Molecular quantum dynamics: Exercise series 12

Problem 1: Classical and quantum thermal energy of the simple harmonic oscillator (SHO)

(a) **Classical thermal energy** $\langle E \rangle_{\mathrm{CL}}$: In class, we used the equipartition theorem to find that $\langle E \rangle_{\mathrm{CL}} = k_B T$. Here, derive the same result using the "molecular dynamics with pen and paper" approach. I.e., start from the phase space average

$$\langle E \rangle_{\mathrm{CL}} = \frac{1}{Z_{\mathrm{CL}}} \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dp\, E(q,p)\, e^{-\beta E(q,p)},$$
$$Z_{\mathrm{CL}} = \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dp\, e^{-\beta E(q,p)}$$

where Z_{CL} is the classical partition function. Insert the energy of the SHO, $E(q,p) = \frac{p^2}{2m} + \frac{1}{2}kq^2$, and evaluate the resulting Gaussian integrals.
Hint: Use the following table for integrals $I(n) = \int_{-\infty}^{\infty} x^n e^{-ax^2} dx$:

$$I(0) = \left(\frac{\pi}{a}\right)^{1/2} \quad \text{and} \quad I(2) = \frac{1}{2}\left(\frac{\pi}{a^3}\right)^{1/2}.$$

(b) **Quantum thermal energy** $\langle E \rangle_{\mathrm{QM}}$**:** In the next lecture, we will show that

$$\langle E \rangle_{\mathrm{QM}} = \frac{\frac{\hbar\omega}{2}}{\tanh \frac{\beta\hbar\omega}{2}}.$$

Show that at very high temperatures the quantum thermal energy approaches the classical result from (a), and that at low temperatures, the quantum thermal energy approaches the zero point energy of the SHO.