm{x}))/Q(N, V, T)$. Show that, for this distribution, this definition of entropy leads to the correct canonical result:

$$S = kT \left(\frac{\partial \ln Q}{\partial T} \right) + k \ln Q$$

   where $Q(N, V, T)$ is the canonical partition function, and k is Boltzmann's constant.

2. Problem 3.1

3. Problem 3.4

4. A single particle of mass m moving in one spatial dimension with coordinate x and momentum p is described by the following Hamiltonian:

$$H(x, p) = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 + \frac{g}{4} x^4$$

   Consider the choice $m = 1$, $\omega = 1$, $g = 1$ with initial conditions $x(0) = 0$, $p(0) = 1$. The Liouville operator for this system is

$$iL = iL_1 + iL_2$$

   where

$$iL_1 = \frac{\partial H}{\partial p} \frac{\partial}{\partial x}, \qquad iL_2 = -\frac{\partial H}{\partial x} \frac{\partial}{\partial p}$$

   a. Write a program for integrating Hamilton's equations of motion for this system based on the propagator factorization scheme

$$e^{iL\Delta t} \approx e^{iL_2 \Delta t/2} e^{iL_1 \Delta t} e^{iL_2 \Delta t/2}$$

   Run your program for at least $P = 10^3$ periods of the oscillator for different choices of the time step Δt, and calculate the L_1 norm measure of energy conservation

$$\Delta E(\Delta t) = \frac{1}{P} \sum_{k=1}^{P} \left| \frac{H(x(k\Delta t), p(k\Delta t)) - H(x(0), p(0))}{H(x(0), p(0))} \right|$$

   Plot $\log_{10} E(\Delta t)$ vs. $\log_{10} \Delta t$, and show that the integrator is, indeed, second order.

b. Repeat part a for the following propagator factorization scheme:

$$e^{iL\Delta t} \approx e^{iL_1\Delta t/2} e^{iL_2\Delta t} e^{iL_1\Delta t/2}$$

c. Now consider the choice $g = 0.1$ with all other parameters the same. Write a multiple time-step program to integrate this problem using the harmonic force as the fast force and the quartic force as the slow force. Use a time step of $\delta t = 0.01$ for the fast force, and vary the time step Δt for the slow force. Vary the ratio of $\Delta t/\delta t \equiv n$ and plot $\log_{10} E(\Delta t)$ vs. $\log_{10} \Delta t$ for each value of this ratio when you run your code for several thousand periods of the harmonic motion. Is your algorithm second order in Δt?