Lecture 5: Quantized Molecular Dynamics

In the preceding classes, we have emphasize that imaginary-time Feynman path integrals provide an appealing and computationally tractable strategy for evaluating quantum Boltzmann statistical quantities, expressing the quantum mechanical canonical partition function in terms of an isomorphic classical ring-polymer system:

$$Q = \lim_{n\to\infty} (2\pi\hbar)^{-n} \int d\mathbf{x} \int d\mathbf{p}\; e^{-\beta H_n(\mathbf{x},\mathbf{p})}, \tag{1}$$

where

$$H_n(\mathbf{x},\mathbf{p}) = \sum_{j=1}^{n} \frac{p_j^2}{2m_n} + U_{\text{eff}}(\mathbf{x}) \tag{2}$$

is the ring-polymer Hamiltonian,

$$U_{\text{eff}}(\mathbf{x}) = \sum_{j=1}^{n} \frac{1}{2} m_n \omega_n^2 (x_j - x_{j+1})^2 + \frac{1}{n}\sum_{j=1}^{n} V(x_j) \tag{3}$$

is the ring-polymer effective potential, $V(x)$ is the potential energy function for the physical system, and $m_n = m/n$ is the mass of each ring-polymer bead. Using the classical equations of motion for the ring-polymer Hamiltonian

$$\dot{x}_j = \frac{\partial H_n}{\partial p_j}, \qquad \text{and} \qquad \dot{p}_j = -\frac{\partial H_n}{\partial x_j}, \tag{4}$$

it is clear that we can numerically sample the exact quantum Boltzmann distribution for the system. In the last class, we also showed that such imaginary-time path-integral calculations should provide (in principle) all real-time dynamics information via analytical continuation, but this turns out to be numerically intractable in most practical cases.

In the current class, we consider the use of the classical ring-polymer trajectories to conveniently obtain *approximate* quantum mechanical time correlation functions (TCFs), in addition to *exact* statistical quantities.

A. Ring-Polymer Molecular Dynamics

Ring-polymer molecular dynamics (Manolopoulos, 2004) employs the classical mechanical ring-polymer trajectories (Eq. 4) to approximate the Kubo-transformed quantum mechanical

TCF for position-dependent operators A and B:

$$\tilde{C}_{\mathrm{AB}}(t) \equiv \frac{1}{\beta Q}\int_0^\beta d\lambda \; \mathrm{Tr}\left[e^{-(\beta-\lambda)\hat{H}}\hat{A}e^{-\lambda\hat{H}}e^{it\hat{H}/\hbar}\hat{A}e^{-it\hat{H}/\hbar}\right] \tag{5}$$

$$\approx \frac{(2\pi\hbar)^{-n}}{Q}\int d\mathbf{x}_0 \int d\mathbf{p}_0 \; e^{-\beta H_n(\mathbf{x}_0,\mathbf{p}_0)} A_n(\mathbf{x}_0) B_n(\mathbf{x}_t) \tag{6}$$

where $A_n(\mathbf{x}) = \frac{1}{n}\sum_{j=1}^{n} A(x_j)$ and $B_n(\mathbf{x}) = \frac{1}{n}\sum_{j=1}^{n} B(x_j)$ are the bead-averaged evaluation of operators A and B, respectively.

At an intuitive level, the RPMD approximation is compelling: the RHS of Eq. 6 assumes the form of a classical mechanical time-correlation function, and as we have seen previously in the this class, the Kubo-transformed version of the exact quantum mechanical TCF that is most compatible with symmetries and expressions of classical mechanics.

At a formal level, the RPMD approximation can be shown to satisfy many properties of exact quantum mechanics. For example, if we consider the $t = 0$ value of the TCF, it is straightforward to show that this is exactly satisfied in the RPMD approximation. [PUT THIS IN] Similarly, the RPMD approximation can be shown to exhibit other important properties, including

- Exact dynamics in the classical mechanical (high-temperature) limit.
- Exact dynamics for a purely harmonic potential energy surface.
- Exact description of the Kubo-transformed TCF in the $t \rightarrow 0$ limit, with leading-order errors of $O(t^7)$ for linear operators and $O(t^5)$ for non-linear operators.

However, from a practical standpoint, the most important advantage of the RPMD approximation is that it the RPMD equations of motion preserve the quantum Boltzmann-distribution. Therefore, RPMD exactly satisfies the classical Liouville Equation and the classical Liouville theorem, but with respect to the quantum mechanical Boltzmann distribution. To understand the importance of this, recall our derivation of the flux-side formulation of the reaction rate: A critical property of the dynamics that made this formulation possible was that the equilibrium distribution was invariant under the dynamics of the system. If this property were not satisfied, we would not have been able to arrive at the computationally tractable flux-side formulation, with the reaction rate strictly independent of the location of the dividing surface! As another example, consider a simulation of a liquid-phase system that is close to a first-order phase transition, such that quantum zero-point energy is important for keeping the system in the liquid phase; without proper preservation of the quantum Boltzmann distribution, the system might undergo phase separation as a function of time, purely as an artifact of the approximation to the dynamics! (Other examples in slides.)

Of course, an obvious shortcoming of the RPMD approximation is that we have eliminated all phase information from the real-time dynamics (note the lack of imaginary numbers...). We may thus expect RPMD to fail for problems that involve strong real-time quantum coherence effects, which is indeed the case. (Examples in slides.)

B. Centroid Molecular Dynamics

An important method that is closely related to RPMD (and which precedes it by a decade (Voth, 1994)) is centroid molecular dynamics, which reduces the path-integral representation of the ring-polymer with respect to all degrees of freedom other than the centroid mode. Starting from the path-integral representation for the partition function

$$Q = \lim_{n\to\infty} (\mathrm{const}) \int d\mathbf{x}\; e^{-\beta U_{\mathrm{eff}}(\mathbf{x})}, \tag{7}$$

where $U_{\mathrm{eff}}(\mathbf{x})$ is the same ring-polymer effective potential from Eq. 3, we can reduce this distribution with respect to the centroid position of the ring-polymer,

$$\bar{x} = \frac{1}{n}\sum_{j=1}^{n} x_j, \tag{8}$$

such that

$$\begin{aligned} Q &= \lim_{n\to\infty} (\mathrm{const}) \int d\bar{x} \int d\mathbf{x}\; \delta\left(\bar{x} - \frac{1}{n}\sum_{j=1}^{n} x_j\right) e^{-\beta U_{\mathrm{eff}}(\mathbf{x})} && (9)\\ &= \lim_{n\to\infty} (\mathrm{const}) \int d\bar{x}\; e^{-\beta \bar{U}(\bar{x})}, && (10) \end{aligned}$$

where introduced the centroid effective potential

$$U_{\mathrm{eff}}(\mathbf{x}) = -\frac{1}{\beta}\ln\left[d\mathbf{x}\; \delta\left(\bar{x} - \frac{1}{n}\sum_{j=1}^{n} x_j\right) e^{-\beta U_{\mathrm{eff}}(\mathbf{x})}\right] \tag{11}$$

Note that the centroid effective potential is simply the free energy surface for the quantum Boltzmann distribution associated with the centroid collective variable. In this sense, we have “coarse-grained" the original ring-polymer distribution with respect to everything except the centroid coordinate.

Now, introduce a momentum variable for the centroid coordinate (which has no effect on the path-integral Boltzmann distribution), we have

$$Q = \lim_{n\to\infty} (\text{const}) \int d\bar{x} \int d\bar{p}\; e^{-\beta \bar{H}(\bar{p},\bar{x})}, \tag{12}$$

where we have also introduced the centroid Hamiltonian

$$\bar{H}(\bar{p},\bar{x}) = \frac{\bar{p}^2}{2m} + \bar{U}(\bar{x}). \tag{13}$$

This exact form of the quantum Boltzmann distribution could hardly look more classical! Finally, considering the classical equations of motion associated with the centroid Hamiltonian

$$\dot{\bar{x}} = \frac{\partial \bar{H}}{\partial \bar{p}} \qquad \text{and} \qquad \dot{\bar{p}} = -\frac{\partial \bar{H}}{\partial \bar{x}}, \tag{14}$$

we arrive at the centroid molecular dynamics (CMD) approximation for the Kubo-transformed quantum TCF

$$\tilde{C}_{\text{AB}}(t) \approx \frac{(\text{const})}{Q} \int d\bar{x}_0 \int d\bar{p}_0\; e^{-\beta \bar{H}(\bar{p}_0,\bar{x}_0)} A(\bar{x}_0) B(\bar{x}_t). \tag{15}$$

Like RPMD, the CMD approximation provides a purely classical description of the real-time quantum dynamics that rigorously preserves the quantum Boltzmann statistics while neglecting real-time coherence. Although there are technical advantages/disadvantages of one method versus the other, they are very closely related and should be expected to succeed and fail in similar regimes. Specifically, they should be expected to succeed for quantum mechanical problems that are dominated by statistical quantum effects (such as zero-point energy or static tunneling) and they should be expected to fail in systems (such as a double-slit experiment) where real-time quantum coherence plays an important role.

For additional reading about RPMD and CMD, the following reviews provide a good starting point:

- “Ring polymer molecular dynamics: Quantum effects in chemical dynamics from classical trajectories in an extended phase space" S. Habershon, D. E. Manolopoulos, T. E. Markland, and T. F. Miller III, Annu. Rev. Phys. Chem., 64, 387 (2013).

- “Path-integral centroid methods in quantum statistical mechanics and dynamics." G. A. Voth. Adv. Chem. Phys., 93,135 (1996).