

$$\begin{aligned}
 c &= 299792458 = \mathbf{2.998e+08} \text{ m s}^{-1} \\
 k &= 1.3806485e-23 = \mathbf{1.381e-23} \text{ J K}^{-1} \\
 NA &= 6.0221409e+23 = \mathbf{6.022e+23} \text{ mol}^{-1} \\
 e &= 1.6021766e-19 = \mathbf{1.602e-19} \text{ C} \\
 h &= 6.62607e-34 = \mathbf{6.626e-34} \text{ Js}
 \end{aligned}$$

### 1. Boltzmann probability

The first excited state ( $n = 2$ ) of a hydrogen atom 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  $8 = [1(s)+3(p)] \times 2$ .

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$$\begin{aligned}
 T &= 5800 = \mathbf{5800} \text{ K} \\
 DE &= 10.2 * e = \mathbf{1.634e-18} \text{ J} \\
 p &= 8 * \exp(-DE/k/T) / (2 + 8 * \exp(-DE/k/T)) = \mathbf{5.483e-09}
 \end{aligned}$$

### 2. Entropy

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

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$$\begin{aligned}
 T &= 300 = \mathbf{300} \text{ K} \\
 E_{\text{perbit}} &= k * T * \ln 2 = \mathbf{2.871e-21} \text{ J} \\
 E_{\text{min}} &= 8e12 * E_{\text{perbit}} = \mathbf{2.297e-08} \text{ J}
 \end{aligned}$$

### 3. 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 O...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  $104.5^\circ$ . Explain the difference.

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$$\begin{aligned}
 NA &= 6.0221418e+23 = \mathbf{6.022e+23} \text{ mol}^{-1} \\
 T &= 298 = \mathbf{298} \text{ K} \\
 R &= 8.3144598 = \mathbf{8.314} \text{ J mol}^{-1} \text{ K}^{-1} \\
 E &= (46e3 - R * T) / 2 / NA = \mathbf{3.614e-20} \text{ J} \\
 \rho &= 1000 = \mathbf{1000} \text{ kg m}^{-3} \\
 V &= 0.018 / \rho / NA = \mathbf{2.989e-29} \text{ m}^3 \\
 d_{00} &= V^{**}(1/3) = \mathbf{3.103e-10} \text{ m} \\
 d &= d_{00} - 1e-10 = \mathbf{2.103e-10} \text{ m} \\
 \epsilon_0 &= 8.8541878e-12 = \mathbf{8.854e-12} \text{ F m}^{-1} \\
 q &= \sqrt{E * 4 * \pi * \epsilon_0 * d / 2} = \mathbf{2.056e-20} \text{ C} \\
 q/e &= \mathbf{0.1283} \\
 \mu &= 1.85 * 3.335641e-30 = \mathbf{6.171e-30} \text{ C m} \\
 \mu_0 &= 2 * \cos(104.5 / 2 * \pi / 180) * 1e-10 = \mathbf{1.224e-10} \text{ m} \\
 q &= \mu / \mu_0 = \mathbf{5.04e-20} \text{ C} \\
 q/e &= \mathbf{0.3146}
 \end{aligned}$$

### 4. 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. Use

formula from talk simen02.pdf, slide 12. The density of silicon is  $2.329 \text{ g cm}^{-3}$ . The parameters of the Lennard-Jones potential of Si are  $\epsilon = 0.31 \text{ kcal mol}^{-1}$ ,  $\sigma = 4.1 \text{ \AA}$ ,  $M = 28 \text{ g mol}^{-1}$ . Nd 89

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eps=0.31*4184/NA = 2.154e-21 J
sig=4.1e-10 = 4.1e-10 m
rho=2329/28e-3*NA = 5.009e+28 m^-3
def f=-2*pi*eps*rho*sig**3*(-sig**3/r**4+2/5*sig**9/r**10) = (defined) N
max r=sig/2,sig*2 f = 4.098e-10 max=6.83691903865e-11 m
r=sig = 4.1e-10 m
f = 6.837e-11 N
    
```

### 5. Thermal wavelength

Calculate the de Broglie wavelength

- a) of a water molecule at  $0^\circ\text{C}$ ,
- b) of a hydrogen atom at the same temperature.

Discuss the consequences for classical simulations.

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def Lambda=sqrt(h**2/2/pi/m/k/T) = (defined) m
T=273 = 273 K
m=0.018/NA = 2.989e-26 kg
Lambda = 2.49e-11 m
Lambda/d00 = 0.08025
m=.001/NA = 1.661e-27 kg
Lambda = 1.057e-10 m
Lambda/d00 = 0.3405
    
```

### 6. Verlet and leap-frog

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

$$\begin{aligned}
 v(t + \frac{h}{2}) &= v(t - \frac{h}{2}) + h \frac{f}{m} && \left. \begin{array}{l} \\ \\ \end{array} \right\} \text{leap-frog} \\
 r(t + h) &= r(t) + h v(t + \frac{h}{2}) && \oplus \\
 \downarrow t \rightarrow t-h &&& \\
 r(t) &= r(t-h) + h v(t - \frac{h}{2}) && \ominus \\
 r(t+h) &= 2r(t) - r(t-h) && \\
 &+ h [v(t + \frac{h}{2}) - v(t - \frac{h}{2})] && \\
 &= 2r(t) - r(t-h) + h^2 \frac{f}{m} \equiv \text{Verlet} &&
 \end{aligned}$$

### 7. Boltzmann probability again

Water ( $\text{H}_2^{16}\text{O}$ ) vibrations are (in  $\text{cm}^{-1}$ ): 3657.1, 1594.7, 3755.9. Calculate the population of water molecules in the ground state at the boiling point. %8'66

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nu=1594.7*100*c = 4.781e+13 Hz
E=nu*h = 3.168e-20 J
    
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$$T=373.15 = \mathbf{373.1} \text{ K}$$

$$p=\exp(-E/k/T) = \mathbf{0.002136}$$

$$1-p = \mathbf{0.9979}$$

## 8. 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)	$H$ ( $1 \times 10^{-18}$ J)
310	-65.186(23)
290	-67.671(21)

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

$$1-8 \text{ J mol}^{-1} \text{ K}^{-1}, 4.16(5) \text{ J mol}^{-1} \text{ K}^{-1}$$

$$N=1000 = \mathbf{1000}$$

$$H_{310} = -65.186 \times 10^{-18} \times N_A / N = \mathbf{-3.926 \times 10^4} \text{ J mol}^{-1}$$

$$H_{290} = -67.671 \times 10^{-18} \times N_A / N = \mathbf{-4.075 \times 10^4} \text{ J mol}^{-1}$$

$$C_{\text{pm}} = (H_{310} - H_{290}) / 20 = \mathbf{74.83} \text{ J mol}^{-1} \text{ K}^{-1}$$

$$C_{\text{sp}} = C_{\text{pm}} / 18 = \mathbf{4.157} \text{ J g}^{-1} \text{ K}^{-1}$$

$$\text{sig}H_{310} = 0.023 \times 10^{-18} \times N_A / N = \mathbf{13.85} \text{ J mol}^{-1}$$

$$\text{sig}H_{290} = 0.021 \times 10^{-18} \times N_A / N = \mathbf{12.65} \text{ J mol}^{-1}$$

$$\text{sig}C_{\text{pm}} = \sqrt{(\text{sig}H_{310})^2 + (\text{sig}H_{290})^2} / 20 = \mathbf{0.9378} \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\text{sig}C_{\text{sp}} = \text{sig}C_{\text{pm}} / 18 = \mathbf{0.0521} \text{ J g}^{-1} \text{ K}^{-1}$$