

1. Boltzmann probability

The first excited state ($n = 2$) of hydrogen lies by 10.2 eV above the ground state ($n = 1$). Calculate the fraction of hydrogen atoms in the excited state in the solar photosphere ($T = 5800$ K). Neglect higher excited states.

*Discuss convergence/divergence of the sum over all excited states.

Hint: The multiplicity of the $n = 1$ level is 2 (2 spin projections), the multiplicity of the $n = 2$ level is $8 = [1(s)+3(p)] \times 2$.

qdd 9.9

2. Boltzmann probability again

Water (H_2^{16}O) vibrations are (in cm^{-1}): 3657.1, 1594.7, 3755.9. Calculate the population of water molecules in the ground state at the boiling point. Is the rigid water molecule approximation appropriate?

8.66

3. Entropy

Calculate the minimum energy (as required by the Second Law of Thermodynamics) needed at temperature 300 K to store 1TB of data.

1.87

4. Hydrogen bond

- Estimate the energy of a hydrogen bond from the vaporization enthalpy of water (25°C : $\Delta_{\text{vap}}H_m = 46 \text{ kJ mol}^{-1}$).
- Estimate the mean $\text{O}\cdots\text{O}$ distance in water from water density.
- *Estimate the partial charges from the experimental dipole moment of water ($\mu = 1.85 \text{ D}$, where $1 \text{ D} = 1 \text{ Debye} = 3.335641 \times 10^{-30} \text{ C m}$). The HOH angle is 104.5° .

a) $4 \times 10^{-20} \text{ J}$, b) 3 \AA , c) 0.315 e

5. Atomic force microscope (AFM)

Estimate the maximum attractive force between an atom-size tip and a silicon substrate. Approximate the substrate by a wall with uniform distribution of atoms and the tip by a single atom. The density of silicon is 2.329 g cm^{-3} . The parameters of the Lennard-Jones potential of Si are $\epsilon = 0.31 \text{ kcal mol}^{-1}$, $\sigma = 4.1 \text{ \AA}$, $M = 28 \text{ g mol}^{-1}$.

Hint: Use formula from talk [simen02.pdf](#), slide 11.

Nd 89

6. Thermal wavelength

Calculate the de Broglie wavelength

- of a water molecule at 0°C ,
- of a hydrogen atom at the same temperature.

Discuss the consequences for classical simulations.

a) 0.25 \AA , b) 1.1 \AA

7. Verlet and leap-frog

Prove that the Verlet and leap-frog methods are equivalent.

8. Uncertainties

Simulation of a fluid in the NPT ensemble gave the averaged density $\rho = m/\langle V \rangle = 0.7813(32) \text{ g cm}^{-3}$, where the standard stochastic error is given in the parentheses in the unit of the least significant digit. The simulation took 4 hours of CPU time. We are not satisfied with the accuracy and want to know the density with uncertainty $\pm 0.001 \text{ g cm}^{-3}$ at 95% confidence level. How much CPU time do we need on the same computer?

164 h = 1 week

9. Uncertainties

You calculated the following enthalpies ($H = \langle U_{\text{pot}} + pV \rangle$) of a box with with $N = 1000$ model water molecules in the NPT ensemble:

T (K)	H (1×10^{-18} J)
310	-65.186(23)
290	-67.671(21)

The values in parentheses are the estimated uncertainties in the unit of the least significant digit. Calculate the molar and specific heat capacities of the model including the error estimates (standard deviation).

74.8(9) J mol⁻¹ K⁻¹, 4.16(5) J g⁻¹ K⁻¹