

Statistical Mechanics – Problem Set

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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 $\sqrt{\frac{k}{m}}$.

- What is the (classical) Hamiltonian?
- Write down Hamilton's Equations — *i.e.*, what are \dot{x} and \dot{p} as a function of x and p ?
- 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: $\cos \theta = \frac{1}{2} (e^{i\theta} + e^{-i\theta})$ and $\sin \theta = \frac{1}{2i} (e^{i\theta} - e^{-i\theta})$

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

- 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.

- 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.
- 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 defined by,

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

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

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.)

- Evaluate W using the classical Harmonic Oscillator solution with $x(0) = 0$ at $t_0 = 0$, and arbitrary t_1 .
- 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!)
- Using your result in part (c), evaluate I explicitly.
- 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) explicitly.
 - (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.*, $\Delta E \equiv V(x) - V_0(x)$.

- What is the zeroth-order partition function? [*I.e.*, what is Q_0 ?]
- What is the first-order partition function? [Call this Q_1 .]
- What is the second-order partition function? [Call this Q_2 .]
- 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,

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

- Integrate out all the R_i degrees of freedom with i an odd number to obtain a probability distribution in only N bonds: $P(\{R_{2i}\})$.
 - 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 ?
 - 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, $\mathcal{H} = \mathcal{H}_0(x) - xf + \mathcal{H}_b(y_1, \dots, y_N)$ in the notation of Chandler's green book (page 261). (This is also called the Zwanzig Hamiltonian or the Mori-Zwanzig Hamiltonian; particularly when \mathcal{H}_b consists of N harmonic oscillators.)

- Calculate the potential of mean force on x , *i.e.*,

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

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