Problem Set 8   **Due Friday, March 31, 2006**

Reading: Landau and Lifshitz, Secs. 81–86

LD 26: The high temperature behavior of Z_{rot}: Euler-Maclaurin summation and Mulholland's formula.

The quantum corrections to the rotational partition function of a heteronuclear diatomic molecule with characteristic rotational temperature Θ_r can be evaluated for $T > \Theta_r$ by applying the Euler-Maclaurin summation formula to the series for Z_{rot}.

(a) Derive the first three terms in the high-temperature expansion for Z_{rot} (Mulholland's formula). [See, *e.g.*, Abramowitz and Stegun, *Handbook of Mathematical Functions*, Sec. 3.6.28, for the Euler-Maclaurin formula. Be sure to keep enough of the derivative terms, and expand all results to a consistent order in Θ_{rot}/T.]

(b) Use your result to determine S_{rot} and c_{rot}, the rotational specific heat per molecule, to the same order.

LD 27: The rotational partition function and specific heat of H_2^+: the remarkable effect of statistics.

(a) The proton has spin $s = \frac{1}{2}$. The equilibrium separation of the protons in the H_2^+ molecule is 1.06 Å. Obtain an expression for the rotational partition function of H_2^+ in terms of appropriate statistical weights and the rotational partition functions Z_{even} and Z_{odd}, defined as sums over even and odd values of ℓ. Explain your reasoning carefully.

Calculate Z_{even} and Z_{odd} numerically for $0 \leq T/\Theta_r \leq 4$ by using the series expansions carried to a sufficient number of terms. Plot the results and compare with that given by the appropriate multiple of Mulholland's formula. Mark the boiling points of H_2 (20.3 K) and N_2 (77.4 K) for reference. Plot in addition the ratio $Z^{S=1}/Z^{S=0}$ of the equilibrium fractions of H_2^+ molecules with total nuclear spins $S = 0, 1$, and comment on the limiting behaviors for $T \to 0, \infty$.

(b) Calculate the rotational specific heat per molecule c_{rot} numerically using the series expansion for Z_{rot}. Plot c_{rot} carefully for H_2^+ as a function of T/Θ_r for $0 \leq T/\Theta_r \leq 4$. Determine the limiting forms of c_{rot} (not just the limits) analytically for $T \gg \Theta_r$ and $T \ll \Theta_r$, and compare them with the numerical result. For what range of temperatures (in K) is the system essentially classical? [Hint: the analytic result for c_{rot} is simple when expressed in terms of Z_{rot} and its derivatives with respect to $x = \Theta_r/T$. Write out the series defining the derivatives you need, and expand as appropriate in getting the analytic result for $T \to 0$.]

LD 28: Determining past climates: isotope concentrations and thermal histories

The determination of average paleotemperatures and temperature fluctuations is of great interest, e.g., for tracking the thermal history of the oceans during the ice ages, or for the detection of long-term climatic changes. One method involves the measurement of the relative concentrations of the stable isotopes ^{18}O and ^{16}O in glacial ice cores or in rock cores from precipitates such as calcite ($CaCO_3$). The mean ratio of ^{18}O to ^{16}O in the atmosphere and ocean is $\sim 0.2\%$. Since $CaCO_3$ precipitates mainly as animal shells, the ratio of ^{18}O to ^{16}O in the rock reflects the local ratio near the ocean surface at the time the shells were formed. Similarly, the ratio of ^{18}O to ^{16}O in glacial ice reflects the local ratio in atmospheric water vapor when the snow fell. The ratios are different in the ocean and atmosphere and are observed to vary with temperature.

(a) Show that there can *no* such isotope effect classically for equilibrium systems in which the molecular Hamiltonian has the standard form

$$H^i = \sum_{\text{isotopes } I} \sum_{j=1}^{N_I} \frac{\mathbf{p}_j^2}{2m_I} + U^i(\{\mathbf{q}\}),$$

in each phase i. Here m_I is the mass of a molecule containing the isotope I. The potentials $U^i(q)$ are determined by the electronic properties of the molecules and are independent of the isotope in question. Show, in particular, that the equilibrium ratios $n_I^{i'}/n_I^{i}$ of the number densities in phases i' and i are the same for all isotopes. [Hint: Write the configuration integral as $\int \Pi_j d^3q_j \, e^{-\beta U^i(q)}/V_i^N$ where V_i is the volume of phase i. Show that $\mu_I^i = kT \ln n_I^i \lambda_I^3 + \mu_0^i$ where μ_0^i is the same for all isotopes of a given substance in phase i, then consider the conditions for equilibrium between phases. Note that the configuration integral is independent of the division of the molecules between the isotopes I.]

(b) Suppose the potential $U((\{\mathbf{q}\}) = -U_0$ in phase 1, U_0 constant, and $U((\{\mathbf{q}\}) = 0$ in phase 2. Calculate the number of molecules I that cross from region 1 to region 2 per unit area per second (the number flux), and the number that cross from region 2 to region 1. Show that the condition of equal fluxes in the two directions at a common temperature T leads to a result for the ratio n_I^1/n_I^2 equivalent to that obtained in (a). [Hint: It will be useful to consider the flow across an infinitesimal area dA and to change to the energy associated with the motion perpendicular to dA as a variable in evaluating an integral you will encounter.]

(c) The result of (a) shows that any isotope effect must involve nonequilibrium or quantum effects. The ocean and atmosphere are not in overall equilibrium because of rapid atmospheric motions, heat transport, temperature gradients in the atmosphere, etc. Use the results from (b) for nonequilibruium situations to show that temperature-independent changes in isotope ratios occur (Rayleigh fractionation). Use the result to construct a qualitative argument that shows how the $^{18}O/^{16}O$ ratio should change with temperature in sea water, atmospheric water vapor, and snow during a cold glacial period. Take into account the effects of evaporation and precipitation and the continued lack of equilibrium. What are the expected effects on the ratio in glacial ice deposited as snow, and on the $CaCO_3$ in animal shells deposited from the ocean?