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

(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

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

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

where $p_r = m\dot{r}$ and $p_\theta = mr^2\dot{\theta}$ (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 $\bar{\varepsilon} = 2kT$ (hint: the volume element is $dr\,dp_r\,d\theta\,dp_\theta$ and $0 \le r \le \infty$, $0 \le \theta \le 2\pi$, $-\infty \le p_r \le \infty$, $-\infty \le p_\theta \le \infty$)