PHYS 813: Statistical Mechanics and Thermodynamics
Exam II

May 5, 2009, 75 minutes, closed book.

Please start each solution on a fresh sheet of paper, use only one side of the paper. Try to show how well you understand the problems. Always justify your reasoning. Assemble your solutions in the increasing numerical order. Derive all thermodynamic formulas beyond definitions of thermodynamic functions and Maxwell's relations.

1. Consider a dilute, noninteracting gas of N distinguishable diatomic molecules of mass m. Each molecule is a rigid rotor with $(2J+1)$-degenerate energy levels $\epsilon_J = \hbar^2 J(J+1)/2I$, where I is the moment of inertia. Start from the general expression for the canonical partition function $Q_N(V,T) = \sum_n \mathrm{e}^{-E_n/kT}$ where E_n is the total energy of N-molecule system. Calculate then the average energy, the specific heat at constant volume, and the entropy of the system in the limit $kT \gg \hbar^2/2I$. You may use without proof the partition function for the ideal monoatomic gas $Q_N^{\mathrm{ideal}}(V,T) = \left[V(2\pi mkT)^{3/2}/h^3\right]^N$. *Hint:* In the assumed limit, $\sum_n f(n) = \int_0^\infty f(x)dx$.

2. Consider a system consisting of N particles and described by a quantum mechanical Hamiltonian $\hat{H}(\hat{\boldsymbol{p}}_1, \hat{\boldsymbol{p}}_2, \cdots, \hat{\boldsymbol{p}}_N, \hat{\boldsymbol{r}}_1, \hat{\boldsymbol{r}}_2, \cdots, \hat{\boldsymbol{r}}_N)$ dependent in a general way on the position operators $\hat{\boldsymbol{r}}_i$ and the momentum operators $\hat{\boldsymbol{p}}_i = -i\hbar\boldsymbol{\nabla}_i$. Consider also an analogous Hamiltonian with the position operator of particle 1 scaled by a factor λ and the momentum operator by $1/\lambda$: $\hat{H}^\lambda = \hat{H}(\hat{\boldsymbol{p}}_1/\lambda, \hat{\boldsymbol{p}}_2, \cdots, \hat{\boldsymbol{p}}_N, \lambda\hat{\boldsymbol{r}}_1, \hat{\boldsymbol{r}}_2, \cdots, \hat{\boldsymbol{r}}_N)$ (only particle 1 is scaled). In what follows assume that particles are distinguishable.

   (a) Show that $\hat{H}$ and $\hat{H}^\lambda$ have the same eigenvalues. *Hint:* show first that the eigenfunctions fulfill the following relation: $\Psi_n^\lambda(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N) = \Psi_n(\lambda\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N)$.

   (b) Show that the canonical partition functions for the two Hamiltonians are identical: $Q_N^\lambda(V,T) = Q_N(V,T)$. *Hint:* This is almost obvious.

   (c) Show that the statistical expectation value of the operator $\partial\hat{H}^\lambda/\partial\lambda$ is related to $\partial \ln Q_N^\lambda(V,T)/\partial\lambda$.

   (d) For the Hamiltonian of the form: $\hat{H} = \sum_{i=1}^N \frac{\hat{\boldsymbol{p}}_i^2}{2m} + \hat{V}(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N)$ show the statistical virial theorem: $\left\langle\left\langle \hat{T}_1 \right\rangle\right\rangle = \frac{1}{2}\left\langle\left\langle (\boldsymbol{\nabla}_1\hat{V})\cdot\hat{\boldsymbol{r}}_1 \right\rangle\right\rangle$ where $\hat{T}_1 = \hat{\boldsymbol{p}}_1^2/(2m)$.

3. Consider a macrosystem of a given volume V and number of particles N in equilibrium with a thermal bath. The system contains $\mathcal{N}$ microstates $|\Psi^k(t)\rangle$ with probabilities p^k. The Hamiltonian of the system, $\hat{H}$, is independent of time.

   (a) Show that the density operator $\hat{\rho} = \sum_{k=1}^{\mathcal{N}} p^k |\Psi^k\rangle\langle\Psi^k|$ is diagonal in the eigenbasis of $\hat{H}$, i.e., $\hat{\rho} = \sum_{n=1}^\infty \rho_n |\Phi_n\rangle\langle\Phi_n|$, where Φ_n are the eigenfunctions.

   (b) Find ρ_n's.