

The Path Integral Partition Function

The Problem

The quantum partition function, $Z_{NVT}^{QM} = \text{Tr}(e^{-\beta\hat{H}})$, is the cornerstone of quantum statistical mechanics. In the basis of energy eigenstates, this becomes the familiar sum $Z = \sum_i e^{-\beta E_i}$. The problem is that to calculate this sum, we would first need to solve the time-independent Schrödinger equation ($\hat{H}|i\rangle = E_i|i\rangle$) to find all the energy eigenvalues (E_i), which is prohibitively difficult for any complex system.

The Path Integral Solution

The idea behind the path integral formulation is to evaluate the trace in a different, more convenient basis: the **position basis**, $|\underline{R}\rangle$.

The trace in the position basis is written as:

$$Z = \int d\underline{R} \langle \underline{R} | e^{-\beta(\hat{T} + \hat{V})} | \underline{R} \rangle$$

A key difficulty is that the kinetic (\hat{T}) and potential (\hat{V}) operators do not commute, so we cannot simply split the exponential: $e^{-\beta(\hat{T} + \hat{V})} \neq e^{-\beta\hat{T}} e^{-\beta\hat{V}}$. However, if we do make this approximation (which is only valid in the high-temperature limit), we recover the classical partition function.

The correct way to handle the non-commuting operators is to use **Trotter's theorem**:

$$e^{-\beta(\hat{T} + \hat{V})} = \lim_{P \rightarrow \infty} (e^{-\frac{\beta}{P}\hat{T}} e^{-\frac{\beta}{P}\hat{V}})^P$$

This formula breaks the operator into a product of P "slices," where P is a large integer. This allows us to calculate the partition function by inserting a complete set of position states between each of the P slices.

This mathematical procedure transforms the quantum partition function into the following form:

$$Z = \lim_{P \rightarrow \infty} \int d\underline{R}^{(1)} \dots d\underline{R}^{(P)} \exp \left(-\beta \sum_{s=1}^P \left[\frac{1}{2} m \omega_P^2 (\underline{R}^{(s)} - \underline{R}^{(s+1)})^2 + \frac{1}{P} V(\underline{R}^{(s)}) \right] \right)$$

where $\underline{R}^{(P+1)} = \underline{R}^{(1)}$.

The Classical Isomorphism

The most powerful result of this derivation is that the final expression for the quantum partition function looks exactly like the partition function for a special **classical system**. This mapping is known as the **classical isomorphism**.

In this picture:

- Each single quantum particle is represented by a **classical ring polymer** (or "necklace") made of P beads.
- The beads within a single polymer are connected to their neighbors by **harmonic springs**. The stiffness of these springs, ω_P , depends on the particle's mass, the temperature, and the number of beads, P . This spring term originates from the quantum kinetic energy.
- The actual physical potential, $V(\underline{R})$, acts between beads of the same index (e.g., bead #3 of particle A interacts with bead #3 of particle B), but its strength is scaled down by a factor of $1/P$.

This means we can calculate the exact equilibrium properties of a quantum system by performing a standard classical simulation (like MD or Monte Carlo) on its isomorphic classical system of ring polymers.

The name **path integral** comes from the interpretation that in the limit of $P \rightarrow \infty$, the sum over all possible configurations of the beads is equivalent to integrating over all possible closed "paths" the particle could take in imaginary time.