

PY541 Problem Set 4: Due Thursday, October 24, 2002 in class

1) Consider the vibrational partition function of a diatomic molecule beyond the harmonic approximation. Expand the inter-atomic potential as:

$$V(r) = V_0 + (K/2)(r - r_0)^2 + b(r - r_0)^4, \quad (1)$$

Here r_0 is the equilibrium inter-atomic separation, V_0 , K and b are constants. There is normally a cubic term which can be as important as the quartic one but we ignore it here for simplicity. You may make the approximation that $x = r - r_0$ takes values from $-\infty$ to ∞ .

a) Write the formula for the full vibrational partition function in the classical approximation and then expand it to first order in b assuming b is small, obtaining an explicit formula for this first order correction.

b) Now write an exact formula for the quantum partition function as an operator trace and again expand it to first order b .

Hints: To do this it is convenient to rewrite the operator \hat{x} in terms of raising and lowering operators, a^\dagger and a . (See almost any book on quantum mechanics. Here I write \hat{x} for the operator corresponding to the position.) These obey:

$$\begin{aligned} [a, a^\dagger] &= 1 \\ \hat{x} &= (\hbar/2)^{1/2}(a + a^\dagger)/(K\mu)^{1/4}. \end{aligned} \quad (2)$$

It is convenient to introduce the number operator:

$$\hat{n} \equiv a^\dagger a. \quad (3)$$

This has eigenvalues consisting of the non-negative integers and the Hamiltonian is simply $H = \omega(\hat{n} + 1/2)$. By commuting around factors of a and a^\dagger it is possible to show that:

$$\hat{x}^4 = \alpha \hat{n}^2 + \gamma \hat{n} + \delta + \dots, \quad (4)$$

where α , γ and δ are certain constants which you can find and the \dots represent operators, O which do not commute with \hat{n} and change the quantum number n so that $\langle n|O|n \rangle = 0$. These terms may be discarded and the trace over the other terms reduces to a straightforward sum over n which can be evaluated exactly.

c) Check whether the quantum result reduces to the classical one at high T .

2) The spectral lines from a star produced by atomic transitions are broadened by random Doppler shifts due to the thermal motion of the atoms in the star. Show that the intensity of light at wave-length λ is:

$$I(\lambda) \propto \exp \left[\frac{-mc^2(\lambda - \lambda_0)^2}{2\lambda_0^2 kT} \right]. \quad (5)$$

Here λ_0 is the wave-length for an atom at rest, m is the mass of the atom and T is the temperature of the star. Calculate $\sqrt{(\lambda - \lambda_0)^2}/\lambda_0$ for H-atoms in the sun, where $T=6000\text{K}$.

3) Consider a container of H_2 molecules at $T = 40\text{K}$. Assume that initially the proportion of molecules with total nuclear spin $S_n = 1$ to total nuclear spin $S_n = 0$ is 3:1, the ratio at high temperatures. After about a year the nuclear spin distribution will relax to equilibrium. Calculate the change in entropy per molecule and the change in Helmholtz free energy per molecule from this process. Comment on the sign of each change and explain how it is consistent with the second law of thermodynamics.

4) Assume that the density of H atoms at the surface of the sun is $10^{25}/m^3$ and that the temperature is 6,000K. Assume that the sun is electrically neutral and ignore all other atoms in the sun. Calculate the density of H atoms in the first excited electronic states. The excitation energy is 10.2eV and these states are 4-fold degenerate. Now calculate the number of ionized protons, using the ideal gas approach. The ionization energy is 13.6eV. You should find that the density of ionized protons is greater than the density of H atoms in the first excited state, despite the fact that the energy is higher. Explain how this is possible.