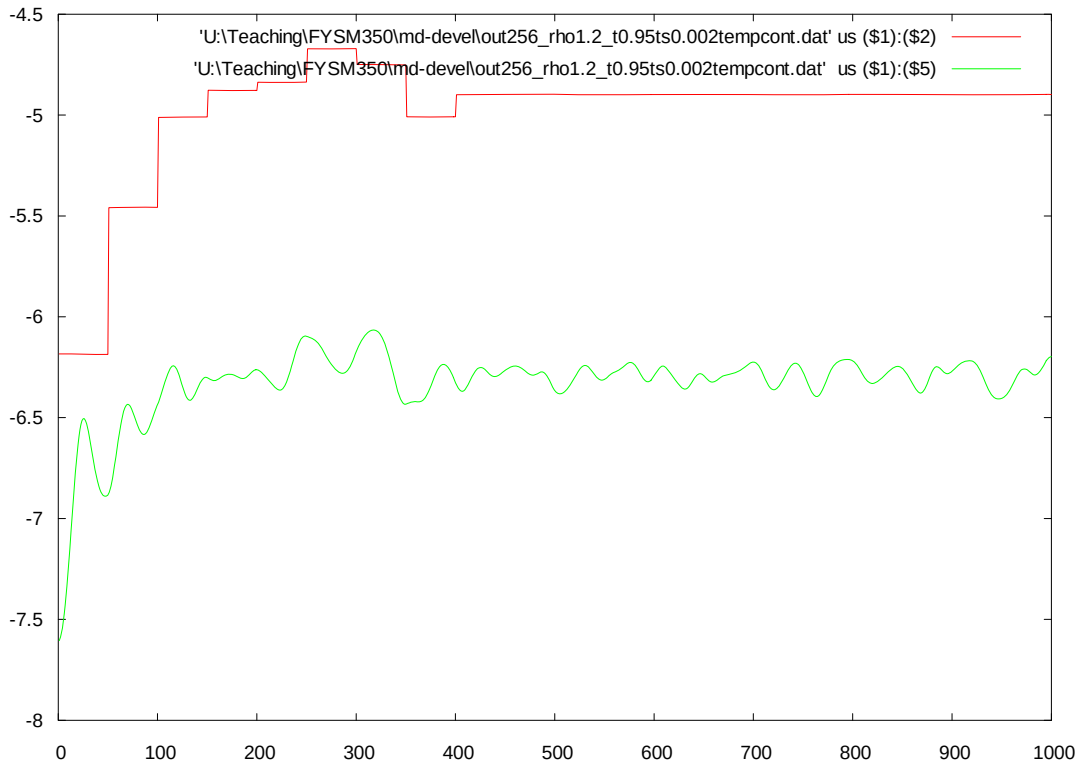
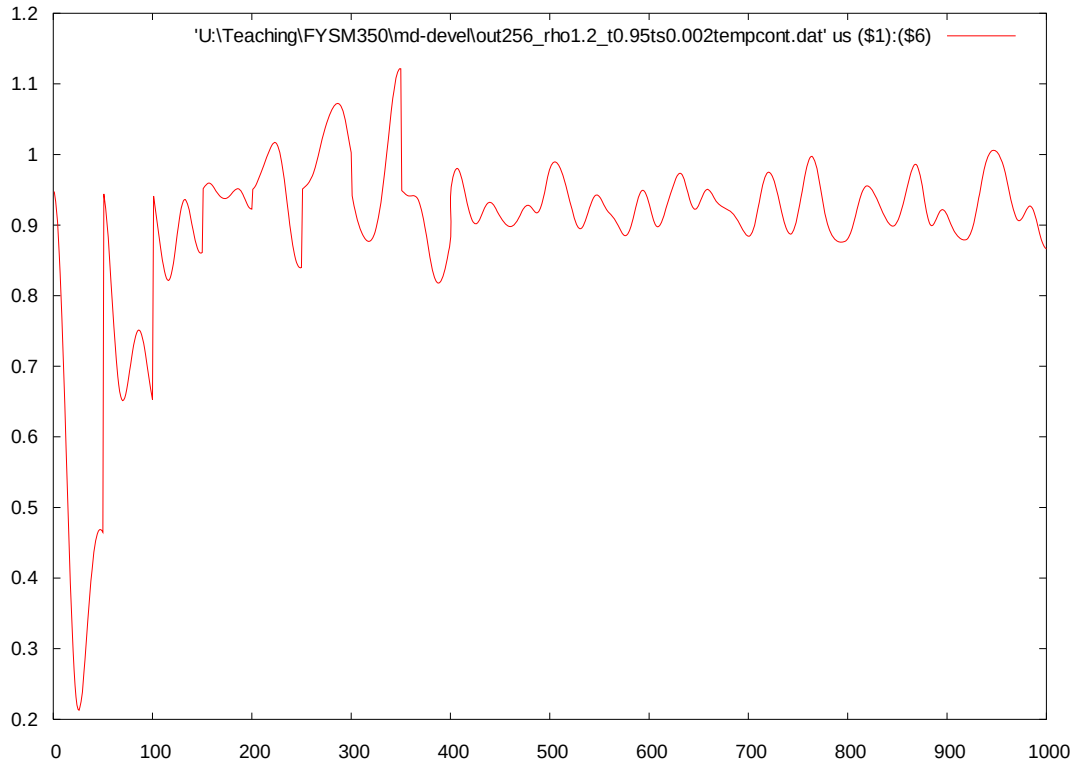
LECTURE 4 SIMULATIONS UNDER VARIOUS THERMODYNAMIC ENSEMBLES

- Standard Newtonian equations of motions create trajectories that "sample" the microcanonical (NVE) ensemble, i.e. thermodynamic averages calculated over sufficiently long trajectories should correspond to those determined from the microcanonical ensemble
- Often a control of temperature and/or pressure is needed
- Sometimes even the shape fluctuations of the simulation shell (=stress fluctuations) are important (i.e. solid-solid phase transitions)
- "temperature control" in the beginning of a NVE simulation can be achieved just by rescaling the velocities for a few times, then let the system evolve (rough method but works always). Below: total energy (red), potential energy (green), 256 atoms, dens=1.2, temp=0.95, Vscaling every 50th step during first 400 steps, calculated T(average) = 0.928 over the last 600 steps





Temperature as a function of time step, T(average)=0.928 +- 0.032

- **More sophisticated methods: Langevin dynamics (stochastic fluctuating force and correlated friction term), Nose-Hoover thermostat (see the handout), etc…**
- **Pressure control: original method by Andersen (1980), modification by Parrinello and Rahman (1980, 1981) (see the handout)**
- **NPT, NPH, NVT simulations often realized by using Gear predictor-corrector algorithms**
- **Original literature:**
  1. **H.C. Andersen, Journal of Chemical Physics 72, 2384 (1980)**
  2. **M. Parrinello and A. Rahman, Physical Review Letters 45, 1196 (1980)**
  3. **M. Parrinello and A. Rahman, Journal of Applied Physics 52, 7182 (1981)**
  4. **S. Nose, Molecular Physics 52, 255 (1984)**
  5. **W.G. Hoover, Physical Review A 31, 1695 (1985)**