Exercise 1

Release:	23.02.2024	online
Hand-in:	28.02.2024	`yuchen.wang@phys.chem.ethz.ch`

In this exercise you will write a program to sample the equilibrium density of a harmonic oscillator, to model the thermodynamic properties of molecular bonds. You may use any programming language, but the official hints and solutions will be written in Python 3. As a starting guide we provide a skeleton code `skeleton.py`. You will continue to build upon this program in future exercises, so keep it tidy and well commented. When submitting, please include your source code as a `.py` file and your (appropriately labelled) plots and answers as a PDF document.

Problem 1: Classical and quantum statistics

The classical Hamiltonian for a one-dimensional harmonic oscillator is

$$H(x,p) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2, \tag{1.1}$$

and the corresponding thermal distribution is

$$\rho_{\mathrm{cl}}(x,p) = \frac{1}{Q_{\mathrm{cl}}}\,\mathrm{e}^{-\beta(\frac{p^2}{2m}+\frac{1}{2}m\omega^2x^2)}, \tag{1.2}$$

where Q_{cl} is the classical partition function in Eq. (22) of your notes.

a) Write a code that samples N phase-space points (x,p) from the classical thermal distribution in Eq. (1.2).
Hint: Note that Eq. (1.2) is a product of two normal distributions. What are their means and standard deviations?

b) Write a code that samples N phase-space points (x,p) from the thermal Wigner distribution[1]

$$\rho_{\mathrm{W}}(x,p) = 2\alpha\,\mathrm{e}^{-\alpha(\frac{m\omega}{\hbar}x^2+\frac{1}{m\omega\hbar}p^2)}, \tag{1.3}$$

where $\alpha = \tanh\frac{\beta\hbar\omega}{2}$.

c) Plot the harmonic potential $V(x) = m\omega^2x^2/2$ for $m=\omega=\hbar=\beta=1$ on the interval $-3 \le x \le 3$. Set your y-axis range to $0 \le y \le 1.5$. Sample $N = 1000$ x-points from the classical and Wigner thermal distribution in Eq. (1.2) and (1.3), and plot a histogram of the result on the same figure as the potential. Use at least 100 bins and make sure to label your histograms. Increase the number of samples N until the distributions appear converged. For comparison, on the same figure plot the ground-state distribution $|\psi_0(x)|^2 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2}\mathrm{e}^{-m\omega x^2/\hbar}$. Don't forget to add comments in your code to make it more legible.
Remark: It might seem unnecessary to sample the densities when you could plot them directly, but sampling is a powerful tool for computing integrals like expectation values. In the following weeks, you will use the samples as starting points for dynamical trajectories.

[1] A derivation can be found in D. J. Tannor, *Introduction to Quantum Mechanics: A Time-Dependent Perspective* (University Science Books, 2007), p. 68–69.

d) Make a new plot displaying the same functions and sampled distributions as in 1c) for $\beta = 10$. Comment on the difference between the two.

e) State what values of m, ω, $\hbar$ and β best describe a stretch mode of a typical molecule at room temperature. For this system, which of the distributions (classical or Wigner) gives a more realistic description of the thermal statistics?

f) Compute the thermal expectation values $\langle x \rangle$, $\langle x^2 \rangle$ and $\langle xp \rangle$ at $\beta = 1$ and 10 for both distributions using sampling. Calculate the corresponding analytical expressions by hand or with Mathematica. Do the numerical values agree with the analytical results?
Hint: To evaluate the integrals by hand, you may use the following formulae

$$\int_{-\infty}^{+\infty} \mathrm{e}^{-ax^2}\,\mathrm{d}x = \sqrt{\frac{\pi}{a}}, \qquad \int_{-\infty}^{+\infty} x^2\,\mathrm{e}^{-ax^2}\,\mathrm{d}x = \frac{1}{2}\sqrt{\frac{\pi}{a^3}}. \tag{1.4}$$

g) Plot two-dimensional histograms of (x, p) at $\beta = 1$ and 10 for each of the two distributions. Set the ranges to $-2 \leq x \leq 2$, $-2 \leq p \leq 2$. Comment on the differences between the plots.