CHEM-GA 2600: Statistical Mechanics

Problem set #1

Due: Feb. 4, 2016

1. *Nonuniqueness of the Lagrangian*: The Lagrangian of a system of N particles in Cartesian coordinates is

$$L(\mathbf{r}, \dot{\mathbf{r}}) = \frac{1}{2}\sum_{i=1}^{N} m_i \dot{\mathbf{r}}_i^2 - U(\mathbf{r}_1, ..., \mathbf{r}_N)$$

Let $F(\mathbf{r}_1, ..., \mathbf{r}_N, t)$ be any differentiable function of the coordinates and of time. Show that the Lagrangian

$$L'(\mathbf{r}, \dot{\mathbf{r}}, t) = L(\mathbf{r}, \dot{\mathbf{r}}) + \frac{dF(\mathbf{r}_1, ..., \mathbf{r}_N, t)}{dt}$$

gives the same equations of motion as $L(\mathbf{r}, \dot{\mathbf{r}})$.

2. It has been suggested that when a system is subject to a shearing force, its Hamiltonian should be modified to read

$$H(\mathbf{r}, \mathbf{p}) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1, ..., \mathbf{r}_N) + \sum_{i=1}^{N}\sum_{\alpha=1}^{3}\sum_{\beta=1}^{3} r_{i,\alpha} B_{\alpha\beta} p_{i,\beta}$$

where α and β index the three spatial components of the vectors $\mathbf{r}_i$ and $\mathbf{p}_i$ such that $r_{i,1} = x_i$, $r_{i,2} = y_i$, $r_{i,3} = z_i$ with analogous idenfitications for $p_{i,\beta}$. $B_{\alpha\beta}$ is a constant matrix.

   a. Derive Hamilton's equations of motion for this Hamiltonian.

   b. Suppose the elements of the matrix $B_{\alpha\beta}$ are $B_{32} = \gamma$ and $B_{\alpha\beta} = 0$ otherwise. Here γ is a constant. Examine the $\dot{\mathbf{r}}_i = \partial H/\partial \mathbf{p}_i$ equation carefully in the limit that $\mathbf{p}_i \to 0$ and show that the $r_{i,\alpha} B_{\alpha\beta} p_{i,\beta}$ term does, indeed, produce a shearing effect. **Hint**: One way to do this is to plot the component of $\dot{\mathbf{r}}_i$ that is affected by this term as a function of $\mathbf{r}_i$ in the limit that $\mathbf{p}_i \to 0$.

3. A particle of mass m with coordinate x and momentum p moves in a double-well potential of the form

$$U(x) = \frac{U_0}{a^4}\left(x^2 - a^2\right)^2.$$

Sketch the contours of the constant-energy surface $H(x, p) = E$ in phase space for the following cases:

   a. $E < U_0$.

   b. $E = U_0 + \epsilon$, where $\epsilon \ll U_0$.

   c. $E > U_0$.

4. Consider a system with coordinate q, momentum p, and Hamiltonian

$$H = \frac{p^n}{n} + \frac{q^n}{n},$$

where n is an integer larger than 2. Show that if the energy E of the system is chosen such that $nE = m^n$, where m is a positive integer, then no phase space trajectory can ever pass through a point for which p and q are both positive integers. Consider a system with coordinate q, momentum p, and Hamiltonian

$$H = \frac{p^n}{n} + \frac{q^n}{n},$$

where n is an integer larger than 2. Show that if the energy E of the system is chosen such that $nE = m^n$, where m is a positive integer, then no phase space trajectory can ever pass through a point for which p and q are both positive integers.

Hint: You might find Fermat's last theorem helpful here.

5. Consider an ensemble of one-particle systems, each evolving in one spatial dimension according to an equation of motion of the form

$$\dot{x} = -\alpha x$$

where $\alpha > 0$, and where $x(t)$ is the particle position at time t. The Liouville equation for the ensemble distribution $f(x,t)$ is

$$\frac{\partial f}{\partial t} - \alpha x \frac{\partial f}{\partial x} = \alpha f$$

a. Suppose that at $t = 0$, the ensemble distribution is given by

$$f(x,0) = \frac{1}{\pi} \frac{\sigma}{\sigma^2 + x^2}$$

where σ is a constant. Find the ensemble distribution $f(x,t)$ at all time, and discuss the behavior of this distribution as $t \to \infty$. Finally, show that your distribution function $f(x,t)$ is normalized for all t.

Hint: Show that the substitution $f(x,t) = e^{\alpha t} \tilde{f}(x,t)$ yields an equation for a conserved distribution $\tilde{f}(x,t)$. Next, try multiplying the x in the initial distribution by a function $g(t)$, where $g(0) = 1$, and use the Liouville equation to derive an equation that $g(t)$ must satisfy.

b. Repeat for the case that the initial distribution is a Gaussian,

$$f(x,0) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-x^2/2\sigma^2}$$

where σ is a constant.