G25.2651: Advanced Statistical Mechanics

Final Exam

Instructions: For this take-home exam, only lecture notes and other course materials will be permitted, and you are on your honor not to consult any outside texts or the Internet. You may consult math books if you have difficulty figuring out how to manipulate a particular expression. Also, do *not* work together on the exam. Each person must turn in her/his own work. Partial credit will be given generously, so it is in your best interest to try to answer *all* parts of *all* problems *and* to present *all* your work in a *neat an organized* fashion. This last point is *important*. Remember, I will not assume that what I cannot read is correct as a matter of course, i.e., you are not likely to get the benefit of the doubt. **The exam is due May 13 before 5 pm**.

1. (**40 points**)
   A simple model for electron transfer is defined by a Hamiltonian of the form

$$H = \frac{\varepsilon}{2}\sigma_z + \frac{\Delta}{2}\sigma_x$$

where ϵ and Δ are constants and σ_x, σ_y and σ_z are the Pauli matrices given by

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The model assumes that there are only two states for the electron and is thus a simplification of the true electron-transfer problem.

a. (**10 points**)
   In the Heisenberg picture, the operators that describe the observables of a system evolve in time according to the equation of motion

$$\frac{dA}{dt} = \frac{1}{i\hbar}[A, H]$$

where A is an arbitrary operator. Write down Heisenberg's equations for σ_x, σ_y and σ_z.

b. (**10 points**)
   Compute the autocorrelation function $\langle \sigma_y(0)\sigma_y(t)\rangle$ assuming an initial canonical distribution.

c. (**10 points**)
   In order to mimic the effect of an environment, the above two-level system is often coupled to a bath of quantum-mechanical harmonic oscillators for which the Hamiltonian is given by

$$H = \frac{\varepsilon}{2}\sigma_z + \frac{\Delta}{2}\sigma_x + \sum_\alpha \hbar\omega_\alpha \left[a_\alpha^\dagger a_\alpha + \frac{1}{2}\right] + \frac{\hbar}{2}\sigma_z \sum_\alpha g_\alpha \left(a_\alpha^\dagger + a_\alpha\right)$$

where α is an index that runs over all of the bath modes, ω_α are the bath frequencies, a_α and $a_\alpha^\dagger$ are the bath annhilation and creation operators, respectively, and g_α are a set of coupling constants. For this Hamiltonian, write down the Heisenberg equations of motion for *all* operators, including the Pauli matrices of the system and the creation and annhilation operators of the bath.

d. (**10 points**)
   Treating the coupling between the system and the harmonic bath as small, we can view this coupling as a perturbation on the Hamiltonian

$$H_0 = \frac{\varepsilon}{2}\sigma_z + \frac{\Delta}{2}\sigma_x + \sum_\alpha \hbar\omega_\alpha \left[a_\alpha^\dagger a_\alpha + \frac{1}{2}\right]$$

By solving the Heisenberg equations for the bath operators, develop expressions for the bath correlation functions $\langle a_\alpha(t)a_{\alpha'}^\dagger(t')\rangle_0$ and $\langle a_\alpha^\dagger(t)a_{\alpha'}(t')\rangle_0$ and show that these can be expressed in terms of the correlation function $\langle \sigma_y(t)\sigma_y(t')\rangle_0$ where $\langle \cdots \rangle_0$ means that any ensemble average is to be computed using the canonical distribution of the unperturbed Hamiltonian.

2. (**20 points**)
For the spin-$\frac{1}{2}$ Ising model in one dimension with $h = 0$, recall that the partition function could be expressed in the form

$$\Delta = \mathrm{Tr}\left(\mathrm{P}^N\right).$$

Consider a RG transformation, called the *pair cell* transformation in which Δ is re-expressed as

$$\Delta = \mathrm{Tr}\left[\left(\mathrm{P}^2\right)^{N/2}\right].$$

The transfer matrix is redefined by $\mathrm{P}' = \mathrm{P}^2$. Find the RG equation corresponding to this transformation and show that it leads to the expected stable fixed point.

Hint: Try redefining the coupling constant by $u = e^K$ and show that P' can be put in the same form as P, i.e., $\mathrm{P}'(u') = c(u)\mathrm{P}(u')$ and that c can be defined implicitly in terms of u'.

3 (**20 points**)
Consider a system of two distinguishable degrees of freedom with position operators $\hat{x}$ and $\hat{X}$ and corresponding momenta $\hat{p}$ and $\hat{P}$, respectively, with Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{\hat{P}^2}{2M} + U(\hat{x}, \hat{X}).$$

Assume that the masses M and m are such that $M \gg m$, meaning that the two degrees of freedom are adiabatically decoupled.

a. (**10 points**)
Show that the partition function of the system can be approximated as

$$Q(\beta) = \sum_n \oint \mathcal{D}X(\tau) \exp\left\{-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau \, \left[\frac{1}{2}M\dot{X}^2(\tau) + \varepsilon_n\left(X(\tau)\right)\right]\right\}$$

where $\varepsilon_n(X)$ are the eigenvalues that result from the solution of the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x, X)\right]\psi_n(x; X) = \varepsilon_n(X)\psi_n(x; X)$$

for the light degree of freedom at a fixed value X of the heavy degree of freedom. This approximation is known as the *path integral Born-Oppenheimer approximation.* The eigenvalues $\varepsilon_n(X)$ are the Born-Oppenheimer surfaces.

b. (**10 points**)
Under what conditions can the sum over n in the above expression be approximated by a single term involving only the ground-state surface $\varepsilon_0(X)$? Why?

4. (**20 points**)

a. (**10 points**)
Prove the following theorem: Let $\{|\phi_n\rangle\}$ be an arbitrary set of orthonormal functions on the Hilbert space of a quantum system whose Hamiltonian is $\hat{H}$. The functions $\{|\phi_n\rangle\}$ are assumed to satisfy the same boundary and symmetry conditions of the physical system. It follows that the canonical partition function $Q(N, V, T)$ satisfies the inequality

$$Q(N, V, T) \geq \sum_n e^{-\beta\langle\phi_n|\hat{H}|\phi_n\rangle},$$

where equality holds only if $\{|\phi_n\rangle\}$ are the eigenfunctions of $\hat{H}$.

Hint: You might find the Ritz variational principle helpful. The Ritz principle states that for an arbitrary wave function $|\Psi\rangle$, the ground-state energy E_0 obeys the inequality

$$E_0 \leq \langle\Psi|\hat{H}|\Psi\rangle$$

where equality only holds if $|\Psi\rangle$ is the ground state wave function of $\hat{H}$.

b. (**10 points**)
Using the result of part a, prove the following inequality: If A_1 and A_2 are the Helmholtz free energies for systems with Hamiltonians $\hat{H}_1$ and $\hat{H}_2$, respectively, then

$$A_1 \leq A_2 + \langle\hat{H}_1 - \hat{H}_2\rangle_2$$

where $\langle\cdots\rangle_2$ indicates an ensemble average calculated with respect to the density matrix of system 2. This inequality is known as the Gibbs-Bogliubov inequality.