Statistical Mechanics – Problem Set
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(Dated: July 2009)

1. In this problem, we will solve the classical Harmonic Oscillator. Recall that for the harmonic oscillator, $V(x) = \frac{1}{2}kx^2$, and that the frequency ω is usually defined as $\sqrt{\frac{k}{m}}$.

   (a) What is the (classical) Hamiltonian?

   (b) Write down Hamilton's Equations — *i.e.*, what are $\dot{x}$ and $\dot{p}$ as a function of x and p?

   (c) Solve the two coupled equations in part (b), and explicitly provide the values of $x(t)$ and $p(t)$. (Assume that the boundary conditions in time — *i.e.* the requirements that the solution must satisfy — are that $x(0) = x_0$ and $p(0) = p_0$.)

   Hint #1: You have two first-order equations. Construct one second-order equation in p, and solve it.

   Hint #2: $\cos\theta = \frac{1}{2}\left(e^{i\theta} + e^{-i\theta}\right)$ and $\sin\theta = \frac{1}{2i}\left(e^{i\theta} - e^{-i\theta}\right)$

   Hint #3: $\frac{d}{dt}e^{ikt} = ike^{ikt}$

   (d) Using your result from part (c), what is the value of the Hamiltonian as a function of t? Is it constant in time? Why or why not?

2. Now we solve problem #2, using the more powerful machinery that we discussed.

   (a) Notice that the classical path for the Harmonic oscillator that you obtained in the previous problem is cyclic in time. Evaluate the action over one period.

   (b) Use θ to denote the cyclic angle, *i.e.*, identify a quantity in the classical path which you will set to take on the value of θ such that the solution takes on the same values at $\theta = 0$ and $\theta = 2\pi$.

   NOTE: There are also other quantities which are sometimes called the action besides the quantity S defined in the notes: I of action-angle variables fame, and Hamilton's Characteristic Function, W, are are defined by,

$$I \equiv \frac{1}{\pi}W(t_<, t_>) \tag{0.1}$$

$$W(t_0, t_1) \equiv \int_{t_0}^{t_1} pdq \, , \tag{0.2}$$

   where the integral in W is over the path from $q(t_0)$ to $q(t_1)$, and the integration interval is provided implicitly with respect to time because the path may retrace itself. The explicit times $t_<$ and $t_>$ in I correspond to the turning points of a cyclic path. (Turning points are the places along the path in which the path reverses its direction, *i.e.*, where it hits the potential barrier.)

   (c) Evaluate W using the classical Harmonic Oscillator solution with $x(0) = 0$ at $t_0 = 0$, and arbitrary t_1.

   (d) Calculate the action S for the same conditions as in the previous part. By comparison with your result for S show that S and W are related by a Legendre transform over the variables E and t. (NOTE: It's because this simple relation holds in general, that they can both be properly called actions!)

   (e) Using your result in part (c), evaluate I explicitly.

   (f) In your solutions for x and p in the Harmonic oscillator, insert I and θ as obtained/defined in the previous parts as much as possible. (When your're done, there should be no reference to t in your expressions, nor should there be any x's or p's, as we will use these expressions to define a canonical transformation between the (x, p) phase space, and the (I, θ) — *vis-a-vis* action-angle — phase space.)

(g) Calculate the energy, E — *i.e.*, the transformed Hamiltonian — in terms of I and θ.

(h) Assuming that the transformation in part (f) is canonical, what are Hamilton's equations for I and θ? Notice that these equations are easy to solve — I and θ are the action-angle variables that correspond to an integrated Hamiltonian! [No surprise, really, since we've used the solution of problem 1 to obtain it. The correct way to solve this problem *a priori* is to develop a systematic method for the construction of canonical transformations. This has been done for special cases, but it's likely that a general solution will never be found.]

(i) **Bonus Question:** Is the transformation of part (f) canonical?

3. The classical partition function for the harmonic oscillator.

   (a) Calculate the classical partition function, Q, for the one-dimensional harmonic oscillator by integrating over the phase space variables, (x, p), explicitly.

   Hint: Use the formula for the Gaussian integral!

   (b) Calculate the classical partition function, Q, for the one-dimensional harmonic oscillator by integrating over the action-angle variables, (I, θ) explicity.

   (c) Did you get the same result? Why or why not?

4. The Classical partition function for an ideal gas.

   (a) Calculate the classical canonical partition function, Q, for an ideal gas of N particles in a 3-dimensional box with sides, L_1, L_2, and L_3, at temperature, T.

   (b) Calculate the equation of state from Q

   (c) Calculate $E(T, V, N)$ and $S(T, V, N)$ for this system.

   (d) Calculate the isothermal-isobaric partition function, $\Delta(T, P, N)$

   (e) Calculate $G(T, P, N)$ and $S(T, P, N)$ for this system.

   (f) Calculate the grand canonical partition function, $\Theta(T, V, \mu)$

   (g) Calculate $S(T, V, \mu)$ for this system.

   (h) Use your results to show that $S(T, V, N)$ and $S(T, V, \mu)$ are related by Legendre transforms.

5. Critical exponents in the spin-Ising system.

   (a) Derive the critical exponents for magnetization and heat capacity near T_c as predicted by mean field theory in one and two dimensions.

   (b) Derive the critical exponents for magnetization and heat capacity near T_c as predicted by renormalization group theory in one and two dimensions.

6. Suppose that your system consists of 1000 diatomic O_2 molecules inside of a cubic box of side L. Assume that each molecule can be described as a harmonic spring, and that every intermolecular O-O contact is described by a Lennard-Jones potential.

   (a) What is the formal expression for $Q(\beta)$ for this system? (Identify all necessary parameters.)

   (b) Without assuming that the Lennard-Jones potential is trivial, what other simplifying assumptions would be required for this system to be nearly ideal?

   (c) What differences (if any) would you expect to see (in terms of the algorithms, the computational performance and the result) within a Metropolis Monte Carlo calculation of $g(r)$ for N_2 versus that of O_2?

7. Perturbation theory.

- Recall that the Gibbs-Bogoliubov-Feynman (GBF) bound gives the partition function,

$$Q \approx Q_0 e^{-\beta\langle\Delta E\rangle_0} ,$$

  where ΔE is the difference in energy between the system we are interested in and that of some other reference system denoted by 0.

- Suppose $V(x) = \frac{1}{2}m\omega^2 x^2 + \frac{1}{24}k^4 x^4$ with $k > 0$ is the potential of interaction for a continuous one-dimensional system.
- Let the harmonic oscillator, $V_0(x) \equiv \frac{1}{2}m\omega^2 x^2$, be the reference potential.
- Treat the quartic term in $V(x)$ as the perturbation, *i.e.*, $\Delta E \equiv V(x) - V_0(x)$.

(a) What is the zeroth-order partition function? [*I.e.*, what is Q_0?]

(b) What is the first-order partition function? [Call this Q_1.]

(c) What is the second-order partition function? [Call this Q_2.]

(d) Are the ratios Q_n/Q_0 smaller or larger than 1, for n equal to 1 and 2? According to the GBF bound, how will the ratio of Q/Q_0 compare to 1? What does this imply about the relative localization of x between the quartic oscillator and the reference harmonic oscillator?

8. Suppose you have a Gaussian polymer with $2N$ bonds in 3 dimensions, whose probability distribution is given by,

$$P(\{R_i\}) = \left(\frac{3}{2\pi b^2}\right)^{3N} \prod_{n=1}^{2N} e^{-\frac{3}{2b^2}(R_n - R_{n-1})^2}$$

(a) Integrate out all the R_i degrees of freedom with i an odd number to obtain a probability distribution in only N bonds: $P(\{R_{2i}\})$.

(b) Your result in part *a* should be a Gaussian distribution. What is the value of the new (effective) bond length, b', in terms of b?

(c) Using the scaling formula in part *b*, obtain $\langle R^2\rangle$ for a system with $N = 2^M$. Compare your result to that in the book obtained by explicitly calculating $\langle R^2\rangle$.

9. Consider the multidimensional Hamiltonian, $\mathcal{H} = \mathcal{H}_0(x) - xf + \mathcal{H}_b(y_1, \ldots, y_N)$ in the notation of Chandler's green book (page 261). (This is also called the Zwanzig Hamiltonian or the Mori-Zwanzig Hamiltnonian; particularly when $\mathcal{H}_b$ consists of N harmonic oscillators.)

(a) Calculate the potential of mean force on x, *i.e.*,

$$e^{-\beta V_{PMF}(x)} = \langle \delta(x - \bar{x})\rangle_{\bar{x}\to x} .$$

(b) Evaluate the potential, $\bar{V}(x)$, of the Langevin Equation given on page 263 in Chandler explicitly in terms of the parameters of the Hamiltonian, $\mathcal{H}$.

(c) Compare your answers in parts *a* and *b*. What does this say about the role of $\bar{V}$ in the Langevin equation?