Chem 534: Problem Set #7

Due in class: Tues., Nov. 17th

(1) Determine the most probable velocity in a Maxwell-Boltzmann velocity distribution.

(2) Determine the fluctuation in the translational kinetic energy $\sigma_\epsilon$ from the Maxwell-Boltzmann velocity distribution.

Hint: your first step is to use the result from class, $\langle v^2 \rangle = \left( \frac{3kT}{m} \right)$, to show that

$$\langle \epsilon \rangle^2 = \left( \frac{3}{2} kT \right)^2.$$

(3) Consider the two-dimensional harmonic oscillator with Hamiltonian

$$H = \frac{1}{2m} \left( p_x^2 + p_y^2 \right) + \frac{k}{2} \left( x^2 + y^2 \right)$$

According to the principle of equipartition of energy, the average energy will be $2kT$. Now transform this Hamiltonian to plane polar coordinates to get

$$H = \frac{1}{2m} \left( m^2 r^2 + m^2 r^2 \dot{\theta}^2 \right) + \frac{k}{2} r^2$$

This can then be further simplified (no need to show) to: $H = \frac{1}{2m} \left( p_r^2 + \frac{p^2_{\theta}}{r^2} \right) + \frac{k}{2} r^2$

where $p_r = m \dot{r}$ and $p_{\theta} = m r^2 \dot{\theta}$ (the dots indicate a time derivative).

Based on the last expression for $H$, can you use the equipartition theorem to predict the average energy? Why or why not? Show by direct integration in plane polar coordinates that $\bar{E} = 2kT$ (hint: the volume element is $dr d\theta d\phi$ and $0 \leq r \leq \infty$, $0 \leq \theta \leq 2\pi$, $-\infty \leq p_r \leq \infty$, $-\infty \leq p_{\theta} \leq \infty$).