

Ring Polymer Molecular Dynamics

For a quantum system of Hamiltonian

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

we are often interested in the partition function

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

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

$$Z = \sum_{|n\rangle} \langle n | e^{-\beta \hat{H}} | n \rangle = \text{tr} e^{-\beta \hat{H}}, \quad (3)$$

assuming convergence.

Claim 1. Next, we want to show that

$$e^{-\beta \hat{H}} = \lim_{N \rightarrow \infty} \left[e^{-\frac{\beta}{N} \hat{H}} \right]^N. \quad (4)$$

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,

$$e^X e^Y = e^Z, \quad (5)$$

where Z is given by

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

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

This simply states that once X and Y are non-commutative, we no longer have $e^X e^Y = e^{X+Y}$ — otherwise this will be same as $e^Y e^X$ 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

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

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 $\rightarrow 0$ as $N \rightarrow \infty$. This gives the *Lie product formula*

$$e^{A+B} = \lim_{N \rightarrow \infty} \left(e^{A/N} e^{B/N} \right)^N. \quad (8)$$

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

This allows us to write

$$Z = \sum_{|n\rangle} \lim_{N \rightarrow \infty} \left\langle n \left| \left[e^{-\frac{\beta}{N} \hat{H}} \right]^N \right| n \right\rangle. \quad (9)$$

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

$$Z = \lim_{N \rightarrow \infty} \int dq_1 \left\langle q_1 \left| \left[e^{-\frac{\beta}{N} \hat{H}} \right]^N \right| q_1 \right\rangle. \quad (10)$$

We have the freedom to inset identity operators

$$1 = \int dq_i |q_i\rangle \langle q_i| \quad (11)$$

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

$$Z = \lim_{N \rightarrow \infty} \int dq_1 \dots dq_N \left\langle q_1 \left| e^{-\frac{\beta}{N} \hat{H}} \right| q_2 \right\rangle \left\langle q_2 \left| e^{-\frac{\beta}{N} \hat{H}} \right| q_3 \right\rangle \dots \left\langle q_N \left| e^{-\frac{\beta}{N} \hat{H}} \right| q_1 \right\rangle. \quad (12)$$

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

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

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

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

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

$$M_i = \int dq_m \left\langle q_i \left| e^{-\frac{\beta}{N} \hat{T}} \right| q_m \right\rangle \left\langle q_m \left| e^{-\frac{\beta}{N} \hat{V}} \right| q_{i+1} \right\rangle. \quad (15)$$

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

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

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

$$\left\langle q_i \left| e^{-\frac{\beta}{N} \hat{T}} \right| q_{i+1} \right\rangle = \int dp \langle q_i | p \rangle \left\langle p \left| e^{-\frac{\beta}{N} \hat{T}} \right| q_{i+1} \right\rangle \quad (17)$$

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

$$\langle q_i | p \rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{ipq_i/\hbar}, \quad (18)$$

while

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

so the second term is

$$\left\langle p \left| e^{-\frac{\beta}{N} \hat{T}} \right| q_{i+1} \right\rangle = e^{-\frac{\beta p^2}{2mN}} \langle p | q_{i+1} \rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{-\frac{\beta p^2}{2mN}} e^{-ipq_{i+1}/\hbar}. \quad (20)$$

Therefore,

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

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

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

and so the matrix elements are

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

The partition function of interest is therefore

$$Z = \lim_{N \rightarrow \infty} \left(\frac{mN}{2\pi\beta\hbar^2}\right)^{N/2} \int dq_1 \dots dq_N \exp\left[-\sum_{i=1}^N \left(\frac{mN}{2\beta\hbar^2}(q_i - q_{i+1})^2 + \frac{\beta}{N}V(q_i)\right)\right]. \quad (24)$$

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

$$\left(\frac{m}{2\pi\beta_N\hbar^2}\right)^{1/2} = \frac{1}{2\pi\hbar} \int dp_i \exp\left(-\frac{\beta_N p_i^2}{2m}\right). \quad (25)$$

This allows us to finally write

$$\begin{aligned} Z &= \lim_{N \rightarrow \infty} \frac{1}{(2\pi\hbar)^N} \int dp_1 dq_1 \dots dp_N dq_N \exp\left[-\beta_N \sum_{i=1}^N \left(\frac{p_i^2}{2m} + \frac{m}{2\beta_N^2\hbar^2}(q_i - q_{i+1})^2 + V(q_i)\right)\right] \\ &= \lim_{N \rightarrow \infty} \frac{1}{(2\pi\hbar)^N} \int d^N \mathbf{p} d^N \mathbf{q} \exp(-\beta_N H_N), \end{aligned} \quad (26)$$

where

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

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 .