

Lecture 3: Path-Integral Statistics

Time-dependent perturbation theory and the fluctuation dissipation theorem enable dynamical quantities of interest - including rate constants, diffusion constants, absorption spectra, etc. - to be expressed in terms of equilibrium time-correlation functions of the form

$$\tilde{C}_{AB}(t) = \frac{1}{Q} \text{Tr} [\rho_0 \tilde{A}(0) B(t)]. \quad (1)$$

For the next few classes, we shall turn our attention to strategies for numerically evaluating these quantum TCFs. However, as an example, we can consider the special case of $B = 1$, such that Eq. 1 simplifies to

$$\tilde{C}_{A1}(t) = \frac{1}{Q} \text{Tr} [\rho_0 \tilde{A}] = \frac{1}{Q} \text{Tr} [\rho_0 A] = \langle A \rangle_0, \quad (2)$$

the equilibrium quantum mechanical expectation value of operator A . Therefore, before launching into the discussion of how to calculate quantum-mechanical equilibrium (i.e., thermal) TCFs, we must first discuss how to calculate quantum-mechanical thermal expectation values.

A. Boltzmann Statistics for a quantum system

Consider a system with Hamiltonian operator

$$\hat{H} = \hat{K}(\hat{p}) + \hat{V}(\hat{x}), \quad (3)$$

where \hat{K} is the kinetic energy operator, which is a pure function of the momentum, \hat{p} . We consider a system with one dimension, although generalization of the results presented here is straightforward. The Boltzmann statistics for this system is given by the canonical partition function

$$Q = \sum_{\nu} e^{-\beta E_{\nu}}, \quad (4)$$

where $\{E_{\nu}\}$ are the energy eigenvalues of the Hamiltonian, with associated eigenfunctions, $\{\psi_{\nu}\}$. Bear in mind that exact calculation of each of these eigenstates scales exponentially in cost with the dimension of the system, and also bear in mind that large systems with many thermally accessible states (such as the vibrational manifold of liquids) would require a huge number of states to converge this sum. From this perspective, the exact evaluation of the partition function in Eq. 4 is a daunting challenge.

B. Path-integral discretization

To obtain a more computationally tractable form of Eq. 4, we begin by exactly rewriting it in the position representation:

$$Q = \sum_{\nu} \langle \psi_{\nu} | e^{-\beta \hat{H}} | \psi_{\nu} \rangle = \text{Tr} \left[e^{-\beta \hat{H}} \right] = \int dx \langle x | e^{-\beta \hat{H}} | x \rangle \quad (5)$$

Then, using that $e^{-\beta \hat{H}} = e^{-\beta \hat{H}/2} e^{-\beta \hat{H}/2}$ and the resolution of the identity in the position representation,

$$1 = \int dx |x\rangle \langle x|, \quad (6)$$

then Eq. 5 becomes

$$Q = \int dx \int dx' \langle x | e^{-\beta \hat{H}/2} | x' \rangle \langle x' | e^{-\beta \hat{H}/2} | x \rangle \quad (7)$$

$$= \int dx_1 \dots \int dx_n \prod_{j=1}^n \langle x_j | e^{-\beta_n \hat{H}} | x_{j+1} \rangle, \quad (8)$$

where $\beta_n = \beta/n$ and $x_{n+1} = x_1$.

At first, this would not seem to have provided any real advantage. After all, through the various exact manipulations, we have simply rewritten the original trace in terms of other matrix elements that are equally hard to evaluate exactly. And yet there is an advantage, which arises from the fact that the matrix elements in Eq. 8 correspond to arbitrarily high temperature ($\beta_n = (k_B n T)^{-1}$) and thus may be expected to become more classical mechanical in nature. This can be seen upon considering the matrix element:

$$\langle x | e^{-\beta_n \hat{H}} | x' \rangle = \langle x | e^{-\beta_n (\hat{K}(\hat{p}) + \hat{V}(\hat{x}))} | x' \rangle = \langle x | e^{-\beta_n \hat{K}(\hat{p})} e^{-\beta_n \hat{V}(\hat{x})} | x' \rangle + O(\beta_n^2), \quad (9)$$

where the error term vanishes with increasing n (i.e., increasing temperature of the matrix element). Note that this error term is identical to the one previously encountered in our discussion of the split-operator approach to integrating wavepacket dynamics; in the path-integral context, neglect of this error term is often called the Trotter approximation.

As seen previously for the SOFT method, the advantage of introducing the Trotter approximation is that it allows for simple evaluation of the potential energy operator in the position representation,

$$\langle x | e^{-\beta_n \hat{H}} | x' \rangle = \langle x | e^{-\beta_n \hat{K}(\hat{p})} | x' \rangle e^{-\beta_n V(x')} + O(\beta_n^2), \quad (10)$$

and it allows for simple evaluation of the kinetic energy operator in Fourier space, such that by following the steps:

- Express $\hat{K} = \frac{\hat{p}^2}{2m}$,
- Introduce the resolution of the identity in the momentum representation: $1 = \int dx |x\rangle\langle x|$,
- Introduce the free particle wavefunction in the position rep.: $\langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{-ipx/\hbar}$,
- Complete the square and evaluate a Gaussian integral in p ,

we obtain

$$\langle x|e^{-\beta_n \hat{K}(\hat{p})}|x'\rangle = \left(\frac{m\omega_n}{2\pi\hbar}\right)^{1/2} e^{-\beta_n(\frac{1}{2}m\omega_n^2(x-x')^2)}, \quad (11)$$

where $\omega_n = (\beta_n \hbar)^{-1}$.

Finally, combining the results from Eqs. 8, 10, and 11, we obtain the path-integral representation for the canonical partition function

$$Q = \lim_{n \rightarrow \infty} \left(\frac{m\omega_n}{2\pi\hbar}\right)^{n/2} \int dx_1 \dots \int dx_n e^{-\beta U_{\text{eff}}(\mathbf{x})} \quad (12)$$

where

$$U_{\text{eff}}(\mathbf{x}) = \frac{1}{n} \sum_{j=1}^n \frac{1}{2} m\omega_n^2 (x_j - x_{j+1})^2 + \frac{1}{n} \sum_{j=1}^n V(x_j). \quad (13)$$

Remarkably, Eq. 12 is an exact expression for the quantum Boltzmann statistics of the system, expressed in terms of a classical mechanical configuration integral for ring-polymer with each bead in the ring polymer comprised of a copy of the system at a different position. This rigorous mapping is called the quantum-classical isomorphism, which was originally derived by Feynman and brought into the chemistry literature by Chandler and Wolynes (1981).