Phys. 807 — Statistical Mechanics

HW4 due Thu Oct 13 at 4 p.m. in my mailbox.

Problem 1 (on classical statistical mechanics).

The total energy of a diatomic molecule is given by

$$T + U = \frac{1}{2m_1}(p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2) + \frac{1}{2m_2}(p_{x_2}^2 + p_{y_2}^2 + p_{z_2}^2) + U(r)$$

where $m_1, x_1, y_1, z_1, p_{x_1}, p_{y_1}, p_{z_1}$ and $m_2, x_2, y_2, z_2, p_{x_2}, p_{y_2}, p_{z_2}$ are the masses, coordinates and momenta of atoms 1 and 2, respectively, and r is the relative distance between them. Assuming the potential energy $U(r)$ to have the form

$$U(r) = A\left[\left(\frac{r_0}{r}\right)^9 - \left(\frac{r_0}{r}\right)^6\right] \ : \ A > 0$$

a) find the value r^* for which $U(r)$ has its minimum and give an expression of $U(r)$ in two forms:

$$U(r) = U_{\rm min}\left[a\left(\frac{r^*}{r}\right)^9 + b\left(\frac{r^*}{r}\right)^6\right] \text{ and } U = U_{\rm min} + B(r-r^*)^2 + C(r-r^*)^3 \,,$$

where $U_{\rm min}, B, C$ should be expressed in terms of A and r^*.

b) Take $U_{\rm min} = -1$ eV and verify that $A \gg k_B T$ at room temperatures. Neglecting the cubic and higher terms in $U(r)$ and the variation in the moment of inertia due to deviations of r from r^*, calculate the root mean square $\sqrt{\overline{(r-r^*)^2}} \equiv \Delta$ and the specific heat of N molecules at the absolute temperature T.

c) As an estimate of the importance of the cubic term, take $C\Delta^3$ and determine a temperature T^* such that for $T < T^*$ one finds $C\Delta^3 < \frac{1}{10}B\Delta^2$. [$Hint$: Use 1 eV$\approx$ 12000 k_B °K.]

d) By expanding partition function in βC find correction to the specific heat induced by the cubic term.

Problem 2:

Express the mean square fluctuation of energy in quantum statistical mechanics

$$\langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2$$

in terms of heat capacity C_V (and temperature T).

Problem 3:

A harmonic oscillator is kept at a low temperature T such that $\frac{k_B T}{\hbar\omega} \ll 1$. Assuming that only the ground state and the first excited state are occupied, find the mean energy of the oscillator as a function of the temperature T.