Ring Polymer Molecular Dynamics and Matsubara Dynamics

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1 Partition Function

For a quantum system of Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} = \frac{\hat{p}^2}{2m} + V(q)\,, \tag{1.1}$$

we are often interested in the partition function

$$\begin{aligned} Z &= \sum_{|k\rangle} \mathrm{e}^{-\beta E_k} \\ &= \sum_{|k\rangle} \mathrm{e}^{-\beta \langle k|\hat{H}|k\rangle}\,, \end{aligned} \tag{1.2}$$

where $\{|k\rangle\}$ are the energy eigenstates. Defining the exponential of an operator via power series, one can write

$$Z = \sum_{|k\rangle} \left\langle k \middle| \mathrm{e}^{-\beta\hat{H}} \middle| k \right\rangle = \operatorname{tr} \mathrm{e}^{-\beta\hat{H}}\,, \tag{1.3}$$

assuming convergence.

Since the Hamiltonian commutes with itself, one can show, by Taylor expansion, that

$$\mathrm{e}^{-\beta\hat{H}} = \left[\mathrm{e}^{-\frac{\beta}{N}\hat{H}}\right]^N \tag{1.4}$$

We will take the $N \to \infty$ limit of the above decomposition, which is known as the *Trotter splitting*, to write

$$Z = \operatorname{tr}\left[\lim_{N\to\infty}\left(\mathrm{e}^{-\frac{\beta}{N}\hat{H}}\right)^N\right]\,. \tag{1.5}$$

The trace has the nice property that it is independent of the basis that we evaluate it in. We now expand the trace in the position basis $\{|q_1\rangle\}$, giving

$$Z = \lim_{N\to\infty} \int \mathrm{d}q_1 \left\langle q_1 \middle| \left[\mathrm{e}^{-\frac{\beta}{N}\hat{H}}\right]^N \middle| q_1 \right\rangle\,. \tag{1.6}$$

We have the freedom to insert identity operators

$$1 = \int \mathrm{d}q_i\ |q_i\rangle\langle q_i| \tag{1.7}$$

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

$$Z = \lim_{N\to\infty} \int \mathrm{d}q_1 \ldots \mathrm{d}q_N \left\langle q_1 \middle| \mathrm{e}^{-\frac{\beta}{N}\hat{H}} \middle| q_2 \right\rangle \left\langle q_2 \middle| \mathrm{e}^{-\frac{\beta}{N}\hat{H}} \middle| q_3 \right\rangle \ldots \left\langle q_N \middle| \mathrm{e}^{-\frac{\beta}{N}\hat{H}} \middle| q_1 \right\rangle\,. \tag{1.8}$$

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

$$M_i = \left\langle q_i \middle| \mathrm{e}^{-\beta_N \hat{H}} \middle| q_{i+1} \right\rangle\,, \tag{1.9}$$

where we have identified $q_1 \equiv q_{N+1}$ and denoted $\beta_N \coloneqq \beta/N$. We would like to evaluate this matrix element, but the Hamiltonian in the exponent will cause us some trouble, since it is made of two operators, $\hat{H} = \hat{T} + \hat{V}$, which does not commute. To proceed, we need the following result from Lie algebra.

Lemma 1.1 (Baker–Campbell–Hausdorff formula). For possibly non-commutative X and Y in the Lie algebra of a Lie group,

$$\mathrm{e}^X \mathrm{e}^Y = \mathrm{e}^Z \,, \tag{1.10}$$

where Z is given by

$$Z = X + Y + \frac{1}{2}[X, Y] + \frac{1}{12}([X,[X,Y]] + [Y,[Y,X]]) + \ldots, \tag{1.11}$$

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

This simply states that once X and Y are non-commuting, we no longer have $\mathrm{e}^X\mathrm{e}^Y = \mathrm{e}^{X+Y}$ — otherwise this would be the same as $\mathrm{e}^Y\mathrm{e}^X$ 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.

This means that if we break $\beta_N\hat{H} = \beta_N\hat{T} + \beta_N\hat{V}$, this will lead to an error term $\frac{1}{2}[\beta_N\hat{T}, \beta_N\hat{V}] + \cdots = O(N^{-2})$. We have N such terms, so the global error is $O(N^{-1})$, which vanishes in the $N \to \infty$ limit.

However, we can do better than that. We can symmetrically break the Hamiltonian to

$$M_i \simeq \left\langle q_i \middle| \mathrm{e}^{-\beta_N\hat{V}/2}\mathrm{e}^{-\beta_N\hat{T}}\mathrm{e}^{-\beta_N\hat{V}/2} \middle| q_{i+1} \right\rangle . \tag{1.12}$$

By Baker–Campbell–Hausdorff formula, this symmetric decomposition will only introduce a $O(N^{-3})$ error in each term due to cancellation of $O(N^{-2})$ terms, leading to a $O(N^{-2})$ error globally in Z. There are no difference in the above two splitting schemes as $N \to \infty$ as both errors converges to zero, but the error in symmetric splitting is smaller when N is finite.

Since $\{|q_i\rangle\}$ is an eigenbasis of $\hat{V}$

$$\begin{aligned} M_i &\simeq \left\langle q_i \middle| \mathrm{e}^{-\beta_N\hat{V}/2}\mathrm{e}^{-\beta_N\hat{T}}\mathrm{e}^{-\beta_N\hat{V}/2} \middle| q_{i+1} \right\rangle \\ &= \mathrm{e}^{-\beta_N V(q_i)/2} \left\langle q_i \middle| \mathrm{e}^{-\beta_N\hat{T}} \middle| q_{i+1} \right\rangle \mathrm{e}^{-\beta_N V(q_{i+1})/2} . \end{aligned} \tag{1.13}$$

To evaluate the matrix element in the middle, we again use the trick of inserting an identity operator between the exponentials, but this time is the momentum basis, giving

$$\begin{aligned} M_i &\simeq \mathrm{e}^{-\beta_N V(q_i)/2}\mathrm{e}^{-\beta_N V(q_{i+1})/2} \int \mathrm{d}p \, \left\langle q_i \middle| \mathrm{e}^{-\beta_N\hat{T}} \middle| p \right\rangle \langle p|q_{i+1}\rangle \\ &= \mathrm{e}^{-\beta_N V(q_i)/2}\mathrm{e}^{-\beta_N V(q_{i+1})/2} \int \mathrm{d}p \, \mathrm{e}^{-\frac{\beta_N p^2}{2m}} \langle q_i|p\rangle \langle p|q_{i+1}\rangle \, . \end{aligned} \tag{1.14}$$

The bra-kets are just the position representation of momentum eigenstates

$$\langle q_i|p\rangle = \frac{1}{\sqrt{2\pi\hbar}} \mathrm{e}^{\mathrm{i}pq_i/\hbar} . \tag{1.15}$$

Therefore,

$$M_i \simeq \frac{1}{2\pi\hbar} \mathrm{e}^{-\beta_N V(q_i)/2}\mathrm{e}^{-\beta_N V(q_{i+1})/2} \int \mathrm{d}p \, \mathrm{e}^{\mathrm{i}p(q_i - q_{i+1})/\hbar} \mathrm{e}^{-\frac{\beta_N p^2}{2m}} . \tag{1.16}$$

We are only left with a simple Gaussian integral (after completing the square), which evaluates to

$$\int \mathrm{d}p \, \mathrm{e}^{\mathrm{i}p(q_i - q_{i+1})/\hbar} \mathrm{e}^{-\frac{\beta_N p^2}{2m}} = \sqrt{\frac{2\pi m}{\beta_N}} \exp\left(-\frac{m}{2\beta_N\hbar^2}(q_i - q_{i+1})^2 \right) , \tag{1.17}$$

and so the matrix elements are

$$M_i \simeq \sqrt{\frac{m}{2\pi\beta_N\hbar^2}} \exp\left[-\frac{m}{2\beta_N\hbar^2}(q_i - q_{i+1})^2 - \frac{\beta_N[V(q_i) + V(q_{i+1})]}{2} \right] . \tag{1.18}$$

The partition function of interest is therefore

$$Z = \lim_{N\to\infty} \left(\frac{m}{2\pi\beta_N\hbar^2}\right)^{N/2} \int \mathrm{d}q_1 \ldots \mathrm{d}q_N \, \exp\left[-\sum_{i=1}^{N}\left(\frac{m}{2\beta_N\hbar^2}(q_i - q_{i+1})^2 + \beta_N V(q_i)\right)\right] . \tag{1.19}$$

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 $\beta_N \equiv \beta/N$ here. This is the effective (inverse) temperature of our ring polymer. Observe that

$$\left(\frac{m}{2\pi\beta_N\hbar^2}\right)^{1/2} = \frac{1}{2\pi\hbar}\int \mathrm{d}p_i \, \exp\left(-\frac{\beta_N p_i^2}{2m}\right) . \tag{1.20}$$

This allows us to finally write

$$\begin{aligned} Z &= \lim_{N\to\infty} \frac{1}{(2\pi\hbar)^N} \int \mathrm{d}p_1 \, \mathrm{d}q_1 \ldots \mathrm{d}p_N \, \mathrm{d}q_N \, \exp\left[-\beta_N \sum_{i=1}^{N}\left(\frac{p_i^2}{2m} + \frac{m}{2\beta_N^2\hbar^2}(q_i - q_{i+1})^2 + V(q_i)\right)\right] \\ &= \lim_{N\to\infty} \frac{1}{(2\pi\hbar)^N} \int \mathrm{d}^N\mathbf{p}\, \mathrm{d}^N\mathbf{q} \, \exp\left(-\beta_N H_N\right) \\ &=: \lim_{N\to\infty} Z_N \, , \end{aligned} \tag{1.21}$$

where

$$H_N = \sum_{i=1}^{N}\left[\frac{p_i^2}{2m} + \frac{m}{2\beta_N^2\hbar^2}(q_i - q_{i+1})^2 + V(q_i)\right] . \tag{1.22}$$

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 $\omega_N = \frac{1}{\beta_N\hbar}$, placed on a potential V at inverse temperature β_N. If we take the $N \to \infty$ limit, the partition function this polymer ring with N particles becomes that of a single quantum particle!

2 Thermal Average of an Operator

Suppose now we are interested in the thermal average of an operator $\hat{A}$,

$$\langle A \rangle = \frac{1}{Z} \sum_{|k\rangle} \mathrm{e}^{-\beta E_k} \left\langle k \middle| \hat{A} \middle| k \right\rangle . \tag{2.1}$$

If we pick $\{|k\rangle\}$ to be the eigenstate of the Hamiltonian, then

$$\mathrm{e}^{-\beta \hat{H}} |k\rangle = \mathrm{e}^{-\beta E_k} |k\rangle , \tag{2.2}$$

so

$$\begin{aligned} \langle A \rangle &= \frac{1}{Z} \sum_{|k\rangle} \left\langle k \middle| \mathrm{e}^{-\beta \hat{H}} \hat{A} \middle| k \right\rangle \\ &= \frac{1}{Z} \operatorname{tr}[\mathrm{e}^{-\beta \hat{H}} \hat{A}] . \end{aligned} \tag{2.3}$$

We use the same trick to split the $\mathrm{e}^{-\beta \hat{H}}$ into $N \to \infty$ parts, and equate Z with the ring polymer partition function

$$\langle A \rangle = \lim_{N\to\infty} \frac{1}{Z_N} \operatorname{tr}\left[\left(\mathrm{e}^{-\beta_N \hat{H}} \right)^N \hat{A} \right] . \tag{2.4}$$

A nice property of the trace is that it is cyclic invariant, meaning that we can move any number of slices of $\mathrm{e}^{-\beta_N \hat{H}}$ after $\hat{A}$

$$\langle A \rangle = \lim_{N\to\infty} \frac{1}{Z_N} \operatorname{tr}\left[\left(\mathrm{e}^{-\beta_N \hat{H}} \right)^j \hat{A} \left(\mathrm{e}^{-\beta_N \hat{H}} \right)^{N-j} \right] , \tag{2.5}$$

where $0 \le j \le N$. We take one step further and write $\langle A \rangle$ as the average of the right hand sides with $1 \le j \le N$:

$$\langle A \rangle = \lim_{N\to\infty} \frac{1}{N Z_N} \sum_{j=1}^{N} \operatorname{tr}\left[\left(\mathrm{e}^{-\beta_N \hat{H}} \right)^j \hat{A} \left(\mathrm{e}^{-\beta_N \hat{H}} \right)^{N-j} \right] . \tag{2.6}$$

For each j, we can use our good old trick of inserting identity operators between each pair of slices, giving

$$\langle A \rangle = \lim_{N\to\infty} \frac{1}{N Z_N} \sum_{j=1}^{N} \int \mathrm{d}^N \mathbf{q} \left\langle q_1 \middle| \mathrm{e}^{-\beta_N \hat{H}} \middle| q_2 \right\rangle \dots \left\langle q_j \middle| \mathrm{e}^{-\beta_N \hat{H}} \hat{A} \middle| q_{j+1} \right\rangle \dots \left\langle q_N \middle| \mathrm{e}^{-\beta_N \hat{H}} \middle| q_1 \right\rangle . \tag{2.7}$$

Notice the extra $\hat{A}$ in the j^{th} matrix element.

2.1 Coordinate-Dependent Quantities

To proceed, we assume that the operator of interest $\hat{A} = A(\hat{q})$ is a function of coordinate only, and so $\hat{A}\,|q_i\rangle = A(q_i)\,|q_i\rangle$. An example is the potential energy $\hat{V} = V(\hat{q})$. Then since $\hat{A}\,|q\rangle = A(q)\,|q\rangle$,

$$\langle A \rangle = \lim_{N\to\infty} \frac{1}{N Z_N} \sum_{j=1}^{N} \int \mathrm{d}^N \mathbf{q}\, A(q_{j+1}) \left\langle q_1 \middle| \mathrm{e}^{-\beta_N \hat{H}} \middle| q_2 \right\rangle \dots \left\langle q_N \middle| \mathrm{e}^{-\beta_N \hat{H}} \middle| q_1 \right\rangle . \tag{2.8}$$

This now reduces to what we have seen before, just with an extra scalar function in the integral. We can write it as

$$\begin{aligned} \langle A \rangle &= \lim_{N\to\infty} \frac{1}{(2\pi\hbar)^N Z_N} \int \mathrm{d}^N \mathbf{p}\, \mathrm{d}^N \mathbf{q} \left[\frac{1}{N} \sum_{j=1}^{N} A(q_j) \right] \mathrm{e}^{-\beta_N H_N} \\ &= \lim_{N\to\infty} \frac{1}{(2\pi\hbar)^N Z_N} \int \mathrm{d}^N \mathbf{p}\, \mathrm{d}^N \mathbf{q}\, \mathcal{A}_N \mathrm{e}^{-\beta_N H_N} \end{aligned} \tag{2.9}$$

which is the classical thermal average of $\mathcal{A}_N$ for the polymer ring, where

$$\mathcal{A}_N(\mathbf{q}) = \frac{1}{N}\sum_{i=1}^{N} A(q_i) \tag{2.10}$$

is the average value of A for the N particles on the polymer ring. We reduced the quantum thermal average into the classical thermal average in a polymer ring,

$$\langle A \rangle = \lim_{N\to\infty} \langle \mathcal{A}_N \rangle \ . \tag{2.11}$$

Therefore, if we are interested in the thermal average of some coordinate-dependent quantity of a quantum particle, we can replace it with a ring polymer of large N, propagate the ring polymer classically and sample $\langle \mathcal{A}_N \rangle$. This will give us $\langle A \rangle$ exactly in the $N \to \infty$ limit.

2.2 Kinetic Energy

We can also evaluate the thermal average of some other quantities, despite involving a bit more effort. We will take the kinetic energy operator $\hat{T} = \frac{\hat{p}^2}{2m}$ as an example.

For symmetry, we move a half extra slice of $\mathrm{e}^{-\beta_N \hat{H}}$ after $\hat{T}$ and get

$$\langle T \rangle = \lim_{N\to\infty} \sum_{j=1}^{N} \int \mathrm{d}^N\mathbf{q} \left\langle q_1 \middle| \mathrm{e}^{-\beta_N \hat{H}} \middle| q_2 \right\rangle \dots \left\langle q_j \middle| \mathrm{e}^{-\beta_N \hat{H}/2} \hat{T} \mathrm{e}^{-\beta_N \hat{H}/2} \middle| q_{j+1} \right\rangle \dots \left\langle q_N \middle| \mathrm{e}^{-\beta_N \hat{H}} \middle| q_1 \right\rangle \ . \tag{2.12}$$

Splitting $\hat{H} = \hat{T} + \hat{V}$ again gives

$$\begin{aligned}
\left\langle q_j \middle| \mathrm{e}^{-\beta_N \hat{H}/2} \hat{T} \mathrm{e}^{-\beta_N \hat{H}/2} \middle| q_{j+1} \right\rangle &= \exp\left[-\beta_N \frac{V(q_j)+V(q_{j+1})}{2}\right] \left\langle q_j \middle| \mathrm{e}^{-\beta_N \hat{T}/2} \hat{T} \mathrm{e}^{-\beta_N \hat{T}/2} \middle| q_{j+1} \right\rangle \\
&= \exp\left[-\beta_N \frac{V(q_j)+V(q_{j+1})}{2}\right] \left\langle q_j \middle| \hat{T} \mathrm{e}^{-\beta_N \hat{T}} \middle| q_{j+1} \right\rangle \\
&= -\exp\left[-\beta_N \frac{V(q_j)+V(q_{j+1})}{2}\right] \frac{\partial}{\partial \beta_N} \left\langle q_j \middle| \mathrm{e}^{-\beta_N \hat{T}} \middle| q_{j+1} \right\rangle \\
&= -\exp\left[-\beta_N \frac{V(q_j)+V(q_{j+1})}{2}\right] \frac{\partial}{\partial \beta_N} \left[\left(\frac{m}{2\pi\hbar^2\beta_N}\right)^{\frac{1}{2}} \exp\left(-\frac{m(q_j-q_{j+1})^2}{2\hbar^2\beta_N}\right)\right] \\
&= \exp\left[-\beta_N \frac{V(q_j)+V(q_{j+1})}{2}\right] \left[\frac{1}{2\beta_N} - \frac{m(q_j-q_{j+1})^2}{2\hbar^2\beta^2}\right] \left\langle q_j \middle| \mathrm{e}^{-\beta_N \hat{T}} \middle| q_{j+1} \right\rangle \\
&= \left[\frac{1}{2\beta_N} - \frac{1}{2} m\omega_N^2 (q_j - q_{j+1})^2\right] \left\langle q_j \middle| \mathrm{e}^{-\beta_N \hat{H}} \middle| q_{j+1} \right\rangle \ .
\end{aligned} \tag{2.13}$$

Therefore, the quantum thermal average of kinetic energy is identical to $N \to \infty$ limit of classical thermal average of the kinetic energy estimator T_N

$$\langle T \rangle = \lim_{N\to\infty} \frac{1}{(2\pi\hbar)^N Z_N} \int \mathrm{d}^N\mathbf{q}\, \mathrm{d}^N\mathbf{p}\, \mathcal{T}_N \mathrm{e}^{-\beta_N H_N} = \lim_{N\to\infty} \langle \mathcal{T}_N \rangle \ , \tag{2.14}$$

where

$$\mathcal{T}_N = \frac{1}{2\beta_N} - \frac{1}{2N}\sum_{j=1}^{N} m\omega_N^2 (q_j - q_{j+1})^2 \ . \tag{2.15}$$

2.3 Total Energy

We can trivially work out the total energy estimator by summing up the kinetic and potential energy estimators:

$$\mathcal{E}_{N,\mathrm{TD}} = \mathcal{T}_N + \mathcal{V}_n = \frac{1}{2\beta_N} - \frac{1}{2N}\sum_{j=1}^{N} m\omega_N^2 (q_j - q_{j+1})^2 + \frac{1}{N}\sum_{j=1}^{N} V(q_j)\,, \tag{2.16}$$

where the extra subscript TD stands for 'thermodynamic' as this estimator is known as the *thermodynamic energy estimator*. This is to distinguish with another total energy estimator that will be introduced later. We than have

$$\langle E\rangle = \lim_{N\to\infty} \frac{1}{(2\pi\hbar)^N Z_N} \int \mathrm{d}^N\mathbf{p}\,\mathrm{d}\mathbf{q}\,\mathcal{E}_{N,\mathrm{TD}}\mathrm{e}^{-\beta_N H_N} = \langle \mathcal{E}_{N,\mathrm{TD}}\rangle\;. \tag{2.17}$$

An alternative approach is to use the thermodynamic relation

$$\langle E\rangle = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_V\,, \tag{2.18}$$

where we already have the ring polymer expression of partition function Z_N. This gives the same thermodynamic energy estimator $\mathcal{E}_{N,\mathrm{TD}}$.

$\mathcal{E}_{N,\mathrm{TD}}$ is not the only estimator that gives the total energy. The *centroid virial energy estimator*

$$\mathcal{E}_{N,\mathrm{CV}} = \frac{1}{2\beta} + \frac{1}{2N}\sum_{j=1}^{N}(q_j - \overline{q})\frac{\mathrm{d}V(q_j)}{\mathrm{d}q_j} + \frac{1}{N}\sum_{j=1}^{N} V(q_j)\,, \tag{2.19}$$

where $\overline{q} = \frac{1}{N}\sum_{k=1}^{N} q_k$ is the centroid coordinate of the polymer beads, can be shown to have the same average $\langle\mathcal{E}_{N,\mathrm{CV}}\rangle = \langle\mathcal{E}_{N,\mathrm{TD}}\rangle$ as the thermodynamics energy estimator, but with a way smaller variance. In the example above, both thermodynamic energy estimator and centroid virial estimator

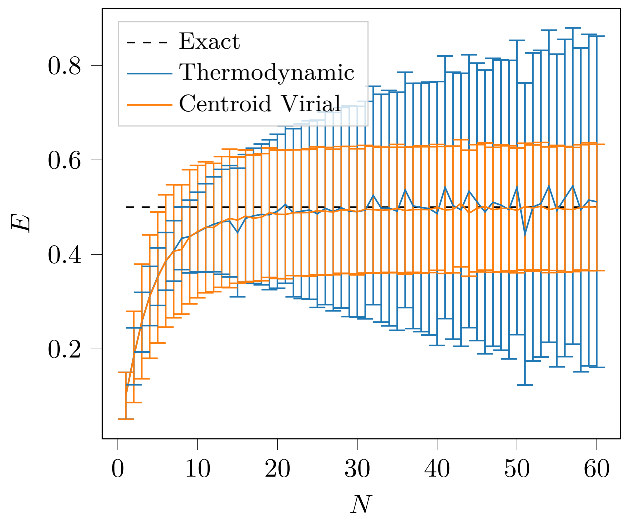

Figure 1: Average energies of a harmonic oscillator with $\beta\hbar\omega = 10$, sampled with 20000 runs using the two estimators. The error bars are the standard deviation of the energies.

converges to the exact $\langle E\rangle$ as $N\to\infty$. However, the standard deviation of the thermodynamic estimator grows asymptotically as $\sqrt{N}$, so the required number of sample would increase linearly with N to keep the standard error in the mean constant. By contrast, the standard deviation of the centroid virial estimator is asymptotically constant of N.

3 Propagating the Ring Polymer Dynamics

3.1 Integrating the Equations of Motion

In the previous section, we have established that to sample the equilibrium thermal average of some quantum system, we can instead propagate the dynamics of a classical ring polymer system and sample the thermal average of the corresponding classical estimator. This is known as the *path integral molecular dynamics* (PIMD).

Given a classical Hamiltonian $H(\mathbf{p}, \mathbf{q})$ with initial conditions $\mathbf{p}(0) = \mathbf{p}_0$, $\mathbf{q}(0) = \mathbf{q}_0$, the evolution of the system is governed deterministically by the Hamilton's equation

$$\dot{\mathbf{p}} = -\frac{\partial H}{\partial \mathbf{q}} \tag{3.1}$$

$$\dot{\mathbf{q}} = +\frac{\partial H}{\partial \mathbf{p}}\,. \tag{3.2}$$

For our Hamiltonian $H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{q})$, this is

$$\dot{\mathbf{p}} = -\frac{\partial V}{\partial \mathbf{q}} \tag{3.3}$$

$$\dot{\mathbf{q}} = +\frac{\mathbf{p}}{m} \tag{3.4}$$

as one would expect from Newton's second law.

These are a set of differential equations, and to work out the trajectory, we need to integrate these equations of motion. The most common way to do this is to use the velocity Verlet algorithm (see my notes on NST Part II C8: *Computer Simulation Methods*), in which the following steps are carried out iteratively to propagate the dynamics (the subscript denotes the time step):

$$\mathbf{p}_{n+\frac{1}{2}} = \mathbf{p}_n - \frac{\delta t}{2}\frac{\partial V}{\partial \mathbf{q}}(\mathbf{q}_n) \tag{3.5}$$

$$\mathbf{q}_{n+1} = \mathbf{q} + \delta t \frac{\mathbf{p}_{n+\frac{1}{2}}}{m} \tag{3.6}$$

$$\mathbf{p}_{n+1} = \mathbf{p}_{n+\frac{1}{2}} - \frac{\delta t}{2}\frac{\partial V}{\partial \mathbf{q}}(\mathbf{q}_{n+1})\,. \tag{3.7}$$

This propagates the momenta under V by half a time step, propagates the coordinates by a full time step, and then propagate the momenta by another time step, corresponding to symmetrically splitting the time evolution operator by

$$\mathrm{e}^{\mathcal{L}\delta t} \simeq \mathrm{e}^{\mathcal{L}_V \delta t/2}\mathrm{e}^{\mathcal{L}_T \delta t}\mathrm{e}^{\mathcal{L}_V \delta t/2}\,. \tag{3.8}$$

This is accurate to $O(\delta t^3)$ for each time step ($O(\delta t^2)$ globally), and is better than propagating the coordinates and momenta by a full time step simultaneously, which is known as the Euler's algorithm and is accurate to $O(\delta t^2)$ each step and $O(\delta t)$ globally.

For path integral molecular dynamics, we can of course directly use the standard velocity Verlet algorithm with Hamiltonian

$$H_N(\mathbf{p}, \mathbf{q}) = \frac{\mathbf{p}^2}{2m} + V(\mathbf{q})\,, \tag{3.9}$$

where

$$V(\mathbf{q}) = \sum_{j=1}^{N}\left[\frac{1}{2}m\omega_N^2(q_j - q_{j+1})^2 + V(q_j)\right]\,, \tag{3.10}$$

to propagate the dynamics. However, the harmonic springs between the beads are stiff, especially with large N ($\omega_N = N/\beta\hbar$). This requires a very small time step for us to propagate the internal vibrations of the ring polymer beads accurately. (Usually a time step of 1/20 of the shortest characteristic vibrational time scale of the system is safe.)

Luckily, we know how to solve the vibrational motions of systems connected by harmonic springs exactly! We can break them down to normal modes and propagate these internal normal modes exactly. (See NST Part II C8: *Further Quantum Mechanics* or NST Part IB Mathematical Methods.) We break down the Hamiltonian as

$$H_N(\mathbf{p},\mathbf{q}) = H_{N,0}(\mathbf{p},\mathbf{q}) + V_N(\mathbf{q})\,, \tag{3.11}$$

where

$$H_{N,0} = \sum_{j=1}^{N}\left[\frac{p_j^2}{2m} + \frac{1}{2}m\omega_N^2(q_j - q_{j+1})^2\right] \tag{3.12}$$

is the free ring polymer Hamiltonian without the external potential and

$$V_N(\mathbf{q}) = \sum_{j=1}^{N} V(q_j) \tag{3.13}$$

is the external potential. Since the potential of the free ring polymer Hamiltonian $H_{N,0}(\mathbf{p},\mathbf{q})$ is harmonic, it can be diagonalised with a normal mode transformation

$$\begin{cases} P_n = \sum_{j=1}^{N} T_{jn} p_j \\ Q_n = \sum_{j=1}^{N} T_{jn} q_j\,, \end{cases} \tag{3.14}$$

where

$$T_{jn} = \begin{cases} \sqrt{1/N} & n = 0 \\ \sqrt{2/N}\sin(2\pi jn/N) & 1 \le n \le N/2 - 1 \\ \sqrt{1/2}(-1)^j & n = N/2 \text{ (if } N \text{ is even)} \\ \sqrt{2/N}\cos(2\pi jn/N) & N/2 + 1 \le n \le N\,, \end{cases} \tag{3.15}$$

giving

$$H_{N,0}(\mathbf{P},\mathbf{Q}) = \sum_{k=0}^{N-1}\left[\frac{P_k^2}{2m} + \frac{1}{2}m\omega_k^2 Q_k^2\right] \tag{3.16}$$

with

$$\omega_k = 2\omega_N \sin\left(\frac{k\pi}{N}\right)\,. \tag{3.17}$$

Notice that we have shifted the range of indices from $1 \le j \le N$ to $0 \le k \le N-1$. You should be familiar with this because T_{jk} and ω_k^2 are actually exactly the Hückel molecular orbital coefficients and the orbital energies of a cyclic polyene. This is because the Hückel matrix of a cyclic polyene and the potential energy matrix of a ring polymer are exactly the same:

$$\mathsf{H}_{\text{polyene}} = \begin{pmatrix} \alpha & \beta & 0 & \cdots & \beta \\ \beta & \alpha & \beta & \cdots & 0 \\ 0 & \beta & \alpha & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \beta & 0 & 0 & \cdots & \alpha \end{pmatrix} \quad \xleftrightarrow{\alpha=2,\beta=-1} \quad \mathsf{V} = \begin{pmatrix} 2 & -1 & 0 & \cdots & -1 \\ -1 & 2 & -1 & \cdots & 0 \\ 0 & -1 & 2 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ -1 & 0 & 0 & \cdots & 2 \end{pmatrix} \tag{3.18}$$

such that $\sum_{j=1}^{N}(q_j - q_{j+1})^2 = \mathbf{q}^{\mathrm{T}}\mathsf{V}\mathbf{q}$. Moreover, the normal mode transformation (3.14) is exactly the discrete Fourier transform, which can be efficiently carried out using the Fast Fourier Transform (FFT) algorithm with a scaling no larger than $O(N\log N)$.

In the normal mode coordinates, the Hamiltonian $H_{0,N}$ is broken down into N independent harmonic oscillators, each evolving sinusoidally

$$\begin{cases} Q_k = A_k\sin(\omega_k t) + B_k\cos(\omega_k t) \\ P_k = mA_k\omega_k\cos(\omega_k t) - mB_k\omega_k\sin(\omega_k t)\,. \end{cases} \tag{3.19}$$

To overall idea is therefore breaking down the ring polymer evolution by

$$\mathrm{e}^{\mathcal{L}\delta t} = \mathrm{e}^{\mathcal{L}_V \delta t/2}\mathrm{e}^{\mathcal{L}_0 \delta t}\mathrm{e}^{\mathcal{L}_V \delta t/2}\,, \tag{3.20}$$

i.e. evolve the momenta by the external potential for half a time step, transform into the normal mode coordinates, evolve the coordinates and momenta by the internal ring normal modes for a full time step, revert back to the real coordinates, and finally evolve the momenta by the external potential for half a time step. The detailed algorithm is

$$\mathbf{p}' = \mathbf{p}_n - \frac{\delta t}{2}\frac{\mathrm{d}V}{\mathrm{d}\mathbf{q}}(\mathbf{q}_n) \tag{3.21}$$

$$\mathbf{P}' = \mathsf{T}^{\mathrm{T}}\mathbf{p}' \tag{3.22}$$

$$\mathbf{Q}' = \mathsf{T}^{\mathrm{T}}\mathbf{q}_n \tag{3.23}$$

$$\begin{pmatrix} P_k'' \\ Q_k'' \end{pmatrix} = \begin{pmatrix} \cos\omega_k\delta t & -m\omega_k\sin\omega_k\delta t \\ \frac{1}{m\omega_k}\sin\omega_k\delta t & \cos\omega_k\delta t \end{pmatrix}\begin{pmatrix} P_k' \\ Q_k' \end{pmatrix} \tag{3.24}$$

$$\mathbf{p}'' = \mathsf{T}\mathbf{P}'' \tag{3.25}$$

$$\mathbf{q}_{n+1} = \mathsf{T}\mathbf{Q}'' \tag{3.26}$$

$$\mathbf{p}_{n+1} = \mathbf{p}'' - \frac{\delta t}{2}\frac{\mathrm{d}V}{\mathrm{d}\mathbf{q}}(\mathbf{q}_{n+1}) \tag{3.27}$$

3.2 Sampling in Canonical Ensemble

The above algorithm well propagates the dynamics of the ring polymer in a microcanonical ensemble, but we can't use them to calculate canonical thermal averages because

- The above algorithm rigorously conserves the energy H_N. Instead in a canonical ensemble with constant energy, the phase space should be sampled with all possible H_N weighted by their Boltzmann factors.
- It is far from ergodic. If the external potential is harmonic, then the whole H_N is diagonal in the normal mode representation and hence there is no energy flow between the normal modes. If the external potential is instead mildly anharmonic, then the energy exchanges between modes very slowly. It is therefore not even possible to fully sample the microcanonical constant energy hypersurface in the phase space ergodically within the typical timescale of a simulation.

Therefore to meaningfully work out a thermal average, we need to attach a thermostat to our ring polymer system. Here we will briefly introduce the path integral Langevin equation (PILE) thermostat.

3.2.1 The Path Integral Langevin Equation Thermostat

The PILE thermostat attaches a separate Langevin thermostat to each internal mode of the free ring polymer, so that the free polymer would evolve by

$$\frac{\mathrm{d}}{\mathrm{d}t}\tilde{q}_k = \frac{\tilde{p}_k}{m} \tag{3.28}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\tilde{p}_k = -m\omega_k^2\tilde{q}_k - \gamma_k\tilde{p}_k + \sqrt{\frac{2m\gamma_k}{\beta_N}}\xi_k(t)\,, \tag{3.29}$$

where $\gamma_k(t)$ represents an uncorrelated, Gaussian-distributed random form with unit variance and zero mean:

$$\langle\xi_k(t)\rangle = 0 \qquad \langle\xi_k(0)\xi_k(t)\rangle = \delta(t)\,, \tag{3.30}$$

and the *friction coefficients* γ_k governs the rate at which the velocities are thermalised. The first term in (3.29) is the free evolution of a microcanonical harmonic oscillator, and the two extra terms are from the Langevin thermostat. Their origins are explained in NST Part II B7: *Statistical Mechanics*.

The PILE thermostat uses the propagator

$$\mathrm{e}^{\mathcal{L}_\gamma \delta t/2}\mathrm{e}^{\mathcal{L}_V \delta t/2}\mathrm{e}^{\mathcal{L}_0 \delta t}\mathrm{e}^{\mathcal{L}_V \delta t/2}\mathrm{e}^{\mathcal{L}_\gamma \delta t/2}\,, \tag{3.31}$$

where the extra thermostatting steps ($\mathrm{e}^{\mathcal{L}_\gamma \delta t/2}$) implements the last two extra terms in (3.29). They are implemented by

$$\tilde{p}_k = \sum_{j=1}^{N} p_j T_{jk} \tag{3.32}$$

$$\tilde{p}_k = \mathrm{e}^{-\gamma_k \delta t/2}\tilde{p}_k + \sqrt{\frac{m(1-\mathrm{e}^{-\gamma_k \delta t})}{\beta_N}}\xi_k \tag{3.33}$$

$$p_j = \sum_{k=1}^{N} T_{jk}\tilde{p}_k\,, \tag{3.34}$$

where ξ_k is an independent Gaussian number randomly drawn from a Gaussian distribution with zero mean and unit variance each time.

The friction coefficients γ_k govern the rate at which the momenta in each mode are thermalised (randomised). The autocorrelation time

$$\tau_V = \frac{1}{\langle V^2\rangle - \langle V\rangle^2}\int_0^\infty \mathrm{d}t\ \langle (V(0)-\langle V\rangle)(V(t)-\langle V\rangle)\rangle \tag{3.35}$$

of the free ring polymer mode potential $V = \frac{1}{2}m\omega_k^2\tilde{q}_k^2$ can be worked out analytically to be

$$\tau_V = \frac{1}{2\gamma_k} + \frac{\gamma_k}{2\omega_k^2} \tag{3.36}$$

for $\omega_k > 0$. The optimum friction coefficient is the one that minimises τ_V (and hence samples the most efficiently), which is $\gamma_k = \omega_k$. This leaves only a single physical parameter τ_0 to be specified for thermostatting the centroid mode $k = 0$.

$$\gamma_k = \begin{cases} 1/\tau_0 & k = 0 \\ \omega_k & k \neq 0\,. \end{cases} \tag{3.37}$$

4 Generalisation for Multiparticle System

The above equations are derived for the one-particle one-dimensional quantum mechanical problem with Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{q})\,. \tag{4.1}$$

The generalisation to higher dimensions is trivial, and in the absence of quantum mechanical exchange effects for identical particles (fermionic and bosonic), it is also straightforward to generalise to multiparticle systems. For example, the M-particle Hamiltonian

$$\hat{H} = \sum_{i=1}^{M} \frac{\hat{\mathbf{p}}_i^2}{2m_i} + V(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \ldots, \hat{\mathbf{r}}_M) \tag{4.2}$$

have the ring polymer Hamiltonian

$$H_N(\{\mathbf{p}_i\}, \{\mathbf{r}_i\}) = \sum_{i=1}^{M}\sum_{j=1}^{N} \left[\frac{\mathbf{p}_{i,j}^2}{2m_i} + \frac{1}{2} m_i \omega_N^2 \left\|\mathbf{r}_{i,j} - \mathbf{r}_{i,j+1}\right\|^2\right] + \sum_{j=1}^{N} V(\mathbf{r}_{1,j}, \ldots, \mathbf{r}_{M,j})\,. \tag{4.3}$$

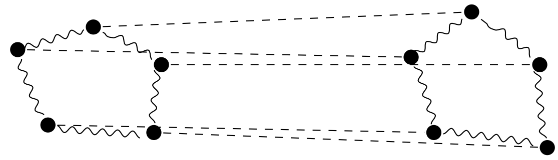

Figure 2: Two interacting ring polymers with $N = 5$.

Identical particle exchange effects become important when the de Broglie thermal wavelengths $\Lambda_i(T) = h/\sqrt{2\pi m_i k_B T}$ exceed the hard sphere diameters of the atoms. These effects can in principle be included by considering dimerisation, trimerisation, etc. of ring polymers (see Chandler and Wolynes). However, it is hardly ever necessary for those of us who work in chemistry departments to have to worry about them, because these effects are almost always negligible, e.g. in liquid para-hydrogen even at its melting temperature (13.8 K).

5 Ring Polymer Molecular Dynamics

Usually we are not just interested in the static thermal average $\langle A \rangle$ of a quantum system. Instead we are interested in time correlation functions.

Definition 5.1. The *correlation function* of two observables A and B is

$$C_{AB}(t) \coloneqq \frac{1}{Z} \operatorname{tr}[\mathrm{e}^{-\beta \hat{H}} \hat{A} \mathrm{e}^{\mathrm{i}\hat{H}t/\hbar} \hat{B} \mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}] . \tag{5.1}$$

The rationalisation of this is that in the Heisenberg picture, the operator $\hat{B}$ evolves as

$$\hat{B}(t) = \mathrm{e}^{\mathrm{i}\hat{H}t/\hbar} \hat{B}(0) \mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar} , \tag{5.2}$$

while the energy eigenstates are not changing, so

$$\begin{aligned} C_{AB}(t) &= \frac{1}{Z} \operatorname{tr}[\mathrm{e}^{-\beta \hat{H}} \hat{A}(0) \hat{B}(t)] \\ &= \frac{1}{Z} \sum_{|n\rangle} \left\langle n \middle| \mathrm{e}^{-\beta \hat{H}} \hat{A}(0) \hat{B}(t) \middle| n \right\rangle \\ &= \frac{1}{Z} \sum_{|n\rangle} \mathrm{e}^{-\beta E_n} \left\langle n \middle| \hat{A}(0) \hat{B}(t) \middle| n \right\rangle \\ &= \langle A(0) B(t) \rangle . \end{aligned} \tag{5.3}$$

These correlation functions are useful because a lot of dynamical properties, like the diffusion coefficient, reaction rate constants and dipole absorption spectra can be related to those correlation functions by Green–Kubo relations. We need to figure out a way to calculate these correlation functions using ring polymers.

Suppose now we have two coordinate-dependent operators $\hat{A}$ and $\hat{B}$ of interest, with classical ring-polymer counterparts $\mathcal{A}_N$ and $\mathcal{B}_N$ defined analogous to (2.10). What does the $N \to \infty$ limit of

$$\langle \mathcal{A}_N \mathcal{B}_N \rangle = \frac{1}{Z_N} \int \mathrm{d}^N \mathbf{p} \, \mathrm{d}^N \mathbf{q} \, \mathcal{A}_N \mathcal{B}_N \mathrm{e}^{-\beta_N H_N} \tag{5.4}$$

corresponds to? A naive guess would be

$$\langle AB \rangle \stackrel{?}{=} \lim_{N \to \infty} \langle \mathcal{A}_N \mathcal{B}_N \rangle , \tag{5.5}$$

but this is actually wrong. To see this, we expand

$$\langle \mathcal{A}_N \mathcal{B}_N \rangle = \frac{1}{N^2} \sum_{i,j=1}^{N} \langle A(q_i) B(q_j) \rangle , \tag{5.6}$$

but to get $\langle AB \rangle$ in the $N \to \infty$ limit, we would need

$$\langle AB \rangle = \lim_{N \to \infty} \frac{1}{N} \sum_{i=1}^{N} \langle A(q_i) B(q_i) \rangle . \tag{5.7}$$

These two are obviously unequal in general. Instead, rather surprisingly, the $N \to \infty$ limit of $\langle \mathcal{A}_N \mathcal{B}_N \rangle$ actually corresponds to something closely related to the correlation function.

Definition 5.2. The *Kubo-transformed correlation function* of two observables A and B is

$$K_{AB}(t) \coloneqq \frac{1}{\beta Z} \int_0^\beta \mathrm{d}\lambda \, \operatorname{tr}[\mathrm{e}^{-(\beta-\lambda)\hat{H}} \hat{A} \mathrm{e}^{-\lambda \hat{H}} \mathrm{e}^{\mathrm{i}\hat{H}t/\hbar} \hat{B} \mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}] . \tag{5.8}$$

Let's have a closer look at what this means. In addition to the Boltzmann factor $\mathrm{e}^{-\lambda\hat{H}}$ and evolved $\hat{B}$ operator $\hat{B}(t) = \mathrm{e}^{\mathrm{i}\hat{H}t/\hbar}\hat{B}\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}$ in the trace, we also have changed our $\hat{A}$ operator by

$$\mathrm{e}^{\lambda\hat{H}}\hat{A}\mathrm{e}^{-\lambda\hat{H}} \tag{5.9}$$

with an averaging over λ from 0 to β by the integral $\frac{1}{\beta}\int_0^\beta$. Notice that this is similar to the time evolution we've done on $\hat{B}$, but this time there is no factor of i in the exponent. We can interpret this as *imaginary-time evolution*,

$$\hat{A}(-\mathrm{i}\hbar\lambda) = \mathrm{e}^{\lambda\hat{H}}\hat{A}\mathrm{e}^{-\lambda\hat{H}}\,. \tag{5.10}$$

Hence in the Kubo-transformed correlation function, we are also averaging over the imaginary time of $\hat{A}$ from $t = 0$ to $t = -\mathrm{i}\hbar\beta$. This allows us to compactly denote the Kubo-transformed correlation function as

$$K_{AB}(t) = \frac{1}{\beta}\int_0^\beta \mathrm{d}\lambda \left\langle \hat{A}(-i\hbar\lambda)\hat{B}(t)\right\rangle\,. \tag{5.11}$$

The ordinary correlation function and the Kubo-transformed one are more closely related in the Fourier domain. This is easily seen if we work in the basis of energy eigenstates. Inserting the resolution of identity operators in the energy basis,

$$\begin{aligned} C_{AB}(t) &= \frac{1}{Z}\sum_{|k\rangle}\sum_{|\ell\rangle}\sum_{|m\rangle}\left\langle k\middle|\mathrm{e}^{-\beta\hat{H}}\hat{A}\middle|\ell\right\rangle\left\langle \ell\middle|\mathrm{e}^{\mathrm{i}\hat{H}t/\hbar}\middle|m\right\rangle\left\langle m\middle|\hat{B}\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}\middle|k\right\rangle \\ &= \frac{1}{Z}\sum_{|k\rangle}\sum_{|\ell\rangle}\sum_{|m\rangle}\mathrm{e}^{-\beta E_k}\mathrm{e}^{-\mathrm{i}E_k t/\hbar}\mathrm{e}^{\mathrm{i}E_\ell t/\hbar}\delta_{m\ell}A_{km}B_{\ell k} \\ &= \frac{1}{Z}\sum_{|k\rangle}\sum_{|m\rangle}\mathrm{e}^{-\beta E_k}\mathrm{e}^{-\mathrm{i}(E_k-E_m)t/\hbar}A_{km}B_{mk}\,. \end{aligned} \tag{5.12}$$

Doing the same for the Kubo-transformed correlation function, we get

$$\begin{aligned} K_{AB}(t) &= \frac{1}{\beta Z}\int_0^\beta \mathrm{d}\lambda\sum_{|k\rangle}\sum_{|\ell\rangle}\sum_{|m\rangle}\left\langle k\middle|\mathrm{e}^{-\beta\hat{H}\mathrm{e}^{\lambda\hat{H}}}\hat{A}\middle|\ell\right\rangle\left\langle \ell\middle|\mathrm{e}^{-\lambda\hat{H}}\mathrm{e}^{\mathrm{i}\hat{H}t/\hbar}\middle|m\right\rangle\left\langle m\middle|\hat{B}\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}\middle|k\right\rangle \\ &= \frac{1}{Z}\sum_{|k\rangle}\sum_{|m\rangle}\mathrm{e}^{-\beta E_k}\mathrm{e}^{-\mathrm{i}(E_k-E_m)t/\hbar}A_{km}B_{mk}\frac{1}{\beta}\int_0^\beta \mathrm{d}\lambda\,\mathrm{e}^{\lambda(E_k-E_m)} \\ &= \frac{1}{Z}\sum_{|k\rangle}\sum_{|m\rangle}\mathrm{e}^{-\beta E_k}\mathrm{e}^{-\mathrm{i}(E_k-E_m)t/\hbar}A_{km}B_{mk}\frac{\mathrm{e}^{\beta(E_k-E_m)}-1}{\beta(E_k-E_m)}\,. \end{aligned} \tag{5.13}$$

It has got some extra bit comparing with the normal correlation function — but it is dependent on $E_k - E_m$, so we can't easily pull it out from the sum. Nice things happen if we move to the Fourier domain. We get

$$\begin{aligned} \tilde{K}_{AB}(\omega) &= \int_{-\infty}^{\infty}\mathrm{d}t\,\mathrm{e}^{-\mathrm{i}\omega t}K_{AB}(t) \\ &= \frac{1}{Z}\sum_{|k\rangle}\sum_{|m\rangle}\mathrm{e}^{-\beta E_k}A_{km}B_{mk}\frac{\mathrm{e}^{\beta(E_k-E_m)}-1}{\beta(E_k-E_m)}\int_{-\infty}^{\infty}\mathrm{d}t\,\mathrm{e}^{-\mathrm{i}\omega t}\mathrm{e}^{-\mathrm{i}(E_k-E_m)t/\hbar}\,. \end{aligned} \tag{5.14}$$

If you're familiar with Fourier transform, you should identify that this is exactly the delta function,

$$\int_{-\infty}^{\infty}\mathrm{d}t\,\mathrm{e}^{-\mathrm{i}\omega t}\mathrm{e}^{-\mathrm{i}(E_k-E_m)t/\hbar} = 2\pi\delta\left(\frac{E_m-E_k}{\hbar}-\omega\right)\,, \tag{5.15}$$

and so

$$\tilde{K}_{AB}(\omega) = \frac{1}{Z}\sum_{|k\rangle}\sum_{|m\rangle}\mathrm{e}^{-\beta E_k}A_{km}B_{mk}\frac{\mathrm{e}^{\beta(E_k-E_m)}-1}{\beta(E_k-E_m)}2\pi\delta\left(\frac{E_m-E_k}{\hbar}-\omega\right)\,. \tag{5.16}$$

The delta function naturally imposes the condition $E_m = E_k + \hbar\omega$, so it reduces the double sum to a single sum,

$$\tilde{K}_{AB}(\omega) = \frac{1}{Z}\sum_{|k\rangle} \mathrm{e}^{-\beta E_k} A_{km} B_{mk} \frac{1-\mathrm{e}^{-\beta\hbar\omega}}{\beta\hbar\omega} 2\pi\delta(0)\,. \tag{5.17}$$

Now the extra factor from the integral over λ is independent of $|k\rangle$, so we can pull it out from the sum

$$\tilde{K}_{AB}(\omega) = \frac{1-\mathrm{e}^{-\beta\hbar\omega}}{\beta\hbar\omega} \frac{2\pi}{Z} \sum_{|k\rangle} \mathrm{e}^{-\beta E_k} A_{km} B_{mk} \delta(0)\,. \tag{5.18}$$

The Fourier transform of the normal correlation function is exactly the same except without this extra factor

$$\tilde{C}_{AB}(\omega) = \frac{2\pi}{Z} \sum_{|n\rangle} \mathrm{e}^{-\beta E_k} A_{km} B_{mk} \delta(0)\,, \tag{5.19}$$

and so

$$\tilde{K}_{AB}(\omega) = \frac{1-\mathrm{e}^{-\beta\hbar\omega}}{\beta\hbar\omega} \tilde{C}_{AB}(\omega)\,. \tag{5.20}$$

Notice also that in the classical limit, the energy spectrum becomes a continuum with $\beta\hbar\omega \to 0$, and so

$$\tilde{K}_{AB}(\omega) \to \tilde{C}_{AB}(\omega)\,. \tag{5.21}$$

5.1 Relation to Ring Polymer Average

Having established what the Kubo-transformed correlation function is, let's see how it is related to the ring-polymer average of two observables.

Claim 5.3. The $N \to \infty$ limit of $\langle \mathcal{A}_N \mathcal{B}_N \rangle$ for the classical ring polymer is the $t \to 0$ limit of the Kubo-transformed correlation function

$$\lim_{N\to\infty} \langle \mathcal{A}_N \mathcal{B}_N \rangle = K_{AB}(0)\,. \tag{5.22}$$

Proof. At $t = 0$,

$$K_{AB}(0) = \frac{1}{\beta Z} \int_0^\beta \mathrm{d}\lambda\ \mathrm{tr}[\mathrm{e}^{-(\beta-\lambda)\hat{H}} \hat{A} \mathrm{e}^{-\lambda\hat{H}} \hat{B}]\,. \tag{5.23}$$

Consider again Trotter-splitting the exponential of the Hamiltonians, but this time

$$\mathrm{e}^{-(\beta-\lambda)\hat{H}} = \left(\mathrm{e}^{-\beta\hat{H}}\right)^{\frac{\beta-\lambda}{\beta}} = \lim_{N\to\infty} \left(\mathrm{e}^{-\beta_N\hat{H}}\right)^{N(1-\frac{\lambda}{\beta})}\,, \tag{5.24}$$

and similarly

$$\mathrm{e}^{-\lambda\hat{H}} = \lim_{N\to\infty} \left(\mathrm{e}^{-\beta_N\hat{H}}\right)^{N\frac{\lambda}{\beta}}\,. \tag{5.25}$$

Therefore,

$$K_{AB}(0) = \lim_{N\to\infty} \frac{1}{\beta Z_N} \int_0^\beta \mathrm{d}\lambda\ \mathrm{tr}\left[\left(\mathrm{e}^{-\beta_N\hat{H}}\right)^{N(1-\frac{\lambda}{\beta})} \hat{A} \left(\mathrm{e}^{-\beta_N\hat{H}}\right)^{N\frac{\lambda}{\beta}} \hat{B}\right]\,. \tag{5.26}$$

Let's consider the effect of the integral averaging over λ: $\frac{1}{\beta}\int_0^\beta$. There are $N(1-\frac{\lambda}{\beta})$ pieces of $\mathrm{e}^{-\beta_N\hat{H}}$ in front of $\hat{A}$ and $N\frac{\lambda}{\beta}$ between $\hat{A}$ and $\hat{B}$. What the integral does is averaging over the number of $\mathrm{e}^{-\beta_N\hat{H}}$ pieces distributed between these two places, while making sure that there are N of them in total. When N is large, this can be replaced by the sum

$$\frac{1}{\beta}\int_0^\beta \mathrm{d}\lambda\, f(\lambda) \longmapsto \lim_{N\to\infty} \frac{1}{N} \sum_{\lambda=1}^{N} f(\lambda\beta_N)\,. \tag{5.27}$$

Therefore we can write

$$K_{AB}(0) = \lim_{N\to\infty} \frac{1}{NZ_N} \sum_{k=1}^{N} \mathrm{tr}\left[\left(\mathrm{e}^{-\beta_N \hat{H}}\right)^k \hat{A} \left(\mathrm{e}^{-\beta_N \hat{H}}\right)^{N-k} \hat{B}\right]. \tag{5.28}$$

Now there are $N+2$ operators in the trace. We again use the trick of inserting identity operators between them, while associating $\hat{A}$ and $\hat{B}$ to the $\mathrm{e}^{-\beta_N \hat{H}}$ in front of them, giving

$$\lim_{N\to\infty} \frac{1}{Z_N} \frac{1}{N} \sum_{k=1}^{N} \int \mathrm{d}^N \mathbf{q} \ldots \left\langle q_k \middle| \mathrm{e}^{-\beta_N \hat{H}} \hat{A} \middle| q_{k+1} \right\rangle \ldots \left\langle q_N \middle| \mathrm{e}^{-\beta_N \hat{H}} \hat{B} \middle| q_1 \right\rangle . \tag{5.29}$$

Another property of the trace we can exploit is its cyclic invariance. This means that we can move any slice of bra-kets at front to the end, and vice versa. This means that

$$\begin{aligned} K_{AB}(0) &= \int \mathrm{d}^N \mathbf{q} \ldots \left\langle q_k \middle| \mathrm{e}^{-\beta_N \hat{H}} \hat{A} \middle| q_{k+1} \right\rangle \ldots \left\langle q_N \middle| \mathrm{e}^{-\beta_N \hat{H}} \hat{B} \middle| q_1 \right\rangle \\ &= \int \mathrm{d}^N \mathbf{q} \ldots \left\langle q_i \middle| \mathrm{e}^{-\beta_N \hat{H}} \hat{A} \middle| q_{i+1} \right\rangle \ldots \left\langle q_j \middle| \mathrm{e}^{-\beta_N \hat{H}} \hat{B} \middle| q_{j+1} \right\rangle \ldots , \end{aligned} \tag{5.30}$$

as long as $|j-i| = k$. We average over all possible cyclic permutations of the trace — there are N of them for each interval k. This is effectively putting $\hat{A}$ and $\hat{B}$ into all possible slices of bra-kets. Therefore we can write

$$\begin{aligned} K_{AB}(0) &= \lim_{N\to\infty} \frac{1}{Z_N} \frac{1}{N^2} \sum_{i,j=1}^{N} \int \mathrm{d}^N \mathbf{q} \ldots \left\langle q_i \middle| \mathrm{e}^{-\beta_N \hat{H}} \hat{A} \middle| q_{i+1} \right\rangle \ldots \left\langle q_j \middle| \mathrm{e}^{-\beta_N \hat{H}} \hat{B} \middle| q_{j+1} \right\rangle \ldots \\ &= \lim_{N\to\infty} \frac{1}{Z_N} \int \mathrm{d}^N \mathbf{p}\, \mathrm{d}^N \mathbf{q}\, \mathcal{A}_N \mathcal{B}_N \mathrm{e}^{-\beta_N H_N} \\ &= \lim_{N\to\infty} \langle \mathcal{A}_N \mathcal{B}_N \rangle , \end{aligned} \tag{5.31}$$

which is exactly what we claimed. □

The idea of *ring polymer molecular dynamics* (RPMD) is to claim that the relationship

$$K_{AB}(t) = \lim_{N\to\infty} \langle \mathcal{A}_N(\mathbf{q}(0)) \mathcal{B}_N(\mathbf{q}(t)) \rangle \tag{5.32}$$

not only holds for $t = 0$, as we proved above, but also hold approximately for non-zero t, so that we can propagate the dynamics of a classical ring polymer at β_N and use $\langle \mathcal{A}_N(\mathbf{q}(0)) \mathcal{B}_N(\mathbf{q}(t)) \rangle$ to approximate $K_{AB}(t)$ at β. This is to say that, we are taking the dynamics of the ring polymer literally as the dynamics of a quantum particle, not just as a tool to sample thermal averages.

Initially when this was proposed, there was no rigorous justification why this would necessarily hold true at $t > 0$, but a few rationalisations for doing so include:

1. As we showed above, the relationship (5.31) is exact in the $t \to 0$ limit, and in fact, one can show that the error of RPMD is $O(t^8)$ about $t = 0$ for coordinate dependent operators.
2. This is exact at high temperature classical limit.
3. It is exact if the external potential is harmonic, and at least one of the operators are linear functions of x.
4. Both $K_{AB}(t)$ and $\langle \mathcal{A}_N(0) \mathcal{B}_N(t) \rangle$ obey a few important symmetries:
   - Detailed balance:
$$K_{AB}(t) = K_{BA}(-t) . \tag{5.33}$$

- Reality

$$K_{AB}(t) = K^{*}_{AB}(t)\,. \tag{5.34}$$

- Evenness

$$K_{AB}(t) = K_{AB}(-t)\,. \tag{5.35}$$

It was therefore quite surprising at that time that the RPMD worked surprisingly well in many cases, especially when applied to rate theories.

It is now understood that RPMD can be considered as an approximation of a rigorous first-principle quantum dynamical method called Matsubara dynamics, which we will introduce later. But first, we need some preliminaries.

6 Wigner Transform

The idea of Wigner transform is to make quantum dynamics somewhat similar to classical dynamics. Quantum mechanics and classical mechanics two different worlds. Quantum mechanics happens in the Hilbert space, $\mathcal{H}$. A quantum state is a vector in the Hilbert space, $|\psi\rangle \in \mathcal{H}$, and a physical observable corresponds to an operator $\hat{A} : \mathcal{H} \to \mathcal{H}$. The classical dynamics, however, happens in the 6-dimensional phase space $\Gamma \cong \mathbb{R}^6$ (for one particle in 3D). The state of the system is a point $(\mathbf{p}, \mathbf{q}) \in \Gamma$, and each physical observable corresponds to a phase space function $A(\mathbf{p}, \mathbf{q}) : \Gamma \to \mathbb{R}$.

What Wigner transform does is to make the quantum mechanical operator $\hat{A}$ into a phase space function $A(\mathbf{p}, \mathbf{q})$.[1] We will illustrate the idea for one-dimensional systems, while the idea easily generalises to higher-dimensional systems.

Definition 6.1. For an operator $\hat{A}$, its *Wigner transform* is defined as

$$A_W(p,q) \equiv \mathcal{W}\left[\hat{A}\right](p,q) := \int_{-\infty}^{\infty} \mathrm{d}\Delta \left\langle q - \frac{\Delta}{2} \middle| \hat{A} \middle| q + \frac{\Delta}{2} \right\rangle \mathrm{e}^{\mathrm{i}\Delta p/\hbar} \tag{6.1}$$

By a change of variable $\Delta \to -\Delta$, one can also write this as

$$A_W(p,q) \equiv \mathcal{W}\left[\hat{A}\right](p,q) := \int_{-\infty}^{\infty} \mathrm{d}\Delta \left\langle q + \frac{\Delta}{2} \middle| \hat{A} \middle| q - \frac{\Delta}{2} \right\rangle \mathrm{e}^{-\mathrm{i}\Delta p/\hbar} . \tag{6.2}$$

By the above two expressions, one can show that the Wigner transform of a Hermitian operator is real.

6.1 Wigner Transform of Position and Momentum

To see why the Wigner transform defined above is a good idea, we first calculate the Wigner transform of $\hat{q}$ and $\hat{p}$.

First the position operator $\hat{q}$.

$$\begin{aligned} q_W(p,q) &= \int_{-\infty}^{\infty} \mathrm{d}\Delta \left\langle q - \frac{\Delta}{2} \middle| \hat{q} \middle| q + \frac{\Delta}{2} \right\rangle \mathrm{e}^{\mathrm{i}\Delta p/\hbar} \\ &= \int_{-\infty}^{\infty} \mathrm{d}\Delta \left\langle q - \frac{\Delta}{2} \middle| q + \frac{\Delta}{2} \right\rangle \left(q + \frac{\Delta}{2}\right) \mathrm{e}^{\mathrm{i}\Delta p/\hbar} \\ &= \int_{-\infty}^{\infty} \mathrm{d}\Delta\, \delta\Delta \left(q + \frac{\Delta}{2}\right) \mathrm{e}^{\mathrm{i}\Delta p/\hbar} \\ &= q . \end{aligned} \tag{6.3}$$

The Wigner transform of $\hat{q}$ is just q itself! Similarly, one can show that

$$\mathcal{W}\left[\hat{q}^n\right] = q^n , \tag{6.4}$$

and hence for any operator that is an analytic function of $\hat{q}$,

$$\mathcal{W}\left[f(\hat{q})\right] = f(q) . \tag{6.5}$$

Before moving on for $\hat{p}$, we are introducing a notation that looks weird but is pretty handy and appears everywhere in literatures. Consider the matrix element of a differential operator in the position basis

$$\left\langle q_1 \middle| \frac{\partial}{\partial q} \middle| q_2 \right\rangle = \int \mathrm{d}q\, \delta(q - q_1) \frac{\partial}{\partial q} \delta(q - q_2) \tag{6.6}$$

[1] There is actually a pair of transformations, known as the *Wigner–Weyl transform*. The Wigner transform, as we introduced, transforms an operator into a phase-space function, while the Weyl transform does the opposite thing: it transform a phase-space function into an operator in Hilbert space.

which would occur, for example, in the matrix element of momentum operator. By chain rule, we have

$$\frac{\partial}{\partial q}\delta(q-q_2)=\delta'(q-q_2)=-\frac{\partial}{\partial q_2}\delta(q-q_2)\,, \tag{6.7}$$

so

$$\begin{aligned}\left\langle q_1\middle|\frac{\partial}{\partial q}\middle|q_2\right\rangle &= -\int \mathrm{d}q\,\delta(q-q_1)\frac{\partial}{\partial q_2}\delta(q-q_2)\\ &= -\frac{\partial}{\partial q_2}\int \mathrm{d}q\,\delta(q-q_1)\delta(q-q_2)\\ &= -\frac{\partial}{\partial q_2}\delta(q_1-q_2)\\ &= -\frac{\partial}{\partial q_2}\left\langle q_1|q_2\right\rangle\,. \end{aligned}\tag{6.8}$$

We will denote the differential with respect to the whole content in the ket as a prime over the ket,

$$\frac{\mathrm{d}}{\mathrm{d}q_2}\left\langle q_1|q_2\right\rangle=\left\langle q_1|q_2\right\rangle'\,, \tag{6.9}$$

so perhaps rather counterintuitively

$$\left\langle q_1\middle|\frac{\partial}{\partial q}\middle|q_2\right\rangle=-\left\langle q_1|q_2\right\rangle'\,. \tag{6.10}$$

We can also denote a differentiation over the whole content in the bra as a reversed prime in from of the bra,

$$\frac{\mathrm{d}}{\mathrm{d}q_1}\left\langle q_1|q_2\right\rangle={}^{\backprime}\!\left\langle q_1|q_2\right\rangle, \tag{6.11}$$

and by the antihermiticity of the differential operator, one can show that

$$\left\langle q_1\middle|\frac{\partial}{\partial q}\middle|q_2\right\rangle={}^{\backprime}\!\left\langle q_1|q_2\right\rangle. \tag{6.12}$$

Next let's evaluate the Wigner transform of the momentum operator $\hat{p}$.

$$p_W(p,q)=\int \mathrm{d}\Delta\,\left\langle q-\frac{\Delta}{2}\middle|\hat{p}\middle|q+\frac{\Delta}{2}\right\rangle \mathrm{e}^{\mathrm{i}\Delta p/\hbar}\,.$$

Note that $\hat{p}=\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}q}$ — but this notation is misleading. We are not differentiating against the symbol q's in the ket and the bra. The $q\pm\Delta/2$ there is more like the q_1 and q_2 in our example above, and we should better denote them as q' to avoid confusion.

$$p_W(p,q')=-\mathrm{i}\hbar\int \mathrm{d}\Delta\,\left\langle q'-\frac{\Delta}{2}\middle|\frac{\mathrm{d}}{\mathrm{d}q}\middle|q'+\frac{\Delta}{2}\right\rangle \mathrm{e}^{\mathrm{i}\Delta p/\hbar}\,.$$

However, this is unnecessary once you are used to this notation, just like $\hat{q}\left|q+\frac{\Delta}{2}\right\rangle=\left(q+\frac{\Delta}{2}\right)\left|q+\frac{\Delta}{2}\right\rangle$ wouldn't cause you any confusion (hopefully). The q here are just formal, but for this time only, we will distinguish the formal q by q'. Using our notation above, we can write this equally as

$$\begin{aligned}p_W(p,q') &= -\mathrm{i}\hbar\int \mathrm{d}\Delta\,{}^{\backprime}\!\left\langle q'-\frac{\Delta}{2}\middle|q'+\frac{\Delta}{2}\right\rangle \mathrm{e}^{\mathrm{i}\Delta p/\hbar}\\ &= +\mathrm{i}\hbar\int \mathrm{d}\Delta\,\left\langle q'-\frac{\Delta}{2}\middle|q'+\frac{\Delta}{2}\right\rangle' \mathrm{e}^{\mathrm{i}\Delta p/\hbar}\end{aligned}\tag{6.13}$$

Alternatively, we can write p_W as the average of the above two expressions.

$$p_W(p,q') = \frac{\mathrm{i}\hbar}{2}\int \mathrm{d}\Delta \left[-{}^{\backprime}\!\left\langle q' - \frac{\Delta}{2} \middle| q' + \frac{\Delta}{2} \right\rangle + \left\langle q' - \frac{\Delta}{2} \middle| q' + \frac{\Delta}{2} \right\rangle' \right] \mathrm{e}^{\mathrm{i}\Delta p/\hbar} . \tag{6.14}$$

By chain rule, this is

$$p_W(p,q') = \mathrm{i}\hbar \int \mathrm{d}\Delta \, \frac{\mathrm{d}}{\mathrm{d}\Delta} \left[\left\langle q - \frac{\Delta}{2} \middle| q + \frac{\Delta}{2} \right\rangle \right] \mathrm{e}^{\mathrm{i}\Delta p/\hbar} . \tag{6.15}$$

We integrate by parts to get

$$\begin{aligned} p_W(p,q') &= -\mathrm{i}\hbar \int \mathrm{d}\Delta \left[\left\langle q - \frac{\Delta}{2} \middle| q + \frac{\Delta}{2} \right\rangle \right] \frac{\mathrm{d}}{\mathrm{d}\Delta} \mathrm{e}^{\mathrm{i}\Delta p/\hbar} \\ &= p \int \mathrm{d}\Delta \left\langle q - \frac{\Delta}{2} \middle| q + \frac{\Delta}{2} \right\rangle \mathrm{e}^{\mathrm{i}\Delta p/\hbar} \\ &= p \, , \end{aligned} \tag{6.16}$$

so the Wigner transform of $\hat{p}$ is also p itself.[2] Similarly, one can show that

$$\mathcal{W}[\hat{p}^n] = p^n \tag{6.20}$$

and

$$\mathcal{W}[f(\hat{p})] = f(p) \tag{6.21}$$

for analytic function f.

The above two results shows that the Wigner transform of a Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{q}) \tag{6.22}$$

is just the classical Hamiltonian

$$H_W = H = \frac{p^2}{2m} + V(q) \tag{6.23}$$

provided that the potential function is analytic.

However, when $\hat{p}$ and $\hat{q}$ are in product, the Wigner transform of $\hat{p}\hat{q}$ wouldn't be exactly pq — otherwise $\hat{p}$ and $\hat{q}$ will be commutative and we will lose all the interesting behaviours of quantum mechanics. To calculate the Wigner transform of $\hat{p}\hat{q}$, we break it into

$$\hat{p}\hat{q} = \frac{1}{2}[\hat{p},\hat{q}] + \frac{1}{2}\{\hat{p},\hat{q}\} \, , \tag{6.24}$$

[2] If you are not comfortable with the notation defined above, here is an alternative way to evaluate the Wigner transform of $\hat{p}$.

$$\begin{aligned} p_W(p,q) &= \int \mathrm{d}\Delta \left\langle q - \frac{\Delta}{2} \middle| \hat{p} \middle| q + \frac{\Delta}{2} \right\rangle \mathrm{e}^{\mathrm{i}\Delta p/\hbar} \\ &= \int \mathrm{d}\Delta \int \mathrm{d}p' \left\langle q - \frac{\Delta}{2} \middle| p' \right\rangle \left\langle p' \middle| \hat{p} \middle| q + \frac{\Delta}{2} \right\rangle \mathrm{e}^{\mathrm{i}\Delta p/\hbar} \\ &= \int \mathrm{d}\Delta \int \mathrm{d}p' \, p' \left\langle q - \frac{\Delta}{2} \middle| p' \right\rangle \left\langle p' \middle| q + \frac{\Delta}{2} \right\rangle \mathrm{e}^{\mathrm{i}\Delta p/\hbar} \, , \end{aligned} \tag{6.17}$$

where we have inserted an identity operator in the momentum basis. Using the plane-wave form $\langle q|p\rangle = \exp(\mathrm{i}qp/\hbar)/\sqrt{2\pi\hbar}$, we get

$$\left\langle q - \frac{\Delta}{2} \middle| p' \right\rangle \left\langle p' \middle| q + \frac{\Delta}{2} \right\rangle = \frac{1}{2\pi\hbar} \exp\left[\frac{\mathrm{i}p'}{\hbar} \left(q - \frac{\Delta}{2} - q - \frac{\Delta}{2} \right) \right] = \frac{1}{2\pi\hbar} \mathrm{e}^{-\mathrm{i}p'\Delta/\hbar} \, , \tag{6.18}$$

so

$$\begin{aligned} p_W(p,q) &= \frac{1}{2\pi\hbar} \int \mathrm{d}\Delta \int \mathrm{d}p' \, p' \mathrm{e}^{\mathrm{i}\Delta(p-p')/\hbar} \\ &= \int \mathrm{d}p' \, p' \delta(p-p') = p \, . \end{aligned} \tag{6.19}$$

where $\{-,-\}$ is the anticommutator. We know that $[\hat{p},\hat{q}] = -\mathrm{i}\hbar$, so its Wigner transform is also trivially $-\mathrm{i}\hbar$. The Wigner transform of the anticommutator is not trivial. The matrix element inside the integral is

$$
\begin{aligned}
\left\langle q-\frac{\Delta}{2}\middle|\hat{p}\hat{q}+\hat{q}\hat{p}\middle|q+\frac{\Delta}{2}\right\rangle &= -\mathrm{i}\hbar\left[\left\langle q-\frac{\Delta}{2}\middle|\frac{\partial}{\partial q}\hat{q}\middle|q+\frac{\Delta}{2}\right\rangle + \left\langle q-\frac{\Delta}{2}\middle|\hat{q}\frac{\partial}{\partial q}\middle|q+\frac{\Delta}{2}\right\rangle\right] \\
&= -\mathrm{i}\hbar\left[\left(q-\frac{\Delta}{2}\right)\left\langle q-\frac{\Delta}{2}\middle|\frac{\partial}{\partial q}\middle|q+\frac{\Delta}{2}\right\rangle - \left(q-\frac{\Delta}{2}\right)\left\langle q-\frac{\Delta}{2}\middle|\frac{\partial}{\partial q}\middle|q+\frac{\Delta}{2}\right\rangle\right] \\
&= -\mathrm{i}\hbar\left[\left(q+\frac{\Delta}{2}\right){}^{\backprime}\left\langle q-\frac{\Delta}{2}\middle|q+\frac{\Delta}{2}\right\rangle - \left(q-\frac{\Delta}{2}\right)\left\langle q-\frac{\Delta}{2}\middle|q+\frac{\Delta}{2}\right\rangle'\right] \\
&= \mathrm{i}\hbar q\left[-{}^{\backprime}\left\langle q-\frac{\Delta}{2}\middle|q+\frac{\Delta}{2}\right\rangle + \left\langle q-\frac{\Delta}{2}\middle|q+\frac{\Delta}{2}\right\rangle'\right] \\
&\quad - \frac{\mathrm{i}\hbar}{2}\left[{}^{\backprime}\left\langle q-\frac{\Delta}{2}\middle|q+\frac{\Delta}{2}\right\rangle + \left\langle q-\frac{\Delta}{2}\middle|q+\frac{\Delta}{2}\right\rangle'\right] \\
&= 2\mathrm{i}\hbar q\frac{\mathrm{d}}{\mathrm{d}\Delta}\left\langle q-\frac{\Delta}{2}\middle|q+\frac{\Delta}{2}\right\rangle - \frac{\mathrm{i}\hbar\Delta}{2}\frac{\mathrm{d}}{\mathrm{d}q}\left\langle q-\frac{\Delta}{2}\middle|q+\frac{\Delta}{2}\right\rangle .
\end{aligned}
\tag{6.25}
$$

Note the $\frac{\mathrm{d}}{\mathrm{d}q}$ in the last term is really the derivative over the formal variable q.

Therefore the Wigner transform of the anticommutator is

$$
\mathcal{W}\left[\{\hat{p},\hat{q}\}\right] = 2\mathrm{i}\hbar q\int \mathrm{d}\Delta\,\frac{\mathrm{d}}{\mathrm{d}\Delta}\left\langle q-\frac{\Delta}{2}\middle|q+\frac{\Delta}{2}\right\rangle \mathrm{e}^{\mathrm{i}\Delta p/\hbar} - \frac{\mathrm{i}\hbar}{2}\frac{\mathrm{d}}{\mathrm{d}q}\int \mathrm{d}\Delta\,\Delta\left\langle q-\frac{\Delta}{2}\middle|q+\frac{\Delta}{2}\right\rangle \mathrm{e}^{\mathrm{i}\Delta p/\hbar} . \tag{6.26}
$$

The first term is exactly what we seen in the Wigner transform of $\hat{p}$, multiplied by a factor of $2q$, so it is $2pq$. The second term evaluates to zero because the braket is effectively a delta function. Therefore,

$$
\mathcal{W}\left[\{\hat{p},\hat{q}\}\right] = 2pq\,, \tag{6.27}
$$

and hence

$$
\mathcal{W}\left[\hat{p}\hat{q}\right] = pq - \frac{\mathrm{i}\hbar}{2}\,. \tag{6.28}
$$

In fact, there is a general formula for the Wigner transform of a product of two operators. This is not particularly relevant to us. We will state it here without proof. The Wigner transform of $\hat{A}\hat{B}$ is

$$
\mathcal{W}\left[\hat{A}\hat{B}\right] = A_W * B_W\,, \tag{6.29}
$$

where the $*$ is the *star product* defined by

$$
(A*B)(p,q) = A(p,q)\exp\left[\frac{\mathrm{i}\hbar}{2}\Lambda\right]B(p,q)\,, \tag{6.30}
$$

where

$$
\Lambda \coloneqq \frac{\overleftarrow{\partial}}{\partial q}\frac{\overrightarrow{\partial}}{\partial p} - \frac{\overleftarrow{\partial}}{\partial p}\frac{\overrightarrow{\partial}}{\partial q}\,. \tag{6.31}
$$

The left and right arrows mean the differentials are only acting on the left and right parts of it. You may find this somehow related to the Poisson brackets in Hamiltonian mechanics. We will discuss more on it later when we talk about dynamics.

6.2 Traces and Thermal Average

Let's consider the expression

$$
\frac{1}{2\pi\hbar}\int \mathrm{d}p\,\mathrm{d}q\,A_W(p,q)B_W(p,q)\,, \tag{6.32}
$$

where A_W and B_W are the Wigner transforms of some operators $\hat{A}$ and $\hat{B}$. We can expand this out as

$$\frac{1}{2\pi\hbar}\int \mathrm{d}p\,\mathrm{d}q \int \mathrm{d}\Delta \left\langle q-\frac{\Delta}{2}\middle|\hat{A}\middle|q+\frac{\Delta}{2}\right\rangle \mathrm{e}^{\mathrm{i}\Delta p/\hbar}\int \mathrm{d}\Delta' \left\langle q+\frac{\Delta'}{2}\middle|\hat{B}\middle|q-\frac{\Delta'}{2}\right\rangle \mathrm{e}^{-\mathrm{i}\Delta' p/\hbar}. \tag{6.33}$$

We can identify the integral over p as

$$\frac{1}{2\pi\hbar}\int \mathrm{d}p\,\mathrm{e}^{\mathrm{i}(\Delta-\Delta')p/\hbar} = \delta(\Delta-\Delta')\,, \tag{6.34}$$

so

$$\begin{aligned}\frac{1}{2\pi\hbar}\int \mathrm{d}p\,\mathrm{d}q\,A_W(p,q)B_W(p,q) &= \int \mathrm{d}q\,\mathrm{d}\Delta \left\langle q-\frac{\Delta}{2}\middle|\hat{A}\middle|q+\frac{\Delta}{2}\right\rangle \left\langle q+\frac{\Delta'}{2}\middle|\hat{B}\middle|q-\frac{\Delta'}{2}\right\rangle \\ &= \mathrm{tr}[\hat{A}\hat{B}]\,. \end{aligned} \tag{6.35}$$

This property is especially useful because we can make $\hat{A}$ the density matrix operator

$$\mathrm{tr}[\hat{\rho}\hat{B}] = \frac{1}{2\pi\hbar}\int \mathrm{d}p\,\mathrm{d}q\,\rho_W(p,q)B_W(p,q)\,. \tag{6.36}$$

In this way, we related the quantum average $\langle B\rangle = \mathrm{tr}[\hat{\rho}\hat{B}]$ with the classical phase space average, provided that we use the phase space density ρ_W given by the Wigner transform of the density matrix, and the operator B_W given by the Wigner transform of $\hat{B}$.

6.3 Dynamics

6.3.1 Heisenberg and Hamilton Equations of Motion

Now let's consider how an observable evolve over time. In Heisenberg's picture, the operators evolve via the Heisenberg equation of motion

$$\dot{\hat{A}} = \frac{\mathrm{i}}{\hbar}[\hat{H},\hat{A}]\,. \tag{6.37}$$

Let's consider the Wigner transform of this time derivative

$$\mathcal{W}\left[\dot{\hat{A}}\right] = \frac{\mathrm{i}}{\hbar}\int \mathrm{d}\Delta \left\langle q-\frac{\Delta}{2}\middle|[\hat{H},\hat{A}]\middle|q+\frac{\Delta}{2}\right\rangle \mathrm{e}^{\mathrm{i}\Delta p/\hbar}\,. \tag{6.38}$$

We split $[\hat{H},\hat{A}]$ into $[\hat{T},\hat{A}]+[\hat{V},\hat{A}]$ and evaluate them separately.

First for the T-commutator, the Wigner transform is

$$\begin{aligned}\mathcal{W}\left[\frac{\mathrm{i}}{\hbar}[\hat{T},\hat{A}]\right] &= -\frac{\mathrm{i}\hbar}{2m}\int \mathrm{d}\Delta \left[\left\langle q-\frac{\Delta}{2}\middle|\frac{\mathrm{d}^2}{\mathrm{d}q^2}\hat{A}\middle|q+\frac{\Delta}{2}\right\rangle - \left\langle q-\frac{\Delta}{2}\middle|\hat{A}\frac{\mathrm{d}^2}{\mathrm{d}q^2}\middle|q+\frac{\Delta}{2}\right\rangle\right]\mathrm{e}^{\mathrm{i}\Delta p/\hbar} \\ &= -\frac{\mathrm{i}\hbar}{2m}\int \mathrm{d}\Delta \left[{}^{\backprime\backprime}\left\langle q-\frac{\Delta}{2}\middle|\hat{A}\middle|q+\frac{\Delta}{2}\right\rangle - \left\langle q-\frac{\Delta}{2}\middle|\hat{A}\middle|q+\frac{\Delta}{2}\right\rangle''\right]\mathrm{e}^{\mathrm{i}\Delta p/\hbar} \end{aligned} \tag{6.39}$$

Notice that

$$\begin{aligned}\frac{\partial^2}{\partial q\partial\Delta}\left\langle q-\frac{\Delta}{2}\middle|\hat{A}\middle|q+\frac{\Delta}{2}\right\rangle &= \frac{1}{2}\frac{\partial}{\partial q}\left[-{}^{\backprime}\left\langle q-\frac{\Delta}{2}\middle|\hat{A}\middle|q+\frac{\Delta}{2}\right\rangle + \left\langle q-\frac{\Delta}{2}\middle|\hat{A}\middle|q+\frac{\Delta}{2}\right\rangle'\right] \\ &= \frac{1}{2}\Bigg[-{}^{\backprime\backprime}\left\langle q-\frac{\Delta}{2}\middle|\hat{A}\middle|q+\frac{\Delta}{2}\right\rangle - {}^{\backprime}\left\langle q-\frac{\Delta}{2}\middle|\hat{A}\middle|q+\frac{\Delta}{2}\right\rangle' \\ &\qquad + {}^{\backprime}\left\langle q-\frac{\Delta}{2}\middle|\hat{A}\middle|q+\frac{\Delta}{2}\right\rangle' + \left\langle q-\frac{\Delta}{2}\middle|\hat{A}\middle|q+\frac{\Delta}{2}\right\rangle''\Bigg] \\ &= -\frac{1}{2}\left[{}^{\backprime\backprime}\left\langle q-\frac{\Delta}{2}\middle|\hat{A}\middle|q+\frac{\Delta}{2}\right\rangle - \left\langle q-\frac{\Delta}{2}\middle|\hat{A}\middle|q+\frac{\Delta}{2}\right\rangle''\right], \end{aligned} \tag{6.40}$$

which is what we had in the bracket in the integrand, so

$$\begin{aligned}\mathcal{W}\left[\frac{\mathrm{i}}{\hbar}[\hat{T},\hat{A}]\right] &= \frac{\mathrm{i}\hbar}{m}\int \mathrm{d}\Delta\,\frac{\partial^2}{\partial q\partial\Delta}\left[\left\langle q-\frac{\Delta}{2}\middle|\hat{A}\middle|q+\frac{\Delta}{2}\right\rangle\right]\mathrm{e}^{\mathrm{i}\Delta p/\hbar} \\ &= \frac{p}{m}\frac{\partial}{\partial q}\int \mathrm{d}\Delta\,\left\langle q-\frac{\Delta}{2}\middle|\hat{A}\middle|q+\frac{\Delta}{2}\right\rangle\mathrm{e}^{\mathrm{i}\Delta p/\hbar} \\ &= \frac{p}{m}\frac{\partial A_W}{\partial q}\,. \end{aligned} \tag{6.41}$$

Now let's move on to the commutator with $\hat{V}$. The Wigner transform is

$$\begin{aligned}\mathcal{W}\left[\frac{\mathrm{i}}{\hbar}[\hat{V},\hat{A}]\right] &= \frac{\mathrm{i}}{\hbar}\int \mathrm{d}\Delta\,\left[\left\langle q-\frac{\Delta}{2}\middle|V(\hat{q})\hat{A}\middle|q+\frac{\Delta}{2}\right\rangle-\left\langle q-\frac{\Delta}{2}\middle|\hat{A}V(\hat{q})\middle|q+\frac{\Delta}{2}\right\rangle\right]\mathrm{e}^{\mathrm{i}\Delta p/\hbar} \\ &= \frac{\mathrm{i}}{\hbar}\int \mathrm{d}\Delta\,\left[V\left(q-\frac{\Delta}{2}\right)-V\left(q+\frac{\Delta}{2}\right)\right]\left\langle q-\frac{\Delta}{2}\middle|\hat{A}\middle|q+\frac{\Delta}{2}\right\rangle\mathrm{e}^{\mathrm{i}\Delta p/\hbar} \end{aligned} \tag{6.42}$$

We expand $V(q-\frac{\Delta}{2})-V(q+\frac{\Delta}{2})$ as a Taylor series

$$\begin{aligned}V\left(q-\frac{\Delta}{2}\right)-V\left(q+\frac{\Delta}{2}\right) &= \sum_{\lambda=0}^{\infty}\frac{1}{\lambda!}\frac{\partial^\lambda V}{\partial q^\lambda}\left[\frac{(-\Delta)^\lambda-\Delta^\lambda}{2^\lambda}\right] \\ &= -\sum_{\lambda=1,\mathrm{odd}}\frac{1}{\lambda!}V^{(\lambda)}(q)\frac{\Delta^\lambda}{2^{\lambda-1}}\,. \end{aligned} \tag{6.43}$$

Therefore Wigner transform becomes

$$\mathcal{W}\left[\frac{\mathrm{i}}{\hbar}[\hat{V},\hat{A}]\right] = -\frac{\mathrm{i}}{\hbar}\sum_{\lambda=1,\mathrm{odd}}\frac{1}{\lambda!}\frac{1}{2^{\lambda-1}}V^{(\lambda)}(q)\int \mathrm{d}\Delta\,\left\langle q-\frac{\Lambda}{2}\middle|\hat{A}\middle|q+\frac{\Lambda}{2}\right\rangle\Delta^\lambda\mathrm{e}^{\mathrm{i}\Delta p/\hbar}\,. \tag{6.44}$$

Notice that

$$\Delta^\lambda\mathrm{e}^{\mathrm{i}\Delta p/\hbar} = \left(-\mathrm{i}\hbar\frac{\partial}{\partial p}\right)^\lambda\mathrm{e}^{\mathrm{i}\Delta p/\hbar}\,, \tag{6.45}$$

so

$$\begin{aligned}\mathcal{W}\left[\frac{\mathrm{i}}{\hbar}[\hat{V},\hat{A}]\right] &= -\frac{\mathrm{i}}{\hbar}\sum_{\lambda=1,\mathrm{odd}}\frac{1}{\lambda!}\frac{1}{2^{\lambda-1}}V^{(\lambda)}(q)\int \mathrm{d}\Delta\,\left\langle q-\frac{\Lambda}{2}\middle|\hat{A}\middle|q+\frac{\Lambda}{2}\right\rangle\left(-\mathrm{i}\hbar\frac{\partial}{\partial p}\right)^\lambda\mathrm{e}^{\mathrm{i}\Delta p/\hbar} \\ &= -\frac{\mathrm{i}}{\hbar}\sum_{\lambda=1,\mathrm{odd}}\frac{1}{\lambda!}\frac{1}{2^{\lambda-1}}V^{(\lambda)}(q)\left(-\mathrm{i}\hbar\frac{\partial}{\partial p}\right)^\lambda\int \mathrm{d}\Delta\,\left\langle q-\frac{\Lambda}{2}\middle|\hat{A}\middle|q+\frac{\Lambda}{2}\right\rangle\mathrm{e}^{\mathrm{i}\Delta p/\hbar} \\ &= -\frac{\partial V}{\partial q}\frac{\partial A_W}{\partial p}-\sum_{\lambda=3,\mathrm{odd}}\frac{1}{\lambda!}\left(\frac{\mathrm{i}\hbar}{2}\right)^{\lambda-1}V^{(\lambda)}(q)\frac{\partial^\lambda A_W}{\partial p^\lambda}\,, \end{aligned} \tag{6.46}$$

where we have isolated out the first term.

Combining what we had above, the Wigner transform of a Heisenberg derivative is

$$(\dot{\hat{A}})_W = \mathcal{W}\left[\frac{\mathrm{i}}{\hbar}[\hat{H},\hat{A}]\right] = \frac{p}{m}\frac{\partial A_W}{\partial q}-\frac{\partial V}{\partial q}\frac{\partial A_W}{\partial p}-\sum_{\lambda=3,\mathrm{odd}}\frac{1}{\lambda!}\left(\frac{\mathrm{i}\hbar}{2}\right)^{\lambda-1}V^{(\lambda)}(q)\frac{\partial^\lambda A_W}{\partial p^\lambda}\,. \tag{6.47}$$

You may find this expression quite familiar. In classical mechanics, the Hamilton's equations of motion states that a phase space function $A(p,q)$ evolves over time via the Hamilton's equation of motion

$$\dot{A}(p,q) = \{A,H\} = \frac{\partial A}{\partial q}\frac{\partial H}{\partial p}-\frac{\partial A}{\partial p}\frac{\partial H}{\partial q}\,, \tag{6.48}$$

where

$$\{X, Y\} := \frac{\partial X}{\partial q}\frac{\partial Y}{\partial p} - \frac{\partial X}{\partial p}\frac{\partial Y}{\partial q} \tag{6.49}$$

is the *Poisson bracket.* For the classical Hamiltonian $H = p^2/2m + V(q)$, this is

$$\dot{A}(p, q) = \frac{p}{m}\frac{\partial A}{\partial q} - \frac{\partial V}{\partial q}\frac{\partial A}{\partial p}\,. \tag{6.50}$$

This is the previous two terms in the Wigner transform of Heisenberg derivative (6.47). In quantum mechanics, we have a series of correction terms in the order of $O(\hbar^2)$.

Notice the parallelism between classical and quantum mechanics, specifically between Heisenberg and Hamilton equations of motion

$$\text{classical:} \quad \dot{A} = \{A, H\} \tag{6.51}$$

$$\text{quantum:} \quad \dot{\hat{A}} = -\frac{\mathrm{i}}{\hbar}[\hat{A}, \hat{H}]\,. \tag{6.52}$$

To promote a classical mechanical system to a quantum mechanical one, one replaces the generalised coordinate q and conjugate momentum p by their corresponding operators $\hat{p}$ and $\hat{q}$, and replace the Poisson brackets $\{-,-\}$ by the commutator $-\frac{\mathrm{i}}{\hbar}[-,-]$. This is known as *canonical quantization.* In the classical limit of $\hbar \to 0$, one may identify

$$[\hat{X}, \hat{Y}] \leftrightarrow \mathrm{i}\hbar\{X, Y\}\,. \tag{6.53}$$

6.3.2 von Neumann and Liouville Equations

Alternatively, we can adopt Schrödinger's picture in quantum mechanics, in which the operators are not changing, but the quantum states, or equivalently the density matrix $\hat{\rho}$, are changing. The evolution of density matrix is given by the von Neumann equation

$$\mathrm{i}\hbar\frac{\mathrm{d}\hat{\rho}}{\mathrm{d}t} = [\hat{H}, \hat{\rho}]\,. \tag{6.54}$$

Using the same step as above, we get

$$(\dot{\hat{\rho}})_W = \mathcal{W}\left[-\frac{\mathrm{i}}{\hbar}[\hat{H}, \hat{\rho}]\right] = -\frac{p}{m}\frac{\partial \rho_W}{\partial q} + \frac{\partial V}{\partial q}\frac{\partial \rho_W}{\partial p} + \sum_{\lambda=3,\mathrm{odd}}^{\infty}\frac{1}{\lambda!}\left(\frac{\mathrm{i}\hbar}{2}\right)^{\lambda-1} V^{(\lambda)}(q)\frac{\partial^\lambda \rho_W}{\partial p^\lambda}\,. \tag{6.55}$$

On the other hand, in classical mechanics, we have the Liouville equation, which states that the density in phase space ρ evolves as

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \{H, \rho\} = -\frac{p}{m}\frac{\partial \rho_W}{\partial q} + \frac{\partial V}{\partial q}\frac{\partial \rho_W}{\partial p}\,. \tag{6.56}$$

Quantum mechanics again put extra quantum corrections of the order $O(\hbar^2)$. One often denote the Poisson bracket with the Hamiltonian as the *Liouvillian* $\mathcal{L}$,[3]

$$\mathcal{L}(*) = -\{H, *\} = \{*, H\}\,, \tag{6.57}$$

or

$$\mathcal{L} = \frac{p}{m}\frac{\partial}{\partial q} - \frac{\partial V}{\partial q}\frac{\partial}{\partial p}\,, \tag{6.58}$$

[3] Some people define the Liouvillian (and also the quantum Liouvillian later) as the negative of what we defined here, $\mathcal{L}(*) = +\{H, *\}$. We make our sign choice here to match the definition of Tim Hele's paper in 2015 which first proposed Matsubara dynamics.

so the Liouville equation reads

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\mathcal{L}\rho\,. \tag{6.59}$$

Similarly one may denote the quantum Liouvillian

$$\hat{\mathcal{L}}(*) = \frac{\mathrm{i}}{\hbar}[\hat{H}, *]\,, \tag{6.60}$$

so the von Neumann equation reads

$$\frac{\mathrm{d}\hat{\rho}}{\mathrm{d}t} = -\hat{\mathcal{L}}\hat{\rho}\,. \tag{6.61}$$

The quantum Liouvillian is therefore

$$\begin{aligned}\hat{\mathcal{L}} &= \frac{p}{m}\frac{\partial}{\partial q} - \sum_{\lambda=1,\mathrm{odd}}^{\infty} \frac{1}{\lambda!}\left(\frac{\mathrm{i}\hbar}{2}\right)^{\lambda-1} \frac{\partial^\lambda V}{\partial q^\lambda}\frac{\partial^\lambda}{\partial p^\lambda} \\ &= \frac{p}{m}\frac{\partial}{\partial q} - V(q)\frac{2}{\hbar}\sin\left(\frac{\overleftarrow{\partial}}{\partial q}\frac{\hbar}{2}\frac{\overrightarrow{\partial}}{\partial p}\right)\end{aligned} \tag{6.62}$$

using the series expansion of sin.

6.4 Deformation Quantisation

What we discussed above is yet another formulation of quantum mechanics, known as *deformation quantisation*.

One may define the *Moyal bracket* from the star product defined above as

$$\{A, B\}_M = A * B - B * A\,. \tag{6.63}$$

Then the Wigner transform of a commutator is exactly the Moyal bracket of their Wigner transforms

$$\mathcal{W}\left[[\hat{A}, \hat{B}]\right] = A_W * B_W - B_W * A_W = \{A_W, B_W\}_M\,. \tag{6.64}$$

The Moyal bracket is related to Poisson bracket via the Moral expansion

$$\{A, B\}_M = \{A, B\} + \sum_{\lambda=3,\mathrm{odd}}^{\infty} \frac{1}{\lambda!}\left(\frac{\mathrm{i}\hbar}{2}\right)^{\lambda-1} V^{(\lambda)}(q)\Lambda^\lambda(A, B)\,, \tag{6.65}$$

where

$$\Lambda(A, B) = A\Lambda B = A\left(\frac{\overleftarrow{\partial}}{\partial q}\frac{\overrightarrow{\partial}}{\partial p} - \frac{\overleftarrow{\partial}}{\partial p}\frac{\overrightarrow{\partial}}{\partial q}\right)B\,. \tag{6.66}$$

The leading term is the classical Poisson bracket, and the higher order terms are all purely quantum corrections in even powers of $\hbar$.

In the ordinary classical dynamics on a phase space (p, q), you have three ingredients

1. Observables: they are analytic functions $A(p, q)$.
2. Product: they are just the normal products $A \cdot B$
3. Bracket: the Poisson bracket $\{A, B\}$.

The idea of deformation quantisation is that you keep the same space of observables, as well as functions on phase space, but deform the product and bracket in a parameter $\hbar$ so that you get quantum mechanics. So now you have

1. Observables: still the analytic functions $A(p, q)$.
2. Product: they modified to the star product $A * B$
3. Bracket: now modified to the Moyal bracket $\{A, B\}_M$.

6.5 LSC-IVR

Consider the Kubo-transformed correlation function

$$K_{AB} = \frac{1}{\beta}\int_0^\beta \mathrm{d}\lambda\ \mathrm{tr}[\mathrm{e}^{-(\beta-\lambda)\hat{H}}\hat{A}\mathrm{e}^{-\lambda\hat{H}}\mathrm{e}^{\mathrm{i}\hat{H}t/\hbar}\hat{B}\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}] = \mathrm{tr}[\hat{K}_A\hat{B}_t]\,, \tag{6.67}$$

where we have neglected the normalising partition function factor and denoted

$$\hat{K}_A = \frac{1}{\beta}\int_0^\beta \mathrm{d}\lambda\,\mathrm{e}^{-(\beta-\lambda)\hat{H}}\hat{A}\mathrm{e}^{-\lambda\hat{H}}\,. \tag{6.68}$$

By (6.35), this trace over two operators can be written as

$$K_{AB} = \frac{1}{2\pi\hbar}\int \mathrm{d}p\,\mathrm{d}q\,\mathcal{W}\left[\hat{K}_A\right]\mathcal{W}\left[\hat{B}(t)\right]\,, \tag{6.69}$$

and its time derivative is

$$\frac{\mathrm{d}K_{AB}}{\mathrm{d}t} = \mathrm{tr}[\hat{K}_A\dot{\hat{B}}(t)] = \frac{1}{2\pi\hbar}\int \mathrm{d}p\,\mathrm{d}q\,\mathcal{W}\left[\hat{K}_A\right]\hat{\mathcal{L}}\mathcal{W}\left[\hat{B}_t\right]\,, \tag{6.70}$$

where the quantum Liouvillian is

$$\hat{\mathcal{L}} = \frac{p}{m}\frac{\partial}{\partial q} - \frac{\partial V}{\partial q}\frac{\partial}{\partial p} - \sum_{\lambda=3,\mathrm{odd}}^{\infty}\frac{1}{\lambda!}\left(\frac{\mathrm{i}\hbar}{2}\right)^{\lambda-1}\frac{\partial^\lambda V}{\partial q^\lambda}\frac{\partial^\lambda}{\partial p^\lambda}\,. \tag{6.71}$$

Integrating the equation of motion, we may write the solution formally as

$$K_{AB}(t) = \frac{1}{2\pi\hbar}\int \mathrm{d}p\,\mathrm{d}q\,\mathcal{W}\left[\hat{K}_A\right](p,q)\mathrm{e}^{\hat{\mathcal{L}}t}\mathcal{W}\left[\hat{B}(0)\right](p,q)\,. \tag{6.72}$$

The quantum Liouvillian and the classical Liouvillian are related by

$$\hat{\mathcal{L}} = \mathcal{L}_{\mathrm{cl}} + O(\hbar^2)\,. \tag{6.73}$$

This is the classical Liouvillian plus a $O(\hbar^2)$ quantum correction, so an obvious approximation to do is to discard the quantum correction, and use the classical Liouvillian. This is known as the linearized semiclassical-initial value representation (LSC-IVR), or sometimes classical Wigner approximation. Therefore the correlation function is approximated by

$$K_{AB}(t) \approx K_{AB}^{\mathrm{Wig}}(t) = \frac{1}{2\pi\hbar}\int \mathrm{d}p\,\mathrm{d}q\,\mathcal{W}\left[\hat{K}_A\right](p,q)\mathrm{e}^{\mathcal{L}_{\mathrm{cl}}t}\mathcal{W}\left[\hat{B}(0)\right](p,q) \tag{6.74}$$

$$= \frac{1}{2\pi\hbar}\int \mathrm{d}p\,\mathrm{d}q\,\mathcal{W}\left[\hat{K}_A\right](p,q)\mathcal{W}\left[\hat{B}(0)\right](p_t,q_t)\,, \tag{6.75}$$

where p_t, q_t are the classical position and momentum at time t of a trajectory initiated at (p, q) at $t = 0$.

This scheme is simple, but it causes a lot of problems. An important one is that the Boltzmann distribution is not conserved under classical Liouvillian

$$\mathcal{L}_{\mathrm{cl}}\mathcal{W}\left[\mathrm{e}^{-\beta\hat{H}}\right] \neq 0\,. \tag{6.76}$$

Also since the dynamics are classical, it cannot describe things like zero point energy or tunneling. In simulations, this will often quickly release the zero point energy stored by the system to thermal kinetic energy. For example, an ice simulated at 150 K will melt in less than a picosecond.

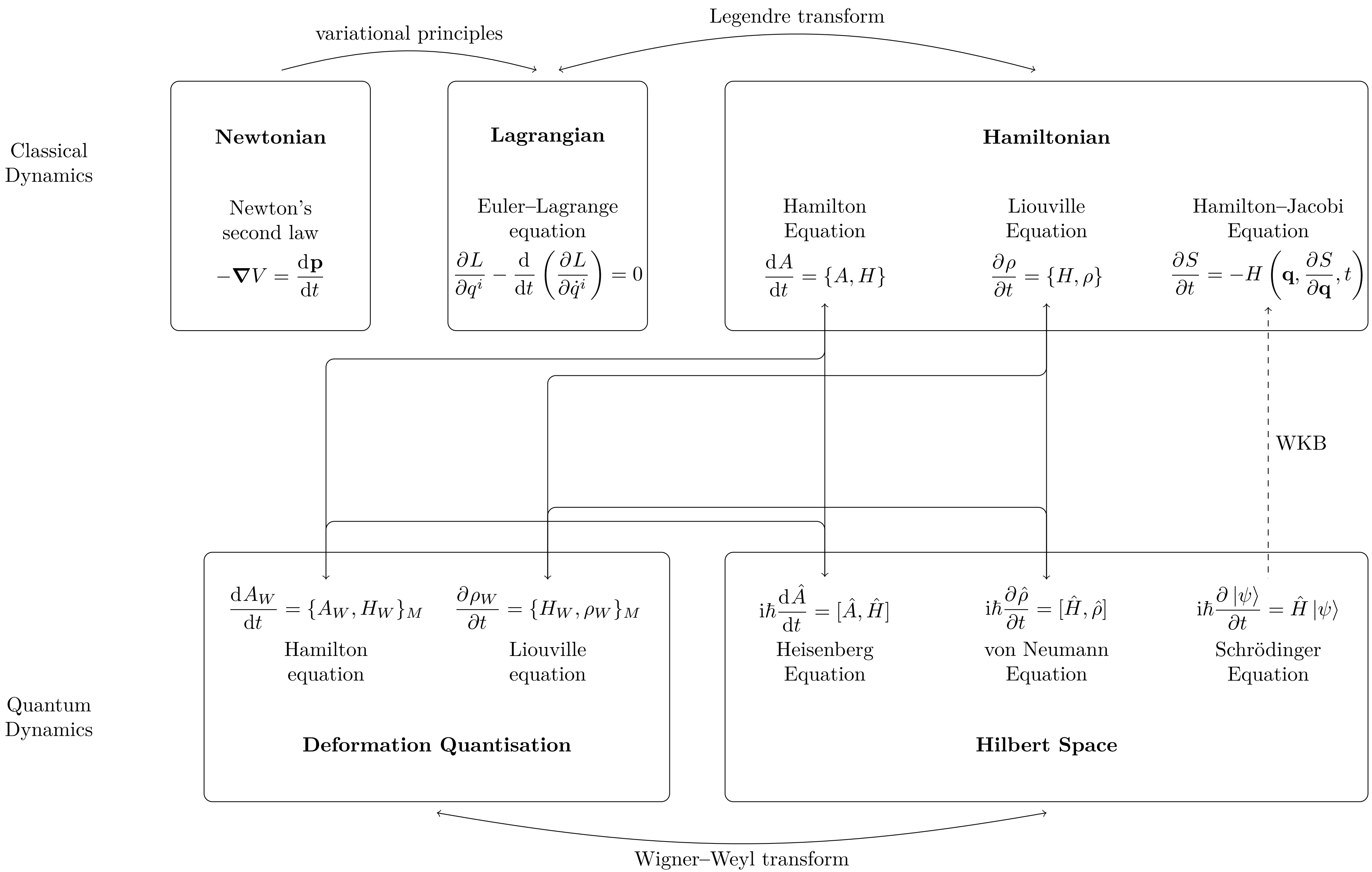

Figure 3: Formulations of Classical and Quantum Dynamics.

7 Matsubara Dynamics

7.1 Correlation Functions with Ring Polymers

Now let's see how the Wigner transform can be applied to correlation functions.

Let's first have a look at the (non-Kubo-transformed) ordinary correlation function

$$C_{AB}(t) = \mathrm{tr}[\mathrm{e}^{-\beta\hat{H}}\hat{A}\mathrm{e}^{\mathrm{i}\hat{H}t/\hbar}\hat{B}\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}]\,. \tag{7.1}$$

We may recast this into an integral

$$C_{AB}(t) = \int \mathrm{d}q\,\mathrm{d}\Delta \left\langle q-\frac{\Delta}{2}\middle|\mathrm{e}^{-\beta\hat{H}}\hat{A}\middle|q+\frac{\Delta}{2}\right\rangle\left\langle q+\frac{\Delta}{2}\middle|\mathrm{e}^{\mathrm{i}\hat{H}t/\hbar}\hat{B}\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}\middle|q-\frac{\Delta}{2}\right\rangle \tag{7.2}$$

$$= \int \mathrm{d}q\,\mathrm{d}\Delta\,\mathrm{d}z\,A\left(q+\frac{\Delta}{2}\right)B(z)\left\langle q-\frac{\Delta}{2}\middle|\mathrm{e}^{-\beta\hat{H}}\middle|q+\frac{\Delta}{2}\right\rangle\left\langle q+\frac{\Delta}{2}\middle|\mathrm{e}^{\mathrm{i}\hat{H}t/\hbar}\middle|z\right\rangle\left\langle z\middle|\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}\middle|q-\frac{\Delta}{2}\right\rangle. \tag{7.3}$$

We can convert this into a more explicit path integral by Trotterizing the imaginary-time evolution $\mathrm{e}^{-\beta\hat{H}}$ and real-time evolution $\mathrm{e}^{\pm\mathrm{i}\hat{H}t/\hbar}$ (although it is unnecessary)

$$\begin{aligned}C_{AB}(t) = \lim_{N\to\infty}\int &\mathrm{d}q\,\mathrm{d}\Delta\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y}\,\mathrm{d}\mathbf{z}\\ &A\left(q+\frac{\Delta}{2}\right)\left\langle q-\frac{\Delta}{2}\middle|\mathrm{e}^{-\beta_N\hat{H}}\middle|x_1\right\rangle\prod_{j=1}^{N-1}\left\langle x_j\middle|\mathrm{e}^{-\beta_N\hat{H}}\middle|x_{j+1}\right\rangle\left\langle x_N\middle|\mathrm{e}^{-\beta_N\hat{H}}\middle|q+\frac{\Delta}{2}\right\rangle\\ &B(z_N)\left\langle q+\frac{\Delta}{2}\middle|\mathrm{e}^{\mathrm{i}\hat{H}t/N\hbar}\middle|y_1\right\rangle\prod_{k=1}^{N-1}\left\langle y_k\middle|\mathrm{e}^{\mathrm{i}\hat{H}t/N\hbar}\middle|y_{k+1}\right\rangle\langle y_N|z_N\rangle\\ &\prod_{k=1}^{N-1}\left\langle z_{k+1}\middle|\mathrm{e}^{-\mathrm{i}\hat{H}t/N\hbar}\middle|z_k\right\rangle\left\langle z_k\middle|\mathrm{e}^{-\mathrm{i}\hat{H}t/N\hbar}\middle|q-\frac{\Delta}{2}\right\rangle\,.\end{aligned} \tag{7.4}$$

This means that we start from a point $q-\frac{\Delta}{2}$, evolve over real time t to $z_N \equiv z$, evaluate B here, then evolve over real time $-t$ back to $t=0$ to some point $q+\frac{\Delta}{2}$, evaluate A there, and evolve over imaginary time $\beta\hbar$ to $q-\frac{\Delta}{2}$ to close the loop. This is averaged over all possible paths and possible end points. The real time propagation is weighted by the path integral propagator $U(t_{k+1}, z_{k+1}; t_k, z_k) = \left\langle z_{k+1}\middle|\mathrm{e}^{\mathrm{i}\hat{H}t/N\hbar}\middle|z_k\right\rangle$ (and similarly for y_k), and the blue imaginary-time evolution at $t=0$ ensures that we are sampling the initial state at the correct Boltzmann distribution.

Now consider the Kubo-transformed correlation function

$$K_{AB}(t) = \frac{1}{\beta}\int_0^\beta \mathrm{d}\lambda\;\mathrm{tr}[\mathrm{e}^{-(\beta-\lambda)\hat{H}}\hat{A}\mathrm{e}^{-\lambda\hat{H}}\mathrm{e}^{\mathrm{i}\hat{H}t/\hbar}\hat{B}\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}]\,. \tag{7.5}$$

We know what the integral over λ does (after Trotterisation) is to put symmetry on the imaginary time evolution: we are evaluating the average of A over all the beads during the imaginary-time evolution.

$$\begin{aligned}K_{AB}(t) = \lim_{N\to\infty}K_{AB}^{[N]}(t) \coloneqq \lim_{N\to\infty}\int \mathrm{d}\mathbf{q}\,\mathrm{d}z\left(\frac{1}{N}\sum_{k=1}^{N}A(q_k)\right)\prod_{j=1}^{N-1}\left\langle q_j\middle|\mathrm{e}^{-\beta_N\hat{H}}\middle|q_{j+1}\right\rangle\\ B(z)\left\langle q_N\middle|\mathrm{e}^{\mathrm{i}\hat{H}t/\hbar}\middle|z\right\rangle\left\langle z\middle|\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}\middle|q_1\right\rangle,\end{aligned} \tag{7.6}$$

where we denoted the N-bead approximation to K_{AB} as $K_{AB}^{[N]}$. We are not breaking the real time evolution explicitly, but do keep in mind that the particle tries all the possible real time evolution path with weights given by the path integral propagator. This means that we are now starting from bead q_1, evolve over real time t to z, evaluate B there, evolve back to $t=0$ to q_N, then evolve over imaginary time $\beta\hbar$ and averaging A over all the beads along the way.

However, due to the cyclic symmetry, the ring polymer beads are not aware which label we gave them. The process we described above is equivalent to starting from an arbitrary bead, say q_{101}, evolve over imaginary time to q_1, evolve over real time forward and backwards, then complete the imaginary time loop to the starting point q_{101}. It completes the same loop. We can see this by shifting the labels of the beads by 100. Therefore, we can evolve over real time in between any two beads in the imaginary-time polymer (open) ring from q_1 to q_N. We take one step further and write the Kubo transformed correlation function to be the average of all possible places the real time evolution can happen,

$$K_{AB}^{[N]}(t) = \frac{1}{N}\sum_{\ell=1}^{N}\int \mathrm{d}\mathbf{q}\,\mathrm{d}z \left(\frac{1}{N}\sum_{k=1}^{N}A(q_k)\right)\prod_{j=1}^{N-1}\left\langle q_j\middle|\mathrm{e}^{-\beta_N\hat{H}}\middle|q_{j+1}\right\rangle B(z)\left\langle q_\ell\middle|\mathrm{e}^{\mathrm{i}\hat{H}t/\hbar}\middle|z\right\rangle\left\langle z\middle|\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}\middle|q_{\ell+1}\right\rangle. \tag{7.7}$$

One might notice that this is in fact equivalent to

$$K_{AB}^{[N]}(t) = \frac{1}{N}\sum_{\ell=1}^{N}\int \mathrm{d}\mathbf{q}\,\mathrm{d}\mathbf{y}\,\mathrm{d}\mathbf{z}\left(\frac{1}{N}\sum_{k=1}^{N}A(q_k)\right)\left(\frac{1}{N}\sum_{\ell=1}^{N}B(z_\ell)\right)\prod_{j=1}^{N}\left\langle q_j\middle|\mathrm{e}^{-\beta_N\hat{H}}\middle|y_j\right\rangle\left\langle y_j\middle|\mathrm{e}^{\mathrm{i}\hat{H}t/\hbar}\middle|z_j\right\rangle\left\langle z_j\middle|\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}\middle|q_{j+1}\right\rangle \tag{7.8}$$

if we pull the red $\frac{1}{N}\sum_\ell$ outside and notice that all other $\int \mathrm{d}y_j\,|y_j\rangle\langle y_j|$ and $\int \mathrm{d}z_j\,|z_j\rangle\langle z_j|$ with $j\neq\ell$ collapse to the identity operator. By a change of variable, we can rewrite this as

$$K_{AB}^{[N]}(t) = \int \mathrm{d}\mathbf{q}\,\mathrm{d}\boldsymbol{\Delta}\,\mathrm{d}\mathbf{z}\,\mathcal{A}_N(\mathbf{q})\mathcal{B}_N(\mathbf{z})\prod_{j=1}^{N}\left\langle q_{j-1}-\frac{\Delta_{j-1}}{2}\middle|\mathrm{e}^{-\beta_N\hat{H}}\middle|q_j+\frac{\Delta_j}{2}\right\rangle\left\langle q_j+\frac{\Delta_j}{2}\middle|\mathrm{e}^{+\mathrm{i}\hat{H}t/\hbar}\middle|z_j\right\rangle\left\langle z_j\middle|\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}\middle|q_j-\frac{\Delta_j}{2}\right\rangle \tag{7.9}$$

We have moved the evaluation of A at the ends of polymer beads $q_i+\frac{\Delta_i}{2}$ to the centers q_i, assuming continuity of $A(q)$. This symmetrisation of z is clearly redundant compared with (7.7), but it better respects the symmetry of the ring polymer.

At $t=0$, the red part becomes

$$\prod_j\left\langle q+\frac{\Delta_j}{2}\middle|z_j\right\rangle\left\langle z_j\middle|q_j-\frac{\Delta_j}{2}\right\rangle = \prod_j\delta(\Delta_j)\delta(z_j-q_j). \tag{7.10}$$

We can imagine this as the blue segments closing up to form a closed polymer, and we are just multiplying $\mathcal{A}_N$ with $\mathcal{B}_N$ for that closed ring polymer.

Next, we insert N identity operators to get

$$K_{AB}^{[N]}(t) = \int \mathrm{d}\mathbf{q}\,\mathrm{d}\boldsymbol{\Delta}\,\mathrm{d}\mathbf{z}\,\mathrm{d}\boldsymbol{\Delta}'\,\mathcal{A}_N(\mathbf{q})\mathcal{B}_N(\mathbf{z})\prod_{j=1}^{N}\delta(\Delta'_j-\Delta_j)\left\langle q_{j-1}-\frac{\Delta_{j-1}}{2}\middle|\mathrm{e}^{-\beta_N\hat{H}}\middle|q_j+\frac{\Delta_j}{2}\right\rangle\left\langle q_j+\frac{\Delta'_j}{2}\middle|\mathrm{e}^{+\mathrm{i}\hat{H}t/\hbar}\middle|z_j\right\rangle\left\langle z_j\middle|\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}\middle|q_j-\frac{\Delta'_j}{2}\right\rangle \tag{7.11}$$

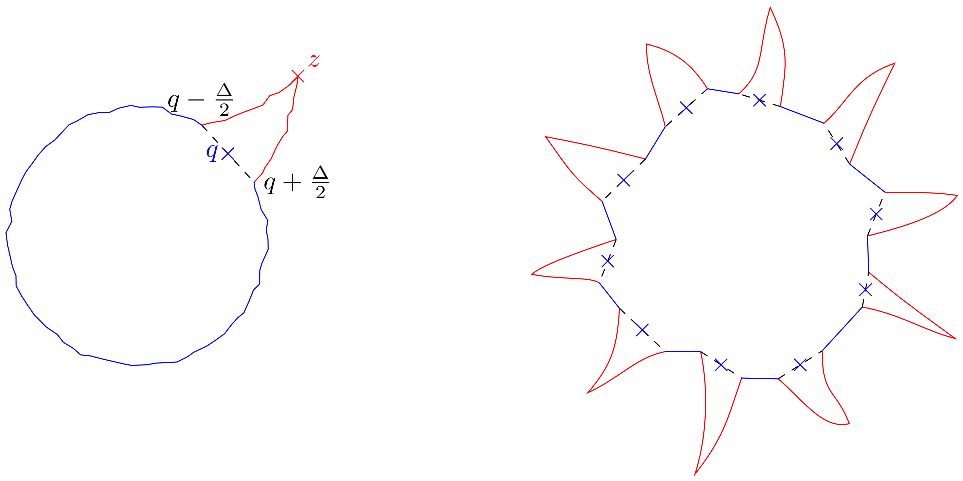

Figure 4: Normal correlation function (left) and Kubo-transformed correlation function (right). We did not Trotterize the real time evolution for the Kubo graph (although we can).

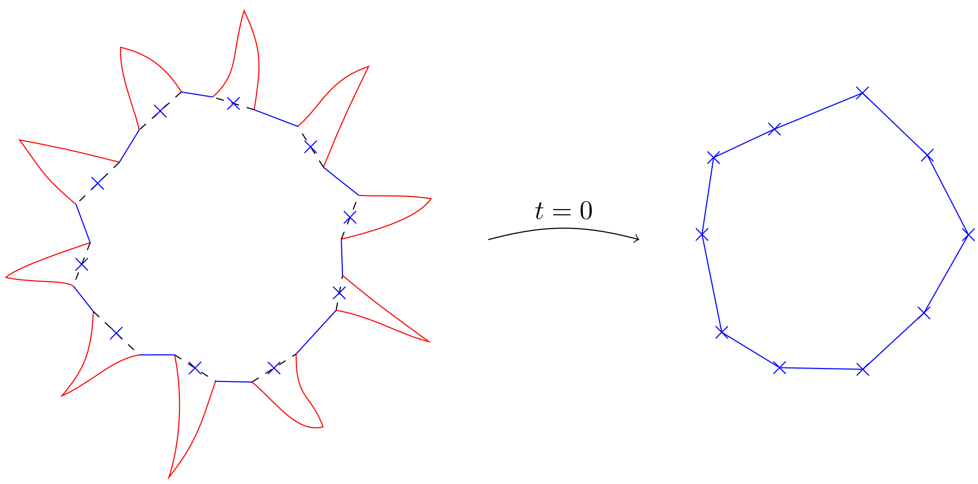

Figure 5: The ring polymer closes up at $t = 0$.

We then further do Fourier expansions of the delta functions to get

$$
\begin{aligned}
K_{AB}^{[N]}(t) = \frac{1}{(2\pi\hbar)^N} \int \mathrm{d}\mathbf{q}\,\mathrm{d}\boldsymbol{\Delta}\,\mathrm{d}\mathbf{z}\,\mathrm{d}\boldsymbol{\Delta'}\,\mathrm{d}\mathbf{p}\,\mathcal{A}_N(\mathbf{q})\mathcal{B}_N(\mathbf{z}) \prod_{j=1}^{N} \mathrm{e}^{\mathrm{i}p_j(\Delta'_j-\Delta_j)/\hbar} \\
\left\langle q_{j-1} - \frac{\Delta_{j-1}}{2} \middle| \mathrm{e}^{-\beta_N \hat{H}} \middle| q_j + \frac{\Delta_j}{2} \right\rangle \left\langle q_j + \frac{\Delta'_j}{2} \middle| \mathrm{e}^{+\mathrm{i}\hat{H}t/\hbar} \middle| z_j \right\rangle \left\langle z_j \middle| \mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar} \middle| q_j - \frac{\Delta'_j}{2} \right\rangle
\end{aligned} \tag{7.12}
$$

That looks a bit complicated, but it nicely factors out, and we can see that this is actually a classical phase space average

$$
\begin{aligned}
K_{AB}^{[N]}(t) &= \frac{1}{(2\pi\hbar)^N} \int \mathrm{d}\mathbf{q}\,\mathrm{d}\mathbf{p} \\
&\quad \mathcal{A}_N(\mathbf{q}) \int \mathrm{d}\boldsymbol{\Delta} \prod_{j=1}^{N} \mathrm{e}^{-\mathrm{i}\Delta_j p_j/\hbar} \left\langle q_{j-1} - \frac{\Delta_{j-1}}{2} \middle| \mathrm{e}^{-\beta_N \hat{H}} \middle| q_j + \frac{\Delta_j}{2} \right\rangle \\
&\quad \int \mathrm{d}\mathbf{z}\,\mathrm{d}\boldsymbol{\Delta'}\,\mathcal{B}_N(\mathbf{z}) \prod_{k=1}^{N} \mathrm{e}^{\mathrm{i}\Delta'_k p_k/\hbar} \left\langle q_k + \frac{\Delta'_k}{2} \middle| \mathrm{e}^{+\mathrm{i}\hat{H}t/\hbar} \middle| z_k \right\rangle \left\langle z_k \middle| \mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar} \middle| q_k - \frac{\Delta'_k}{2} \right\rangle
\end{aligned} \tag{7.13}
$$

The red part is nice. It is the average of Wigner transforms of $\hat{B}(t)$ over all beads. To see this, we expand $\mathcal{B}_N$ to get

$$
\begin{aligned}
&\int \mathrm{d}\mathbf{z}\,\mathrm{d}\boldsymbol{\Delta'}\,\mathcal{B}_N(\mathbf{z}) \prod_{k=1}^{N} \mathrm{e}^{\mathrm{i}\Delta'_k p_k/\hbar} \left\langle q_k + \frac{\Delta'_k}{2} \middle| \mathrm{e}^{+\mathrm{i}\hat{H}t/\hbar} \middle| z_k \right\rangle \left\langle z_k \middle| \mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar} \middle| q_k - \frac{\Delta'_k}{2} \right\rangle \\
&= \frac{1}{N} \sum_{\ell=1}^{N} \int \mathrm{d}z_\ell\,\mathrm{d}\Delta'_\ell\,B(z_\ell)\mathrm{e}^{\mathrm{i}\Delta'_\ell p_\ell/\hbar} \left\langle q_\ell + \frac{\Delta'_k}{2} \middle| \mathrm{e}^{+\mathrm{i}\hat{H}t/\hbar} \middle| z_\ell \right\rangle \left\langle z_\ell \middle| \mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar} \middle| q_\ell - \frac{\Delta'_\ell}{2} \right\rangle \\
&\quad \prod_{k=1,k\neq\ell}^{N} \int \mathrm{d}z_k\,\mathrm{d}\Delta'_k\,\mathrm{e}^{\mathrm{i}\Delta'_k p_k/\hbar} \left\langle q_k + \frac{\Delta'_k}{2} \middle| \mathrm{e}^{+\mathrm{i}\hat{H}t/\hbar} \middle| z_k \right\rangle \left\langle z_k \middle| \mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar} \middle| q_k - \frac{\Delta'_k}{2} \right\rangle \\
&= \frac{1}{N} \sum_{\ell=1}^{N} \mathcal{W}\left[\hat{B}(t)\right](p_\ell, q_\ell) =: \mathcal{W}\left[\hat{B}(t)\right]_N(\mathbf{p},\mathbf{q})\,,
\end{aligned} \tag{7.14}
$$

where in the second line, notice that $k = \ell$ part is just the Wigner transform of B at time t, while the $k \neq \ell$ parts all reduces to the identity. We see this as the Wigner transform generalised for ring polymer, which we denoted as $\mathcal{W}[-]_N(\mathbf{p},\mathbf{q})$. The blue part is, however, not the average of Wigner transforms aver all beads. We will denote it as $\tilde{\mathcal{W}}[-]_N(\mathbf{p},\mathbf{q})$ for simplicity, but do keep in mind that this is not really average of Wigner transforms. Therefore, we have written $K_{AB}^{[N]}(t)$ as

$$
K_{AB}^{[N]}(t) = \frac{1}{(2\pi\hbar)^N} \int \mathrm{d}\mathbf{p}\,\mathrm{d}\mathbf{q}\,\tilde{\mathcal{W}}\left[\hat{A}\right]_N(\mathbf{p},\mathbf{q})\;\mathcal{W}\left[\hat{B}(t)\right]_N(\mathbf{p},\mathbf{q})\,. \tag{7.15}
$$

7.2 Time Evolution and LSC-IVR for Ring Polymer

Luckily, all the time dependence in the correlation function (7.15) is on $\mathcal{W}\left[\hat{B}(t)\right]_N(\mathbf{p},\mathbf{q})$, which is the true (averaged) Wigner transform, and we already know its time evolution from the last chapter. We have

$$
\frac{\mathrm{d}K_{AB}^{[N]}(t)}{\mathrm{d}t} = \frac{1}{(2\pi\hbar)^N} \int \mathrm{d}\mathbf{p}\,\mathrm{d}\mathbf{q}\,\tilde{\mathcal{W}}\left[\hat{A}\right]_N(\mathbf{p},\mathbf{q})\;\mathcal{L}_N\mathcal{W}\left[\hat{B}(t)\right]_N(\mathbf{p},\mathbf{q})\,, \tag{7.16}
$$

where

$$\begin{aligned}\mathcal{L}_N &= \sum_{\ell=1}^{N} \frac{p_\ell}{m}\frac{\partial}{\partial q_\ell} - \sum_{\lambda=1,\mathrm{odd}}^{\infty} \frac{1}{\lambda!}\left(\frac{\mathrm{i}\hbar}{2}\right)^{\lambda-1} \frac{\partial^\lambda V}{\partial {q_\ell}^\lambda}\frac{\partial^\lambda}{\partial {p_\ell}^\lambda} \\ &= \frac{1}{m}\mathbf{p}\cdot\boldsymbol{\nabla}_{\mathbf{q}} - V_N(\mathbf{q})\frac{2}{\hbar}\sin\left(\frac{\hbar}{2}\overleftarrow{\boldsymbol{\nabla}}_{\mathbf{q}}\cdot\overrightarrow{\boldsymbol{\nabla}}_{\mathbf{p}}\right).\end{aligned} \tag{7.17}$$

Recall that $V_N(\mathbf{q}) = \sum_i V(q_i)$.

The LSC-IVR approximation for the ring polymer follows by truncating the Liouvillian to $O(\hbar^0)$ so

$$\mathcal{L}_{\mathrm{cl},N} = \sum_{\ell=1}^{N} \frac{p_\ell}{m}\frac{\partial}{\partial q_\ell} - \frac{\partial V}{\partial q_\ell}\frac{\partial}{\partial p_\ell}. \tag{7.18}$$

The correlation function is then approximated by propagating $\mathbf{p}$ and $\mathbf{q}$ classically so

$$\begin{aligned}K_{AB}(t) \approx K_{AB}^{\mathrm{Wig},[N]} &= \frac{1}{(2\pi\hbar)^N}\int \mathrm{d}\mathbf{p}\,\mathrm{d}\mathbf{q}\,\tilde{\mathcal{W}}\left[\hat{A}\right]_N(\mathbf{p},\mathbf{q})\,\mathrm{e}^{\mathcal{L}_{\mathrm{cl},N}t}\mathcal{W}\left[\hat{B}(0)\right]_N(\mathbf{p},\mathbf{q}) \\ &= \frac{1}{(2\pi\hbar)^N}\int \mathrm{d}\mathbf{p}\,\mathrm{d}\mathbf{q}\,\tilde{\mathcal{W}}\left[\hat{A}\right]_N(\mathbf{p},\mathbf{q})\,\mathcal{W}\left[\hat{B}(0)\right]_N(\mathbf{p}_t,\mathbf{q}_t).\end{aligned}$$

One can show that this agrees with the standard LSC-IVR approximation in the $N\to\infty$ limit by, for example, pulling out the sum and integrating out the irrelevant $(N-1)$ p's:

$$K_{AB}(t) \approx K_{AB}^{\mathrm{Wig}}(t) = \lim_{N\to\infty} K_{AB}^{\mathrm{Wig},[N]}(t). \tag{7.19}$$

7.3 Normal Modes

Recall that we introduced normal mode transformation in section 3.1 as a tool to propagate the dynamics of a ring polymer (classically). It turns out that this will be a particularly useful tool for quantum dynamics, which will eventually lead to the Matsubara dynamics.

To simplify the algebra, suppose we have an odd number of polymer beads N. Now the normal mode coordinates are

$$Q_n = \sum_{\ell=1}^{N} T_{\ell n} q_\ell \tag{7.20}$$

where we take $-\tilde{N} \le n \le \tilde{N}$ with $\tilde{N} = (N-1)/2$, so

$$T_{\ell n} = \begin{cases} \sqrt{1/N} & n = 0 \\ \sqrt{2/N}\sin(2\pi\ell n/N) & 1 \le n \le \tilde{N} \\ \sqrt{2/N}\cos(2\pi\ell n/N) & -1 \ge n \ge -\tilde{N}. \end{cases} \tag{7.21}$$

P_n, D_n *etc.* are the corresponding transformations of $\mathbf{p}$, $\boldsymbol{\Delta}$ *etc.*, respectively. Note that compared to what we defined in section 3.1, the $n = N/2$ mode disappeared because we take N to be odd, and we shifted the label of the cos modes to negative. The benefit for doing that is our normal mode frequency

$$\omega_n = \frac{2}{\beta_N\hbar}\sin\left(\frac{n\pi}{N}\right) \tag{7.22}$$

naturally becomes negative for cos modes (with the same magnitude), which will make our later expressions somewhat neater. The Hamiltonian written in terms of the normal mode coordinates is

$$H_N(\mathbf{P},\mathbf{Q}) = \left(\sum_{n=-\tilde{N}}^{\tilde{N}} \frac{P_n^2}{2m} + \frac{1}{2}m\omega_n^2 Q_n^2\right) + V_N(\mathbf{Q}), \tag{7.23}$$

where $V_N(\mathbf{Q}) = \sum_i^N V(q_i)$. We have invoked several abuses of notations by calling the same quantity in different coordinates (which are mathematically different functions) the same name.

The correlation function can be transformed in the normal mode basis as well:

$$\begin{aligned} K_{AB}^{[N]}(t) = {} & \frac{1}{(2\pi\hbar)^N} \int \mathrm{d}\mathbf{Q}\,\mathrm{d}\mathbf{P} \\ & \mathcal{A}_N(\mathbf{Q}) \int \mathrm{d}\mathbf{D} \prod_{j=-\tilde{N}}^{\tilde{N}} \mathrm{e}^{-\mathrm{i}D_j P_j/\hbar} \left\langle Q_{j-1} - \frac{D_{j-1}}{2} \middle| \mathrm{e}^{-\beta_N \hat{H}} \middle| Q_j + \frac{D_j}{2} \right\rangle \\ & \int \mathrm{d}\mathbf{Z}\,\mathrm{d}\mathbf{D'}\,\mathcal{B}_N(\mathbf{Z}) \prod_{k=-\tilde{N}}^{\tilde{N}} \mathrm{e}^{\mathrm{i}D'_k P_k/\hbar} \left\langle Q_k + \frac{D'_k}{2} \middle| \mathrm{e}^{+\mathrm{i}\hat{H}t/\hbar} \middle| Z_k \right\rangle \left\langle Z_k \middle| \mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar} \middle| Q_k - \frac{D'_k}{2} \right\rangle \end{aligned} \tag{7.24}$$

$$=: \frac{1}{(2\pi\hbar)^N} \int \mathrm{d}\mathbf{Q}\,\mathrm{d}\mathbf{P}\, \tilde{\mathcal{W}}\left[\hat{A}\right]_N (\mathbf{P},\mathbf{Q})\, \mathcal{W}\left[\hat{B}(t)\right]_N (\mathbf{P},\mathbf{Q}), \tag{7.25}$$

where, again, we have abused notations to write $\mathcal{A}_N(\mathbf{Q}) = \mathcal{A}_N(\mathbf{q})$, evaluated by transforming $\mathbf{Q}$ to $\mathbf{q}$ and similarly for $\mathcal{B}_N$. The exact quantum dynamics is described by

$$\frac{\mathrm{d}K_{AB}^{[N]}(t)}{\mathrm{d}t} = \frac{1}{(2\pi\hbar)^N} \int \mathrm{d}\mathbf{Q}\,\mathrm{d}\mathbf{P}\, \tilde{\mathcal{W}}\left[\hat{A}\right]_N (\mathbf{P},\mathbf{Q})\, \mathcal{L}_N \mathcal{W}\left[\hat{B}(t)\right]_N (\mathbf{P},\mathbf{Q}), \tag{7.26}$$

where

$$\mathcal{L}_N = \frac{1}{m}\mathbf{P}\cdot\boldsymbol{\nabla}_{\mathbf{Q}} - V_N(\mathbf{Q})\frac{2}{\hbar}\sin\left(\frac{\hbar}{2}\overleftarrow{\boldsymbol{\nabla}}_{\mathbf{Q}}\cdot\overrightarrow{\boldsymbol{\nabla}}_{\mathbf{P}}\right). \tag{7.27}$$

You may have noticed that all of the formulae above are formally the same as in the physical coordinates $(\mathbf{p},\mathbf{q})$ since the normal mode transformation is orthogonal.

7.4 Matsubara Modes

If we perform the normal mode transformation of N beads, we would get N normal modes. What we can do, however, is to take some very large N, then truncate the normal modes to include the M lowest modes only for some $M \ll N$. In the $N \to \infty$ limit, the frequencies ω_n tends to the values

$$\tilde{\omega}_n = \lim_{N\to\infty} \omega_n = \frac{2n\pi}{\beta\hbar} \tag{7.28}$$

for $-\tilde{M} \le n \le \tilde{M}$, $\tilde{M} = (M-1)/2$. These are known as the *Matsubara frequencies*, which were originally proposed in quantum field theory to Fourier expand finite-temperature quantum fields in Euclidean time. The lowest modes M modes we include are the *Matsubara modes*,

$$\tilde{Q}_n = \lim_{N\to\infty} \frac{Q_n}{\sqrt{N}} \tag{7.29}$$

for $-\tilde{M} \le n \le \tilde{M}$ (and similarly for $\tilde{P}_n$ and $\tilde{D}_n$ *etc.*). Note a few things:

- We have an extra factor of $N^{-1/2}$. This ensures that $\tilde{Q}_n$ scales as N^0, so it is bounded in the limit of $N \to \infty$.
- The transformation from $\mathbf{q}$ to $\mathbf{Q}$ is no longer orthogonal. We need to be careful of factors of N in future expressions.
- $\tilde{P}_n$ is no longer the conjugate momentum of $\tilde{Q}_n$. In classical mechanics, the conjugate momentum of generalised coordinate q^i is $p_i = \partial L/\partial \dot{q}^i$. If we scale q^i by $N^{-1/2}$, then p^i should scale by $N^{+1/2}$. However in our definition, both Q_n and P_n (and other coordinates) are scaled by $N^{-1/2}$, so the conjugated momentum of $\tilde{Q}_n$ should really be $N\tilde{P}_n$. However, this will blow up in the limit of $N \to \infty$, so we instead choose to scale everything by $N^{-1/2}$ uniformly.

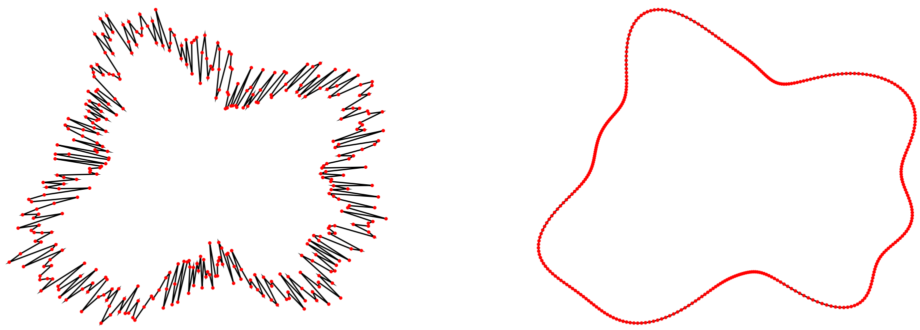

Figure 6: Jagged polymer and smooth polymer including only the lowest M Matsubara modes.

What is good now is that since $N \to \infty$ and we only have a few low frequency modes, the bead coordinates can now be seen as a smooth function of imaginary time $q(\tau)$ such that

$$q_\ell = q(\tau) \tag{7.30}$$

for $\tau = \beta_N \hbar \ell$, $1 \leq \ell \leq N$.

The remaining $N - M$ modes are the "non-Matsubara" modes that gives rises to the jaggedness of the ring polymer.

7.5 Matsubara Dynamics