

Motivation

At low temperatures and for nuclei with small masses (like hydrogen), the quantum nature of the nuclei becomes important. All the molecular dynamics techniques discussed previously have assumed classical nuclei. To account for these quantum effects, we need to return to the principles of statistical mechanics.

Quantum and Classical Distribution Functions

To understand how to include quantum nuclear effects, we first need to establish the connection between the formalisms of quantum and classical statistical mechanics.

In **quantum statistical mechanics**, the partition function for a canonical (NVT) ensemble is a sum over all quantum states i :

$$Z_{NVT}^{QM} = \sum_i e^{-\beta E_i}$$

where $\beta = 1/(k_B T)$. The probability of finding the system in state i is $\rho_i^{QM} = \frac{e^{-\beta E_i}}{Z_{NVT}^{QM}}$.

In **classical statistical mechanics**, the partition function is an integral over all of phase space (all possible positions, q , and momenta, p):

$$Z_{NVT}^{CM} = \frac{1}{h^{3N} N!} \int dp^N dq^N e^{-\beta H(p,q)}$$

Here, $N!$ is the Gibbs factor, which corrects for the indistinguishability of particles.

A more general and powerful way to express these concepts is using the **trace** operation. In this language, the formalisms become directly analogous:

Property	Classical Mechanics (CM)	Quantum Mechanics (QM)
Partition Function	$Z_{NVT}^{CM} = Tr(e^{-\beta H})$	$Z_{NVT}^{QM} = Tr(e^{-\beta \hat{H}})$
Expectation Value	$\langle A \rangle = Tr(A\rho)$	$\langle A \rangle = Tr(\hat{A}\hat{\rho})$

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The quantum statistical operator, $\hat{\rho}$, is also known as the density matrix.

The Thermal de Broglie Wavelength: When is Quantum Important?

Classical mechanics treats particles as points. This is a good approximation when the "size" of the particles is small compared to the distances between them. In a quantum context, the effective size of a particle is given by the **thermal de Broglie wavelength**, Λ .

$$\Lambda = \sqrt{\frac{2\pi\hbar^2\beta}{m}}$$

This wavelength represents the average spatial extent of a free particle with mass m at temperature T .

- For **heavy particles** (large m) or at **high temperatures** (high T), Λ is small, and a classical description is usually sufficient.
- For **light particles** (like hydrogen) or at **low temperatures**, Λ becomes larger, and quantum effects like zero-point energy and tunneling become dominant.

The Harmonic Approximation

A simple way to estimate quantum nuclear effects is the **harmonic approximation**. This method works well for systems near a stable minimum, like atoms in a solid.

1. The potential energy is approximated as a simple parabola (a harmonic oscillator) around the minimum energy position, x_0 .
2. This is done for all the vibrational normal modes of the system.
3. The energy levels of each mode are then quantized: $E^{QM} = \hbar\omega_i(n + \frac{1}{2})$.

A key consequence is the **zero-point energy (ZPE)**, $E^{ZPE} = \frac{1}{2}\hbar\omega$, which is the minimum possible energy the system can have, even at absolute zero temperature. However, this approximation is not suitable for systems that don't have a clear potential minimum, such as liquids.