

Homework 4: Phys 7230 (Spring 2022)

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Problem 1 (Variational approximation): In the lectures we derived the classical variational bound for the free energy, given by

$$F \leq F_{\text{tr}} + \langle \mathcal{H} - \mathcal{H}_{\text{tr}} \rangle_{\text{tr}}, \quad (1.1)$$

where H_{tr} is the variational trial Hamiltonian that best approximates \mathcal{H} . To prove this result we utilize the convexity of a decaying exponential function, namely for a random variable x

$$\langle e^{-x} \rangle \geq e^{-\langle x \rangle}. \quad (1.2)$$

- (a) Prove above convexity inequality at least to lowest order in Taylor series expansion.

Solution.

□

- (b) Show that the variational inequality (1.2) is equivalent to $F \leq F_{\text{v}} = \langle \mathcal{H} \rangle_{\text{tr}} - TS_{\text{tr}}$, where S_{tr} is the Shannon's entropy for the probability distribution $P = Z_{\text{tr}}^{-1} e^{-\beta \mathcal{H}_{\text{tr}}}$, with an extra factor of k_B to make units consistent with our thermodynamics.

Solution.

□

- (c) Consider a particle in a periodic potential described by a Hamiltonian

$$\mathcal{H} = \frac{p^2}{2m} + \alpha(1 - \cos x), \quad (1.3)$$

where I took x to be dimensionless, i.e., measured in units of another length x_0 to simplify the notation. Motivated by the physical expectation that at low T , a particle that starts at $x = 0$ may be trapped in the minimum of the cosine, use $\mathcal{H}_{\text{tr}} = (1/2)kx^2$ to treat this problem variationally.

Specifically, please use the variational procedure to get an implicit equation for the variational parameter function $k(\alpha/k_B T)$. Then solve this equation for the function $k(\alpha/k_B T)$ numerically and/or graphically, giving its two limits, the critical value of $(\alpha/k_B T)_c$ at which the transition occurs, and sketching the function. You will find Mathematica useful.

Hint: (1) You will find our Gaussian integral calculus very useful. (2) You will obtain an implicit equation for the variational parameter k . You can solve this equation numerically or

graphically finding the behavior of $k(\alpha/k_B T)$. From this solution show that the variational theory predicts a phase transition in this problem in the solution for k as a function of $\alpha/k_B T$, namely that the thermodynamics (free energy, etc) has two distinct phases, corresponding to high and low $\alpha/k_B T$. Just for the record, this intriguing finding is an example of a failure of the variational approximation for this single particle (0d) problem, that will, however, become correct for higher dimensional problem, e.g., an extended d -dimensional ($d > 1$) object, e.g., a fluctuating membrane trapped in a periodic potential.

Problem 2 (Propagation in imaginary time, random walk and phantom polymer): (a) Using Gaussian integral calculus demonstrate an important and very useful (e.g., for path integrals and our applications below) Gaussians “propagation” relation,

$$\int_{-\infty}^{\infty} dx_2 \frac{1}{\sqrt{2\pi\tau_2}} e^{-\frac{(x_3-x_2)^2}{2\tau_2}} \frac{1}{\sqrt{2\pi\tau_1}} e^{-\frac{(x_2-x_1)^2}{2\tau_1}} = \frac{1}{\sqrt{2\pi(\tau_2+\tau_1)}} e^{-\frac{(x_3-x_1)^2}{2(\tau_2+\tau_1)}}, \quad (2.1)$$

and thereby prove unnormalized density matrix the “propagator” property for the *free-particle*,

$$\rho^u(x_3, x_1; \tau_1 + \tau_2) = \int dx_2 \rho^u(x_3, x_2; \tau_2) \rho^u(x_2, x_1; \tau_1), \quad (2.2)$$

that, as discussed in class is satisfied by all $\rho^u(x, x', \tau)$.

Solution.

□

(b) Edward’s “phantom” polymer model, coupled harmonic oscillators, and a random walk

As we may discuss in more detail in a few lectures, a simplest model of a polymer (a giant flexible linear molecule of N monomers strung together, illustrated in Fig. 1 below) is that of a freely-joined chain of N links $\mathbf{r}_n = \mathbf{R}_n - \mathbf{R}_{n-1}$. In the continuum, $n \rightarrow s$, the probability of its conformation $\mathbf{R}(s)$ in a d -dimensional space is given by

$$P[\mathbf{R}(s)] = \left(\frac{d}{2\pi b_0^2} \right)^{dN/2} \exp \left[-\frac{d}{2b_0^2} \int_0^N ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 \right], \quad (2.3)$$

where b_0 is the preferred link length and prefactor is a normalization, much like in Eq. (2.1) for 2 links. We can view this system as described by an ideal polymer Hamiltonian

$$\mathcal{H} = \frac{\sigma}{2} \int_0^N ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2, \quad (2.4)$$

where $\sigma = k_B T d / (\pi b_0^2)$ is the entropic polymer free energy per unit of length, i.e., tension, notably proportional to thermal energy $k_B T$.

(i) By discretizing above probability distribution into product of N 1-link probability distributions,

$$p(\mathbf{r}_n) = \left(\frac{d}{2\pi b_0^2} \right)^{d/2} \exp \left[-\frac{d}{2b_0^2} (\mathbf{R}_n - \mathbf{R}_{n-1})^2 \right], \quad (2.5)$$

written in terms of the position \mathbf{R}_n of n -th monomer, and by integrating over all N *intermediate* monomer positions, \mathbf{R}_n for $1 < n < N$ compute the probability distribution $P[\mathbf{R}_N - \mathbf{R}_0]$, for the end-to-end displacement $\mathbf{R}_N - \mathbf{R}_0$.

Hint: Surprise! You have just computed a path-integral for a single polymer statistical mechanics, computing its partition function $Z = \exp(-\beta F)$, for fixed ends $\mathbf{R}_N, \mathbf{R}_0$ of the polymer.

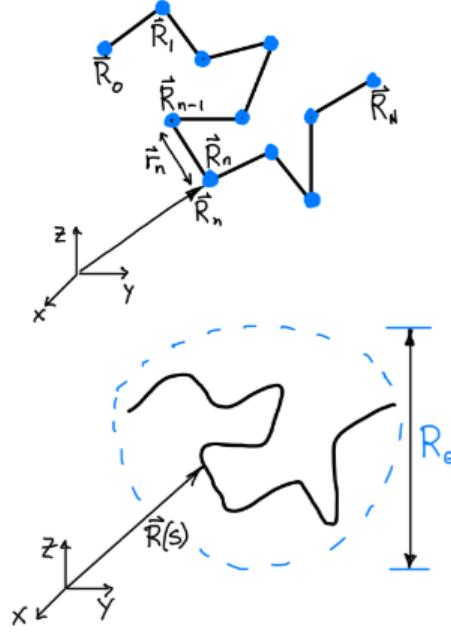


Figure 1: Edward's “phantom” polymer model executing an ideal random walk in d -dimensional space, characterized by $N + 1$ monomer positions, \mathbf{R}_n .

Solution.

□

(ii) Compute the “radius of gyration” $R_g(N)$, defined by

$$R_g^2 = \left\langle (\mathbf{R}_N - \mathbf{R}_0)^2 \right\rangle, \quad (2.6)$$

which characterizes the root-mean-squared radius occupied by a polymer in the d -dimensional embedding space.

Note that, in thinking of the links of the polymer as random steps executed as a function of “time” s , this polymer statistics reproduces the random walk result that after N steps the random walker is only \sqrt{N} away from where she started. All this is of course a consequence of central limit theorem.

Solution.

□

Problem 3 (Free particle density matrix in coordinate representation): In lectures we discussed many properties and forms of the coordinate-space density matrix $\rho(x, x'; \beta)$, including its expected low- and high- T limits, as well as its eigenstates

$$\rho^u(x, x'; \beta) = \sum_n \psi_n(x) \psi_n^*(x') e^{-\beta E_n}, \quad (3.1)$$

and path-integral

$$\rho^u(x, x'; \beta) = \int_{x(0)=x; x(\beta\hbar)=x'} [dx(\tau)] e^{-S_E[x(\tau)]/\hbar} \quad (3.2)$$

formulations, as well as the “imaginary-time” Schrödinger-like equation in β

$$\partial_\beta \rho^u(x, x'; \beta) = -\mathcal{H}(\hat{\rho}, x) \rho^u(x, x'; \beta), \quad (3.3)$$

that it satisfies, where $\hat{\rho} = -i\hbar\partial_x$, i.e., giving the coordinate representation Schrödinger equation in imaginary time. Let us explore the details of this for a free particle here.

(a) For a free particle, use its Hamiltonian inside (3.3), solve the resulting diffusion equation (in “time” β) solve, taking into account the appropriate “initial condition” for $\beta = 0$, discussed in class, required by the general definition of $\hat{\rho}^u$.

Hint: The solution is as simple as solving free-particle Schrödinger equation in imaginary “time” or a real diffusion equation in infinite space.

Solution.

□

(b) Use Hamiltonian eigenbasis representation, Eq. (3.1) and your knowledge of what the free-particle eigenstates are, to rederive the above result for $\rho^u(x, x'; \beta)$, also quoted in the lectures. Note that if you properly take the eigenstates to be normalized in a large box of size L (most convenient with periodic boundary conditions), this analysis automatically gives the correct prefactor for $\rho^u(x, x'; \beta)$.

Solution.

□

(c) Now we will use, perhaps a bit less familiar path-integral formulation. One useful approach to evaluate a path-integral is that of a semi-classical saddle-point approximation.

- An amazing fact, however, that we will see below is that this semi-classical approach is in fact *exact* for a quadratic action, as for e.g., a free particle and harmonic oscillator (the following problem).
- Examining Eq. (3.2), we see that all dependence of $\rho^u(x, x'; \beta)$ on x, x' is in the boundary conditions on $x(0), x(\beta\hbar)$. So let’s introduce new time-dependent coordinates $y(\tau)$, with

$$x(\tau) = x_{\text{cl}}(\tau) + y(\tau), \quad (3.4)$$

where $x_{\text{cl}}(\tau)$ is the classical path satisfying the Euler-Lagrange equation

$$\left. \frac{\delta S_E[x(\tau)]}{\delta x(\tau)} \right|_{x_{\text{cl}}(\tau)} = 0, \quad (3.5)$$

and satisfying $x_{\text{cl}}(0) = x, x_{\text{cl}}(\beta\hbar) = x'$. Thus, $y(0) = y(\beta\hbar) = 0$.

- Inserting Eq. (3.4) into the action in Eq. (3.2) and expanding to lowest nontrivial order in $y(\tau)$ we find

$$\rho^u(x, x'; \beta) \approx e^{-S_E[x_{\text{cl}}(\tau)]/\hbar} \int_{y(0)=y(\beta\hbar)=0} [dy(\tau)] \exp \left[-\frac{1}{2\hbar} \int_0^{\beta\hbar} d\tau y(\tau) S_E''[x_{\text{cl}}] y(\tau) \right], \quad (3.6)$$

where first functional derivative term is absent because it vanishes by virtue of the equation of motion Eq. (3.5) satisfied by $x_{\text{cl}}(\tau)$.

- The key observation in Eq. (3.6) is that for quadratic action $S_E[x(\tau)]$, the kernel $S_E''[x_{\text{cl}}]$ in the exponential is independent of $x_{\text{cl}}(\tau)$. Thus, for such quadratic theory, the remaining functional integral over $y(\tau) \mathcal{N}(\beta\hbar)$ is just a “constant” that only depends on $\beta\hbar$, but *not* on x, x' . We can therefore not worry about this prefactor $\mathcal{N}(\beta\hbar)$ and focus on $\exp \left(-S_E[x_{\text{cl}}(\tau)]/\hbar \right)$ that contains all the key dependence on x, x' , giving us $\rho^u(x, x'; \beta)$ up to the factor $\mathcal{N}(\beta\hbar)$.

Solution.

□

(d) For a free particle, solve the (Euclidean) classical Euler-Lagrange equation of motion Eq. (3.5) for $x(\tau, x, x')$ with initial conditions $x_{\text{cl}}(0) = x, x_{\text{cl}}(\beta\hbar) = x'$, and evaluate

$$S_E[x_{\text{cl}}(\tau)] \equiv S_{\text{cl}}(x, x', \beta\hbar), \quad (3.7)$$

thereby obtaining

$$\rho^u(x, x'; \beta) = \mathcal{N}(\beta\hbar) e^{-S_{\text{cl}}(x, x', \beta\hbar)/\hbar}. \quad (3.8)$$

Demonstrate that up to the unknown prefactor $\mathcal{N}(\beta\hbar)$, you obtain exactly the result found in (a) and (b).

Solution.

□

(e) As a non-required bonus, you can determine the prefactor $\mathcal{N}(\beta\hbar)$, by discretizing the path integral in (3.6) as you did for a polymer in problem 2 (note mathematically it is exactly the same path integral) and then requiring the $\mathcal{N}(\Delta\tau)$ (with $\beta\hbar = N\Delta\tau$) to be special function such that the “propagator” relation, (??) is satisfied.

Alternatively, you can determine $\mathcal{N}(\tau)$ by requiring that (3.8) satisfies the diffusion equation, (3.3), thereby obtaining and solving a differential equation for $\mathcal{N}(\tau)$.

Solution.

□

(f) Now that we have obtained $\rho^u(x, x'; \beta)$ by three methods above, calculate the corresponding (i) partition function $Z(\beta)$ and the (ii) probability $P(x) = \rho^u(x, x, \beta)/Z(\beta)$ of finding a free particle at position x .

Hint: The answer makes sense and is trivial.