Molecular quantum dynamics: Solutions 12

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

$$\beta = \frac{1}{k_B T} \qquad \langle E \rangle_{\mathrm{CL}} = k_B T \qquad E_{\text{zero-point}} = \frac{\hbar\omega}{2}$$

(a)

$$\begin{aligned}
Z_{\mathrm{CL}} &= \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dp \; e^{-\beta E(q,p)} \\
&= \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dp \;\exp\left(-\frac{\beta}{2m}p^2 - \frac{\beta k}{2}q^2\right) \\
&= \int_{-\infty}^{\infty} dp \;\exp\left(-\frac{\beta}{2m}p^2\right) \int_{-\infty}^{\infty} dq \;\exp\left(-\frac{\beta k}{2}q^2\right) \\
&= \left(\frac{2m\pi}{\beta}\right)^{\frac{1}{2}} \left(\frac{2\pi}{\beta k}\right)^{\frac{1}{2}} = \frac{2\pi}{\beta}\left(\frac{m}{k}\right)^{\frac{1}{2}}
\end{aligned}$$

$$\begin{aligned}
\langle E \rangle_{\mathrm{CL}} &= \frac{1}{Z_{\mathrm{CL}}} \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dp \; E(q,p) e^{-\beta E(q,p)} \\
&= \frac{1}{Z_{\mathrm{CL}}} \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dp \;\left(\frac{p^2}{2m} + \frac{1}{2}kq^2\right) \exp\left(-\frac{\beta}{2m}p^2 - \frac{\beta k}{2}q^2\right) \\
&= \frac{1}{Z_{\mathrm{CL}}} \int_{-\infty}^{\infty} dp \;\left[\frac{p^2}{2m}\exp\left(-\frac{\beta}{2m}p^2\right) \int_{-\infty}^{\infty} dq \;\exp\left(-\frac{\beta k}{2}q^2\right)\right. \\
&\qquad\qquad \left. + \frac{k}{2}\exp\left(-\frac{\beta}{2m}p^2\right) \int_{-\infty}^{\infty} dq \; q^2 \exp\left(-\frac{\beta k}{2}q^2\right)\right] \\
&= \frac{1}{Z_{\mathrm{CL}}} \int_{-\infty}^{\infty} dp \;\left[\frac{p^2}{2m}\exp\left(-\frac{\beta}{2m}p^2\right)\left(\frac{2\pi}{\beta k}\right)^{\frac{1}{2}} + \frac{k}{2}\exp\left(-\frac{\beta}{2m}p^2\right)\cdot\frac{1}{2}\left(\frac{2^3\pi}{\beta^3 k^3}\right)^{\frac{1}{2}}\right] \\
&= \frac{1}{Z_{\mathrm{CL}}} \left[\frac{1}{2m}\left(\frac{2\pi}{\beta k}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} dp \; p^2 \exp\left(-\frac{\beta}{2m}p^2\right) + \frac{k}{4}\left(\frac{8\pi}{\beta^3 k^3}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} dp \;\exp\left(-\frac{\beta}{2m}p^2\right)\right] \\
&= \frac{1}{Z_{\mathrm{CL}}} \left[\frac{1}{2m}\left(\frac{2\pi}{\beta k}\right)^{\frac{1}{2}} \cdot \frac{1}{2}\left(\frac{2^3 m^3 \pi}{\beta^3}\right)^{\frac{1}{2}} + \frac{k}{4}\left(\frac{8\pi}{\beta^3 k^3}\right)^{\frac{1}{2}}\left(\frac{2m\pi}{\beta}\right)^{\frac{1}{2}}\right] \\
&= \frac{1}{Z_{\mathrm{CL}}} \left[\frac{\pi}{\beta^2}\left(\frac{m}{k}\right)^{\frac{1}{2}} + \frac{\pi}{\beta^2}\left(\frac{m}{k}\right)^{\frac{1}{2}}\right] \\
&= \frac{2\pi}{\beta^2 Z_{\mathrm{CL}}}\left(\frac{m}{k}\right)^{\frac{1}{2}} = \frac{1}{\beta} = \boxed{k_B T}
\end{aligned}$$

(b) Useful relations:

$$\tanh(x) = \frac{e^{2x}-1}{e^{2x}+1} \qquad e^x = \sum_{k=0}^{\infty} \frac{x^k}{k!} = 1 + x + \cdots$$

$$\langle E \rangle_{\mathrm{QM}} = \frac{\hbar\omega}{2} \frac{1}{\tanh \frac{\beta\hbar\omega}{2}} = \frac{\hbar\omega}{2} \frac{\exp(\beta\hbar\omega)+1}{\exp(\beta\hbar\omega)-1}$$

At a very high temperature (large T), β is small. We approximate the expression using the Taylor series (to the first order):

$$\langle E \rangle_{\mathrm{QM}} = \frac{\hbar\omega}{2} \frac{\beta\hbar\omega + 2}{\beta\hbar\omega} = \frac{\beta\hbar\omega + 2}{2\beta} = \frac{\hbar\omega}{2} + \frac{1}{\beta}.$$

As $T \to \infty$, $\beta \to 0$, the first term can be neglected as it becomes smaller compared to the second term:

$$\langle E \rangle_{\mathrm{QM}} \simeq \frac{1}{\beta} = \boxed{k_B T}$$

As the temperature approaches 0: $T \to 0$, $\beta \to \infty$,

$$\lim_{\beta\to\infty} \langle E \rangle_{\mathrm{QM}} = \frac{\hbar\omega}{2} \lim_{\beta\to\infty} \frac{\exp(\beta\hbar\omega)+1}{\exp(\beta\hbar\omega)-1} = \boxed{\frac{\hbar\omega}{2}}.$$

Alternatively, we can also directly apply the fact $\lim_{x\to\infty} \tanh(x) = 1$ here.