3. Hausübung, **Statistische Physik**

abzugeben am Donnerstag, 3.11.2011

Aufgabe H5 *Equilibrium state from maximum entropy* (6 Punkte)

a. Let A and B be complex matrices. Assuming that we treat a complex number and its conjugate as independent variables (i.e. $\frac{d}{dz}\overline{z} = 0$ and $\frac{d}{dz}z = 1$), show that

$$\frac{\partial}{\partial A_{ij}} \mathrm{tr}\,(AB) = B_{ji}.$$

b. Assuming $\det \rho \neq 0$, one can show that

$$\mathrm{tr}\left[\rho \frac{\partial \ln \rho}{\partial \rho_{ij}}\right] = \delta_{ij}$$

(You are *not* required to show this.) We want to find the state ρ which maximizes the von Neumann entropy $S(\rho) = -\mathrm{tr}\,[\rho \ln \rho]$ with the constraint that the expectation value of the energy be $\mathrm{tr}\,(\rho H) = U$. Using the method of the Lagrange multipliers, with the constraints $\mathrm{tr}\,\rho = 1$ and $\mathrm{tr}\,(\rho H) = U$, show that the entropy is at a local optimum for the quantum state

$$\rho = \frac{e^{-\beta H}}{\mathrm{tr}\; e^{-\beta H}} \tag{1}$$

where $\beta \in \mathbb{R}$ is one of the Lagrange multipliers. Give its *implicit* dependence on U (i.e., write the equation relating β to U, without solving for β.)

c. If a system with Hamiltonian H is at thermal equilibrium with a sufficiently large reservoir at temperature τ, then its state is precisely given by the above density matrix with

$$\beta = \frac{1}{\tau}.$$

The partition function therefore is $Z = \mathrm{tr}\, e^{-\beta H}$, and the free energy is

$$F = -\tau \ln Z.$$

Show that

$$\frac{d}{d\tau} F = -S$$

where S is the von Neumann entropy of the state expressed in Equation 1. Hint: compute both sides independently and compare.

Aufgabe H6 *Rotation of diatomic molecule* (6 Punkte)

Molecules can rotate, which involves kinetic energy. The rotational motion is quantized, and the kinetic energy eigenvalues for a diatomic molecule are of the form

$$\epsilon(j) = j(j+1)\epsilon_0.$$

where $j = 0, 1, 2, \ldots$ and $\epsilon_0 = \frac{\hbar^2}{2I}$, where I is the moment of inertia. The multiplicity of eigenvalue j is

$$g(j) = 2j + 1.$$

a. Write down the partition function $Z(\tau)$.

b. Evaluate $Z(\tau)$ approximately for $\tau \gg \epsilon_0$ by converting the sum to an integral.

c. Do the same for $\tau \ll \epsilon_0$ by truncating the sum after the second term.

d. Give expressions for the energy U and the heat capacity C as functions of τ in both limits. Observe that the rotational contribution to the heat capacity of a diatomic molecule approaches 1 when $\tau \gg \epsilon_0$.