

## Exercise 7 Properties of a liquid

- We would like to determine the radial distribution function of a liquid with a known potential energy function. How would you do this in a Metropolis Monte Carlo simulation? What are the two points for caution when performing an ensemble average in general and the two points of caution when calculating the RDF in particular?
- We would also like to determine the free energy of this liquid. Why is this not possible to determine in the same way as the radial distribution function?
- How would you do it then?

## Exercise 8 Self-diffusion constant

- If you want to determine the self-diffusion constant of water, which property would you sample to achieve this?
- How would you obtain this property practically? What do you need to compute, average, store etc.? Is this the only way?
- Which two simulation methods could you use and why?
- Name an advantage for each method over the other.

## Exercise 9 Rate of a torsion rotation

We consider the rotation of the methyl groups around the C-C bond (torsion angle  $\phi$ ) of the molecule ethane,  $\text{C}_2\text{H}_6$ . The molecules torsion energy,  $\epsilon_t$  around the minimum can be approximated by  $\epsilon_t = k(\phi - \pi/3)^2$  with  $k = 30$  kJ/mol. At the saddle point (eclipsed at  $\phi = 0$  rad), the potential energy can be approximated by  $\epsilon_t = 12\text{kJ/mol} - k(\phi)^2$  with the same value for  $k$ .

- What is the activation energy?
- What assumption is made in harmonic transition state theory on the potential energy surface? Does this apply here?
- For a torsion movement  $\mu$  is not the reduced mass but the reduced moment of inertia. On which coordinates would the reduced moment of inertia belonging to  $\phi$  depend? Assume that all other coordinates remain the same through out the transition. We choose the  $z$ -axis parallel to the C-C bond.
- Determine  $k_{\text{HTST}}$  at 300 K. Use  $\mu = 1 \times 10^{-46}$  kg m<sup>2</sup> for the reduced moment of inertia.
- If we would be able to determine the real rate, we would find that it differs from the HTST rate. Why is this? Which rate is higher?