Ring Polymer Molecular Dynamics

For a quantum system of Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} = \frac{\hat{p}^2}{2m} + V(q)\,, \tag{1}$$

we are often interested in the partition function

$$\begin{aligned} Z &= \sum_{|n\rangle} \mathrm{e}^{-\beta E_n} \\ &= \sum_{|n\rangle} \mathrm{e}^{-\beta \langle n|\hat{H}|n\rangle}\,. \end{aligned} \tag{2}$$

Defining the exponential of an operator via power series, one can write

$$Z = \sum_{|n\rangle} \left\langle n \middle| \mathrm{e}^{-\beta\hat{H}} \middle| n \right\rangle = \operatorname{tr} \mathrm{e}^{-\beta\hat{H}}\,, \tag{3}$$

assuming convergence.

Claim 1. Next, we want to show that

$$\mathrm{e}^{-\beta\hat{H}} = \lim_{N\to\infty} \left[\mathrm{e}^{-\frac{\beta}{N}\hat{H}}\right]^N\,. \tag{4}$$

This seems trivial, but it actually isn't. $\hat{H} = \hat{T} + \hat{V}$, and in general $\hat{T}$ and $\hat{V}$ do not commute with each other. This will cause a little trouble.

We need the following result from Lie algebra.

Lemma 2 (Baker–Campbell–Hausdorff formula). For possibly non-commutative X and Y in the Lie algebra of a Lie group,

$$\mathrm{e}^X \mathrm{e}^Y = \mathrm{e}^Z\,, \tag{5}$$

where Z is given by

$$Z = X + Y + \frac{1}{2}[X,Y] + \frac{1}{12}([X,[X,Y]] + [Y,[Y,X]]) + \dots, \tag{6}$$

in which $[-,-]$ is the commutator.

This simply states that once X and Y are non-commutative, we no longer have $\mathrm{e}^X\mathrm{e}^Y = \mathrm{e}^{X+Y}$ — otherwise this will be same as $\mathrm{e}^Y\mathrm{e}^X$ and the non-commutativity will be broken. Instead, we will have some terms related to the commutators of X and Y introduced into the exponent.

From this, one can show that

$$\left[\exp\left(\frac{A}{N}\right)\exp\left(\frac{B}{N}\right)\right]^N = \exp\left(A + B + \frac{1}{2N}[A,B] + \dots\right)\,. \tag{7}$$

The factor $\frac{1}{2N}$ in front of the commutator is not straightforward to work out, but one can easily see that it is $O(\frac{1}{N})$, and hence all the remainders $\to 0$ as $N \to \infty$. This gives the *Lie product formula*

$$\mathrm{e}^{A+B} = \lim_{N\to\infty} \left(e^{A/N}\mathrm{e}^{B/N}\right)^N\,. \tag{8}$$

Applying this to $\beta\hat{H} = \beta\hat{T} + \beta\hat{V}$, we get out claimed result.

This allows us to write

$$Z = \sum_{|n\rangle} \lim_{N\to\infty} \left\langle n \middle| \left[\mathrm{e}^{-\frac{\beta}{N}\hat{H}} \right]^N \middle| n \right\rangle . \tag{9}$$

We let the complete orthonormal set $\{|n\rangle\}$ be the position basis $\{|q_1\rangle\}$, and correspondingly replace the sum by the integral. This gives

$$Z = \lim_{N\to\infty} \int \mathrm{d}q_1 \left\langle q_1 \middle| \left[\mathrm{e}^{-\frac{\beta}{N}\hat{H}} \right]^N \middle| q_1 \right\rangle . \tag{10}$$

We have the freedom to inset identity operators

$$1 = \int \mathrm{d}q_i \, |q_i\rangle \langle q_i| \tag{11}$$

anywhere we want. We can insert $N-1$ of them, each sandwiched between two of the N exponential operators, giving

$$Z = \lim_{N\to\infty} \int \mathrm{d}q_1 \dots \mathrm{d}q_N \left\langle q_1 \middle| \mathrm{e}^{-\frac{\beta}{N}\hat{H}} \middle| q_2 \right\rangle \left\langle q_2 \middle| \mathrm{e}^{-\frac{\beta}{N}\hat{H}} \middle| q_3 \right\rangle \dots \left\langle q_N \middle| \mathrm{e}^{-\frac{\beta}{N}\hat{H}} \middle| q_1 \right\rangle . \tag{12}$$

Now we have N identical-looking matrix elements in the integrand, each looks like

$$M_i = \left\langle q_i \middle| \mathrm{e}^{-\frac{\beta}{N}\hat{H}} \middle| q_{i+1} \right\rangle , \tag{13}$$

where we have identified $q_1 \equiv q_{N+1}$. This equals to

$$M_i = \left\langle q_i \middle| \mathrm{e}^{-\frac{\beta}{N}\hat{T}} \mathrm{e}^{-\frac{\beta}{N}\hat{V}} \middle| q_{i+1} \right\rangle , \tag{14}$$

because breaking the exponential only introduces error terms $O(\frac{1}{N^2})$ in the exponent, which is a higher order infinitesimal in $N \to \infty$. To evaluate this, we again use the trick of inserting an identity operator between the exponentials, giving

$$M_i = \int \mathrm{d}q_m \left\langle q_i \middle| \mathrm{e}^{-\frac{\beta}{N}\hat{T}} \middle| q_m \right\rangle \left\langle q_m \middle| \mathrm{e}^{-\frac{\beta}{N}\hat{V}} \middle| q_{i+1} \right\rangle . \tag{15}$$

The second term is trivial — $\hat{V}$ is a scalar function of coordinates, so it is diagonal in the coordinate basis, giving

$$\begin{aligned} M_i &= \int \mathrm{d}q_m \left\langle q_i \middle| \mathrm{e}^{-\frac{\beta}{N}\hat{T}} \middle| q_m \right\rangle \mathrm{e}^{-\frac{\beta}{N}\hat{V}(q_{i+1})} \delta(q_m - q_{i+1}) \\ &= \left\langle q_i \middle| \mathrm{e}^{-\frac{\beta}{N}\hat{T}} \middle| q_{i+1} \right\rangle \mathrm{e}^{-\frac{\beta}{N}\hat{V}(q_{i+1})} \end{aligned} \tag{16}$$

The first term is a bit more tricky. Since $\hat{T} = \frac{1}{2m}\hat{p}^2$, it might be a good idea to evaluate it in the momentum basis. We insert the identity operator in the momentum basis, giving

$$\left\langle q_i \middle| \mathrm{e}^{-\frac{\beta}{N}\hat{T}} \middle| q_{i+1} \right\rangle = \int \mathrm{d}p \, \langle q_i | p \rangle \left\langle p \middle| \mathrm{e}^{-\frac{\beta}{N}\hat{T}} \middle| q_{i+1} \right\rangle \tag{17}$$

Both terms are now easy to evaluate: the first one is just the position representation of momentum eigenstates

$$\langle q_i | p \rangle = \frac{1}{\sqrt{2\pi\hbar}} \mathrm{e}^{\mathrm{i}pq_i/\hbar} , \tag{18}$$

while

$$\mathrm{e}^{-\frac{\beta}{N}\hat{T}} |p\rangle = \mathrm{e}^{-\frac{\beta}{N}\frac{p^2}{2m}} |p\rangle , \tag{19}$$

so the second term is

$$\left\langle p \middle| \mathrm{e}^{-\frac{\beta}{N}\hat{T}} \middle| q_{i+1} \right\rangle = \mathrm{e}^{-\frac{\beta p^2}{2mN}} \langle p | q_{i+1} \rangle = \frac{1}{\sqrt{2\pi\hbar}} \mathrm{e}^{-\frac{\beta p^2}{2mN}} \mathrm{e}^{-\mathrm{i}pq_{i+1}/\hbar} . \tag{20}$$

Therefore,

$$\left\langle q_i \middle| \mathrm{e}^{-\frac{\beta}{N}\hat{T}} \middle| q_{i+1} \right\rangle = \frac{1}{2\pi\hbar} \int \mathrm{d}p \, \mathrm{e}^{\mathrm{i}p(q_i - q_{i+1})/\hbar} \mathrm{e}^{-\frac{\beta p^2}{2mN}} \, . \tag{21}$$

This is a Gaussian integral (after completing the square), giving

$$\left\langle q_i \middle| \mathrm{e}^{-\frac{\beta}{N}\hat{T}} \middle| q_{i+1} \right\rangle = \sqrt{\frac{mN}{2\pi\beta\hbar^2}} \exp\left(-\frac{mN}{2\beta\hbar^2} (q_i - q_{i+1})^2 \right) \, , \tag{22}$$

and so the matrix elements are

$$M_i = \sqrt{\frac{mN}{2\pi\beta\hbar^2}} \exp\left[-\frac{mN}{2\beta\hbar^2} (q_i - q_{i+1})^2 - \frac{\beta}{N} V(q_{i+1}) \right] \, . \tag{23}$$

The partition function of interest is therefore

$$Z = \lim_{N\to\infty} \left(\frac{mN}{2\pi\beta\hbar^2} \right)^{N/2} \int \mathrm{d}q_1 \ldots \mathrm{d}q_N \, \exp\left[-\sum_{i=1}^{N} \left(\frac{mN}{2\beta\hbar^2} (q_i - q_{i+1})^2 + \frac{\beta}{N} V(q_i) \right) \right] \, . \tag{24}$$

This form of the partition function starts to reveal its name 'ring polymer'. We just need a few extra steps to get there. In particular, notice the prefactor — it is exactly what is known as the thermal wavelength, which can be obtained by integrating the momentum degrees of freedom when evaluating the classical partition function. It is just instead of β, we have β/N here. Hence, we define $\beta_N = \beta/N$, the effective (inverse) temperature, and observe that

$$\left(\frac{m}{2\pi\beta_N\hbar^2} \right)^{1/2} = \frac{1}{2\pi\hbar} \int \mathrm{d}p_i \, \exp\left(-\frac{\beta_n p_i^2}{2m} \right) \, . \tag{25}$$

This allows us to finally write

$$\begin{aligned} Z &= \lim_{N\to\infty} \frac{1}{(2\pi\hbar)^N} \int \mathrm{d}p_1 \, \mathrm{d}q_1 \, \ldots \mathrm{d}p_N \, \mathrm{d}q_N \, \exp\left[-\beta_n \sum_{i=1}^{N} \left(\frac{p_i^2}{2m} + \frac{m}{2\beta_N^2\hbar^2} (q_i - q_{i+1})^2 + V(q_i) \right) \right] \\ &= \lim_{N\to\infty} \frac{1}{(2\pi\hbar)^N} \int \mathrm{d}^N\mathbf{p} \, \mathrm{d}^N\mathbf{q} \, \exp\left(-\beta_N \hat{H}_N \right) \, , \end{aligned} \tag{26}$$

where

$$\hat{H}_N = \sum_{i=1}^{N} \left(\frac{p_i^2}{2m} + \frac{m}{2\beta_N^2\hbar} (q_i - q_{i+1})^2 + V(q_i) \right) \tag{27}$$

We see something magical here. This is exactly the classical partition function of a N-particle polymer ring system connected by springs of angular frequency $\omega_i = \frac{1}{\beta_N\hbar}$, placed on a potential V at temperature β_N.