# Self-assessment exercises for Molecular and Materials Modeling

## Exercise 1: Volume work

A compressor adiabatically compresses a gas, which originally is at room tem- perature To and ambient pressure Po. After the gas has passed through a water cooled system of pipes (isobaric cooling), it leaves the machine again possessing the temperature To but with the pressure P1.

Calculate the work necessary for this process wa. Also calculate the work wb in the case of a reversible, isothermal compression yielding the identical final state. Sketch the ratio wa/wb as function of P1/Po with CV = (5/2)nR. Hint: Make a sketch of the processes in term of suitable thermodynamic variables. Assume an ideal gas.

## Exercise 2: Classical heat capacity

Demonstrate that the heat capacity, $C_v$, of a classical system can be calculated from fluctuations of the total energy in the canonical ensemble as

$$C_v = \frac{\langle \mathcal{U}^2 \rangle - \langle \mathcal{U} \rangle^2}{k_B T^2}$$

Where $\langle \cdot \rangle$ indicates a canonical Boltzmann average.

## Exercise 3: Variational principle

Estimate the ground state energy of the one-dimensional harmonic oscillator described by the quantum Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + m\omega^2 \hat{x}^2$$

using the trial wavefunction

$$\psi(x;\gamma) = A \exp\left(-\gamma |x|\right)$$

where $A$ is the normalization and $\gamma$ is the variational parameter to be optimized. Compare your result with the exact one, $E_0 = \hbar\omega/2$.

## Exercise 4: Particle in a box

Find eigenfunctions and eigenvalues of the following quantum Hamiltonian describing a particle confined in a one-dimensional box

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$$

where $V(x) = +\infty$ if $|x| > a$ ($a \in \mathbb{R}_{>0}$), and $V(x) = 0$ otherwise.