**10.40 Thermodynamics** **Fall 2003**
**Problem Set 9**

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In this problem set, you will use molecular simulations in order to compute some properties of a simple model of water, TIP3P (CHARMM), as discussed in class. Your calculations will be toy calculations to give you a feel for the application and potential of molecular simulations, without the computational intensity or methodological sophistication of research level computations.

1. For 60 TIP3P (CHARMM) water molecules in a 15Å×15Å×15Å box, compute $P$, $\underline{U}$, and $\underline{C_V}$, at 300 K and at 500K, running for 1000 heat-up steps and 10,000 and 20,000 equilibrium steps. Also, compute the standard deviations of $P$ and $\underline{U}$. If you split up the 20,000 step run into 4 pieces and compute $\underline{C_V}$ and the standard deviations for the averages of $P$ and $\underline{U}$ of the 4 pieces, what do you get? What are the limits of these numbers as the molecular dynamics trajectory lengths get very large? Finally, what is the difference in the meaning of the standard deviations from the whole trajectory and the standard deviations of averages of pieces of the trajectory?

2. Compute at least two $P$-$V$ isotherms. See if you can find one in the liquid-vapor coexistence region. If you can find one, estimate the densities of the two phases at coexistence.

Be sure to state and justify all assumptions made.

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