Path integral molecular dynamics

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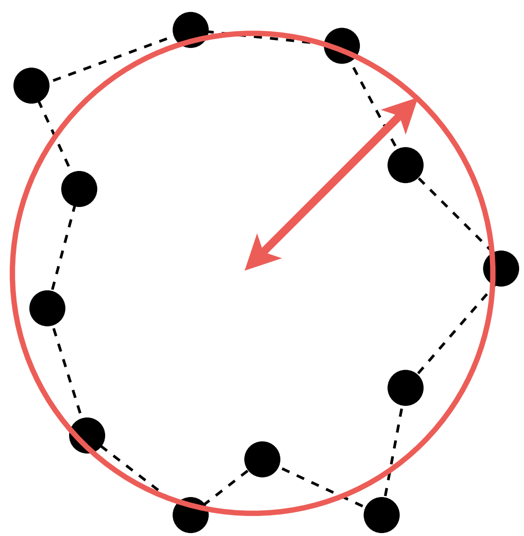
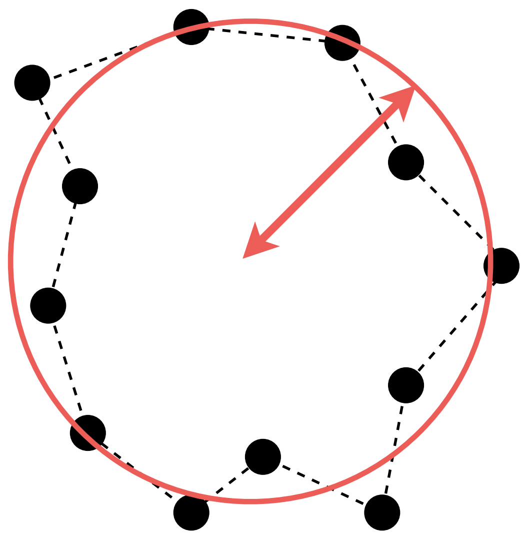


$$\Delta q = \Lambda(T)/\sqrt{8\pi}$$
$$\Lambda(T) = h/\sqrt{2\pi mkT}$$
$$\Delta p = \sqrt{mkT}$$
$$\Rightarrow \Delta p \Delta q = \frac{\hbar}{2}.$$

Mariapfarr Workshop 2019, Lecture I

I. The classical isomorphism[1,2]



$$\Delta q = \Lambda(T)/\sqrt{8\pi}$$

$$\Lambda(T) = h/\sqrt{2\pi mkT}$$

$$\Delta p = \sqrt{mkT}$$

$$\Rightarrow \Delta p \Delta q = \frac{\hbar}{2}.$$

$$Q = \mathrm{tr}\left[e^{-\beta \hat{H}}\right]$$

$$Q = \frac{1}{(2\pi\hbar)^n} \int d\mathbf{p} \int d\mathbf{q}\; e^{-\beta_n H_n(\mathbf{p},\mathbf{q})}$$

$$H_n(\mathbf{p},\mathbf{q}) = \sum_{j=1}^{n} \left[\frac{p_j^2}{2m} + \frac{1}{2} m\omega_n^2 (q_j - q_{j+1})^2 + V(q_j) \right]; \quad \beta_n = \beta/n; \quad \omega_n = 1/(\beta_n \hbar).$$

Background:

In standard (basis set) quantum mechanics

$$\langle \nu | \nu' \rangle = \delta_{\nu\nu'} \quad \hat{1} = \sum_{\nu} |\nu\rangle \langle \nu| \quad \mathrm{tr}\left[\hat{A}\right] = \sum_{\nu} \langle \nu| \hat{A} |\nu\rangle \,.$$

In the position and momentum representations[3]

$$\langle q|p\rangle = \sqrt{\frac{1}{2\pi\hbar}} e^{+ipq/\hbar} \quad \langle p|q\rangle = \langle q|p\rangle^{*} = \sqrt{\frac{1}{2\pi\hbar}} e^{-ipq/\hbar}$$

the analogous results are

$$\langle q|q'\rangle = \delta(q-q') \qquad \langle p|p'\rangle = \delta(p-p')$$

$$\hat{1} = \int dq\, |q\rangle \langle q| \qquad \hat{1} = \int dp\, |p\rangle \langle p|$$

$$\mathrm{tr}\left[\hat{A}\right] = \int dq\, \langle q| \hat{A} |q\rangle \quad \mathrm{tr}\left[\hat{A}\right] = \int dp\, \langle p| \hat{A} |p\rangle \,.$$

Proof of the isomorphism:

$$Q = \mathrm{tr}\left[e^{-\beta\hat{H}}\right] = \mathrm{tr}\left[\left(e^{-\beta_n\hat{H}}\right)^n\right] \text{ where } \beta_n = \beta/n.$$

So

$$Q = \int dq_1 \ldots \int dq_n \, \langle q_1| \, e^{-\beta_n\hat{H}} \, |q_2\rangle \ldots \langle q_n| \, e^{-\beta_n\hat{H}} \, |q_1\rangle \, ,$$

with

$$\begin{aligned}
\langle q| \, e^{-\beta_n\hat{H}} \, |q'\rangle &\simeq \langle q| \, e^{-\beta_n\hat{V}/2} e^{-\beta_n\hat{T}} e^{-\beta_n\hat{V}/2} \, |q'\rangle \\
&= \frac{1}{2\pi\hbar}\int dp \, e^{-\beta_n p^2/2m + ip(q-q')/\hbar - \beta_n[V(q)/2+V(q')/2]} \\
&= \frac{1}{2\pi\hbar}\left(\frac{2\pi m}{\beta_n}\right)^{1/2} e^{-\beta_n[m\omega_n^2(q-q')^2/2+V(q)/2+V(q')/2]} \\
&= \frac{1}{2\pi\hbar}\int dp \, e^{-\beta_n[p^2/2m+m\omega_n^2(q-q')^2/2+V(q)/2+V(q')/2]},
\end{aligned}$$

gives Q with an error of $O(n^{-2})$.

2. Path integral molecular dynamics[4]

PIMD uses the ring polymer trajectories

$$\dot{\mathbf{q}} = +\frac{\partial H_n(\mathbf{p},\mathbf{q})}{\partial \mathbf{p}} \qquad \dot{\mathbf{p}} = -\frac{\partial H_n(\mathbf{p},\mathbf{q})}{\partial \mathbf{q}}$$

as a sampling tool to calculate *exact* values of static equilibrium properties such as

$$\langle A \rangle = \frac{1}{Q}\mathrm{tr}\left[e^{-\beta \hat{H}}\hat{A}\right].$$

Average potential energy

$$\begin{aligned}
\mathrm{tr}\left[e^{-\beta \hat{H}}\,\hat{V}\right] &= \mathrm{tr}\left[\left(e^{-\beta_n \hat{H}}\right)^{j-1}\hat{V}\left(e^{-\beta_n \hat{H}}\right)^{n+1-j}\right] \\
&= \int dq_1 \ldots \int dq_n \, \langle q_1|\, e^{-\beta_n \hat{H}}\, |q_2\rangle \ldots \langle q_j|\, \hat{V} e^{-\beta_n \hat{H}}\, |q_{j+1}\rangle \ldots \langle q_n|\, e^{-\beta_n \hat{H}}\, |q_1\rangle \\
&= \int dq_1 \ldots \int dq_n \, \langle q_1|\, e^{-\beta_n \hat{H}}\, |q_2\rangle \ldots \langle q_n|\, e^{-\beta_n \hat{H}}\, |q_1\rangle \, V(q_j) \\
&= \frac{1}{(2\pi\hbar)^n}\int d\mathbf{p}\int d\mathbf{q}\, e^{-\beta_n H_n(\mathbf{p},\mathbf{q})} V(q_j)
\end{aligned}$$

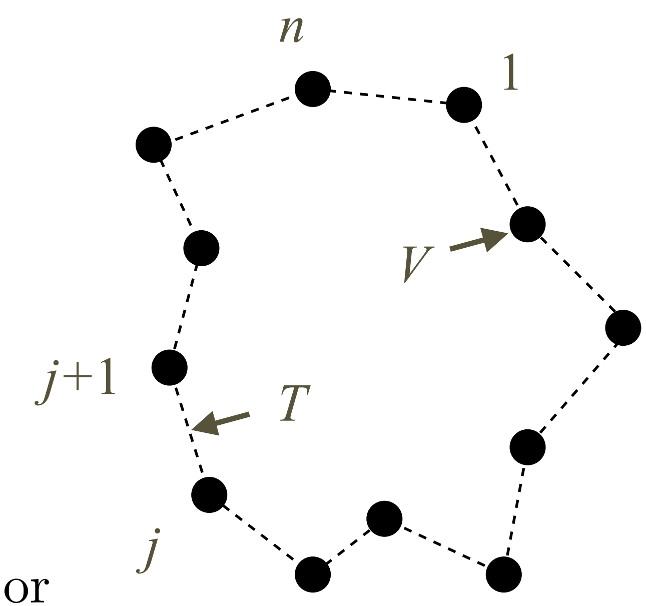
for any bead $j = 1, 2, \ldots, n$, and we can improve the statistics by averaging over the beads:

$$\langle V \rangle = \frac{1}{(2\pi\hbar)^n Q}\int d\mathbf{p}\int d\mathbf{q}\, e^{-\beta_n H_n(\mathbf{p},\mathbf{q})}\mathcal{V}(\mathbf{q}) \equiv \langle \mathcal{V}(\mathbf{q})\rangle\,,$$

where the potential energy estimator is

$$\mathcal{V}(\mathbf{q}) = \frac{1}{n}\sum_{j=1}^{n} V(q_j).$$

Average kinetic energy



By the same argument, the kinetic energy estimator can be constructed from

$$\langle q_j | \, e^{-\beta_n \hat{H}/2} \hat{T} e^{-\beta_n \hat{H}/2} \, | q_{j+1} \rangle \simeq \left[\frac{1}{2\beta_n} - \frac{1}{2} m \omega_n^2 (q_j - q_{j+1})^2 \right] \langle q_j | \, e^{-\beta_n \hat{H}} \, | q_{j+1} \rangle$$

for any bead j, and averaging over the beads to improve the statistics gives

$$\langle T \rangle = \frac{1}{(2\pi\hbar)^n Q} \int d\mathbf{p} \int d\mathbf{q} \, e^{-\beta_n H_n(\mathbf{p},\mathbf{q})} \mathcal{T}(\mathbf{q}) \equiv \langle \mathcal{T}(\mathbf{q}) \rangle$$

where the kinetic energy estimator is

$$\mathcal{T}(\mathbf{q}) = \frac{1}{2\beta_n} - \frac{1}{2n} \sum_{j=1}^{n} m \omega_n^2 (q_j - q_{j+1})^2.$$

Thermodynamic energy estimator

An alternative approach is to note that the average value of the energy $E = T + V$ is given by statistical mechanics as

$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_V = -\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_V$$

which with

$$Q = \frac{1}{(2\pi\hbar)^n}\int d\mathbf{p}\int d\mathbf{q}\, e^{-\beta_n H_n(\mathbf{p},\mathbf{q})}$$

and

$$H_n(\mathbf{p},\mathbf{q}) = \sum_{j=1}^{n}\left[\frac{p_j^2}{2m} + \frac{1}{2}m\omega_n^2(q_j - q_{j+1})^2 + V(q_j)\right]$$

and $\beta_n = \beta/n$ and $\omega_n = 1/(\beta_n\hbar)$ gives

$$\langle E \rangle = \frac{1}{(2\pi\hbar)^n Q}\int d\mathbf{p}\int d\mathbf{q}\, e^{-\beta_n H(\mathbf{p},\mathbf{q})}\mathcal{E}(\mathbf{q}) \equiv \langle \mathcal{E}(\mathbf{q})\rangle\,,$$

where

$$\mathcal{E}(\mathbf{q}) = \frac{1}{2\beta_n} - \frac{1}{2n}\sum_{j=1}^{n} m\omega_n^2(q_j - q_{j+1})^2 + \frac{1}{n}\sum_{j=1}^{n} V(q_j) \equiv \mathcal{T}(\mathbf{q}) + \mathcal{V}(\mathbf{q}).$$

Centroid virial estimator

So the thermodynamic energy estimator

$$\mathcal{E}_{\mathrm{TD}}(\mathbf{q}) = \frac{1}{2\beta_n} - \frac{1}{2n}\sum_{j=1}^{n} m\omega_n^2 (q_j - q_{j+1})^2 + \frac{1}{n}\sum_{j=1}^{n} V(q_j)$$

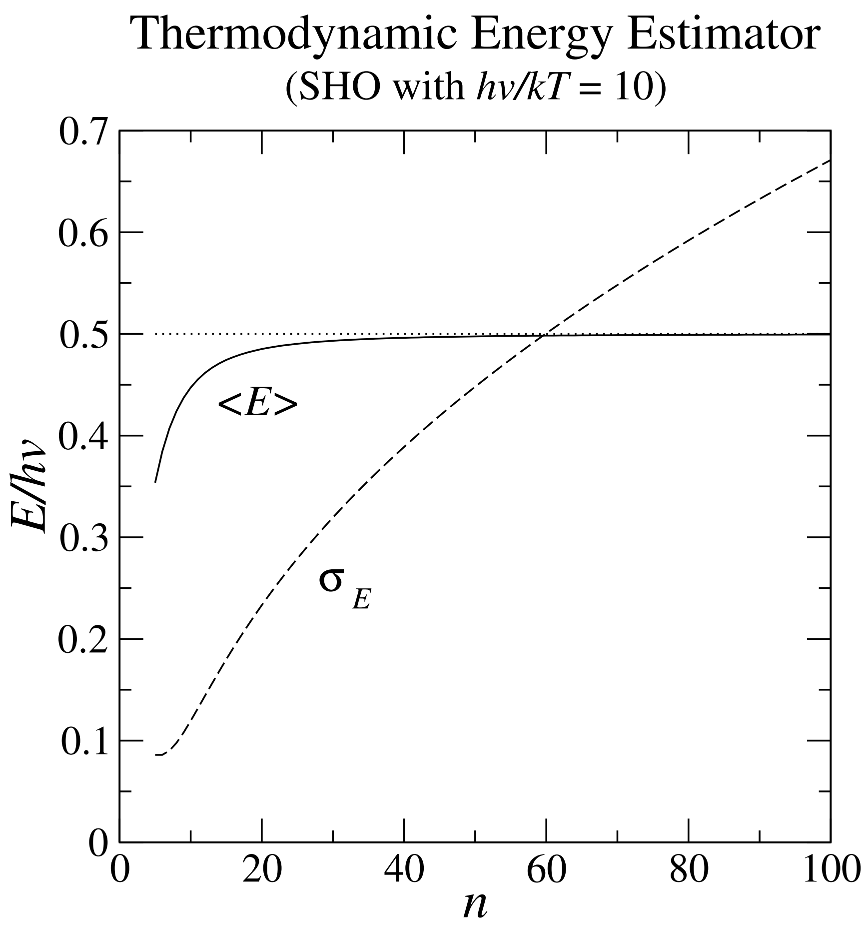
can be derived in two different ways, both of which show that its ring polymer average $\langle \mathcal{E}_{\mathrm{TD}}(\mathbf{q})\rangle$ will give the correct result $\langle E\rangle = \mathrm{tr}\left[e^{-\beta\hat{H}}\hat{H}\right]/Q$ for the average energy in the canonical ensemble.

But this is not the only estimator that will do so. The *centroid virial* energy estimator[5,6]

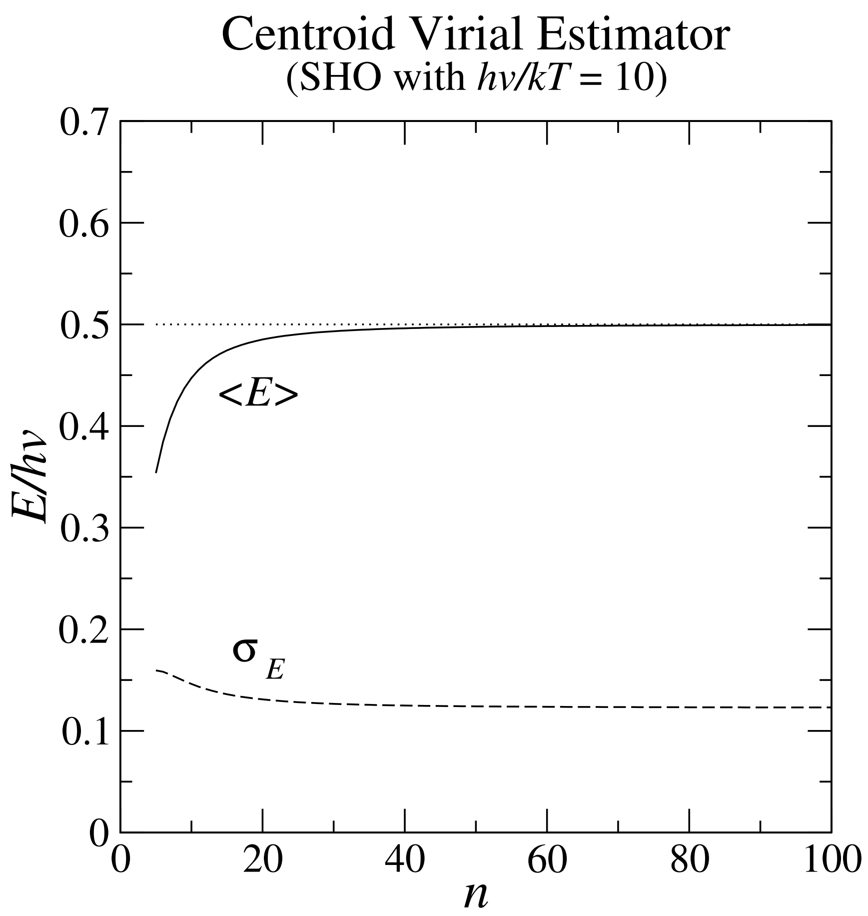
$$\mathcal{E}_{\mathrm{CV}}(\mathbf{q}) = \frac{1}{2\beta} + \frac{1}{2n}\sum_{j=1}^{n}(q_j - \bar{q})\frac{dV(q_j)}{dq_j} + \frac{1}{n}\sum_{j=1}^{n} V(q_j),$$

where $\bar{q} = (1/n)\sum_{j=1}^{n} q_j$, can be shown to have the same average $\langle \mathcal{E}_{\mathrm{CV}}(\mathbf{q})\rangle = \langle \mathcal{E}_{\mathrm{TD}}(\mathbf{q})\rangle$ as the thermodynamic energy estimator, with a *way* smaller variance $\Delta E = \sigma_E^2 = \left\langle \mathcal{E}(\mathbf{q})^2\right\rangle - \langle \mathcal{E}(\mathbf{q})\rangle^2$:

Comparison:



Thermodynamic Energy Estimator
(SHO with hν/kT = 10)
E/hν
n
<E>
σ E
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
20
40
60
80
100



Centroid Virial Estimator
(SHO with hν/kT = 10)
E/hν
n
<E>
σ E
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
20
40
60
80
100

Note that:

1. $\langle E \rangle$ is the same in both cases, and converges on the correct result with an error of $O(n^{-2})$.

2. $\langle E \rangle$ is converged to graphical accuracy by the time $n \simeq 5h\nu/kT = 5\beta\hbar\omega$.

3. The standard deviation of the thermodynamic estimator increases asymptotically as $n^{1/2}$.

4. If $\langle E \rangle$ were calculated using this estimator by Monte Carlo integration, the required number of samples M would increase linearly with n (because the standard error in the mean is proportional to $\sigma_E/M^{1/2}$).

5. By contrast, the standard deviation of the centroid virial estimator is *independent of* n for large n.

3. Integrating the equations of motion[7]

The standard way to integrate classical trajectories in molecular dynamics

$$\dot{\mathbf{p}} = -\frac{\partial H(\mathbf{p},\mathbf{q})}{\partial \mathbf{q}} = -\frac{\partial V(\mathbf{q})}{\partial \mathbf{q}}$$

$$\dot{\mathbf{q}} = +\frac{\partial H(\mathbf{p},\mathbf{q})}{\partial \mathbf{p}} = +\frac{\mathbf{p}}{m}$$

is to use the velocity Verlet algorithm ($e^{-\mathcal{L}\delta t} \simeq e^{-\mathcal{L}_V \delta t/2} e^{-\mathcal{L}_T \delta t} e^{-\mathcal{L}_V \delta t/2}$):

$$\mathbf{p} := \mathbf{p} - \frac{\delta t}{2}\frac{\partial V(\mathbf{q})}{\partial \mathbf{q}}, \quad \text{exact evolution under } H = V \text{ for time } \delta t/2$$

$$\mathbf{q} := \mathbf{q} + \delta t \frac{\mathbf{p}}{m}, \quad \text{exact evolution under } H = T \text{ for time } \delta t$$

$$\mathbf{p} := \mathbf{p} - \frac{\delta t}{2}\frac{\partial V(\mathbf{q})}{\partial \mathbf{q}}, \quad \text{exact evolution under } H = V \text{ for time } \delta t/2.$$

For PIMD, one could write the ring polymer Hamiltonian as

$$H_n(\mathbf{p}, \mathbf{q}) = \frac{|\mathbf{p}|^2}{2m} + V(\mathbf{q})$$

with

$$V(\mathbf{q}) = \sum_{j=1}^{n} \left[\frac{1}{2} m \omega_n^2 (q_j - q_{j+1})^2 + V(q_j) \right]$$

and use the standard velocity Verlet algorithm.

However, this would require a very small time step δt because of the stiff harmonic springs between the beads $[\omega_n = n/(\beta\hbar)]$.

So we prefer to write

$$H_n(\mathbf{p}, \mathbf{q}) = H_0(\mathbf{p}, \mathbf{q}) + V(\mathbf{q})$$

where

$$H_0(\mathbf{p}, \mathbf{q}) = \sum_{j=1}^{n} \left[\frac{p_j^2}{2m} + \frac{1}{2} m \omega_n^2 (q_j - q_{j+1})^2 \right]$$

and

$$V(\mathbf{q}) = \sum_{j=1}^{n} V(q_j),$$

and to use the following time evolution algorithm:

$$e^{-\mathcal{L}\delta t} \simeq e^{-\mathcal{L}_V \delta t/2} e^{-\mathcal{L}_0 \delta t} e^{-\mathcal{L}_V \delta t/2}.$$

Because it is harmonic,

$$H_0(\mathbf{p}, \mathbf{q}) = \sum_{j=1}^{n} \left[\frac{p_j^2}{2m} + \frac{1}{2} m\omega_n^2 (q_j - q_{j+1})^2 \right]$$

can be diagonalised with a normal mode transformation

$$\tilde{p}_k = \sum_{j=1}^{n} p_j C_{jk} \quad \text{and} \quad \tilde{q}_k = \sum_{j=1}^{n} q_j C_{jk}$$

$$C_{jk} = \begin{cases} \sqrt{1/n}, & k = 0 \\ \sqrt{2/n}\cos(2\pi jk/n), & k = 1 \ldots n/2 - 1 \\ \sqrt{1/n}(-1)^j, & k = n/2 \\ \sqrt{2/n}\sin(2\pi jk/n), & k = n/2 + 1 \ldots n - 1, \end{cases}$$

which gives

$$H_0(\tilde{\mathbf{p}}, \tilde{\mathbf{q}}) = \sum_{k=0}^{n-1} \left[\frac{\tilde{p}_k^2}{2m} + \frac{1}{2} m\omega_k^2 \tilde{q}_k^2 \right]$$

with

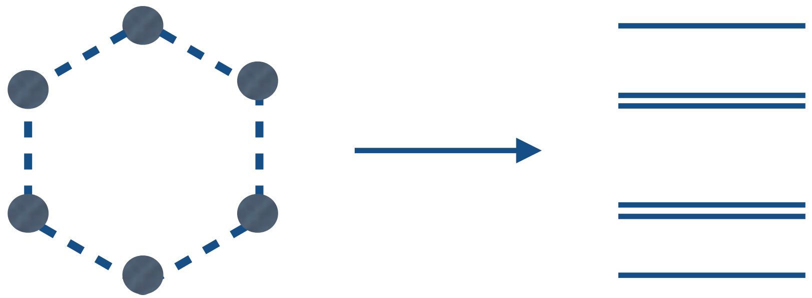
$$\omega_k = 2\omega_n \sin(k\pi/n).$$

Normal mode transformation

In fact

$$\sum_{j=1}^{n}(q_j - q_{j+1})^2 = \mathbf{q}^T(2\mathbf{I} - \mathbf{A})\mathbf{q},$$

where $\mathbf{A}$ is the adjacency matrix of the cyclic hydrocarbon C_nH_n in Hückel theory. So the ring polymer normal mode transformation corresponds to doing a simple HMO calculation:



Moreover

$$\tilde{p}_k = \sum_{j=1}^{n} p_j C_{jk} \quad \text{and} \quad \tilde{q}_k = \sum_{j=1}^{n} q_j C_{jk}$$

is just a pair of discrete Fourier transforms, which can be done very efficiently for large n using the FFT algorithm.

Ring polymer evolution

Bringing all of this together, the (microcanonical) ring polymer evolution

$$e^{-\mathcal{L}\delta t} = e^{-\mathcal{L}_V \delta t/2} e^{-\mathcal{L}_0 \delta t} e^{-\mathcal{L}_V \delta t/2}$$

proceeds as follows:[7]

$$p_j := p_j - \frac{\delta t}{2} \frac{dV(q_j)}{dq_j}$$

$$\tilde{p}_k := \sum_{j=1}^{n} p_j C_{jk} \qquad \tilde{q}_k := \sum_{j=1}^{n} q_j C_{jk}$$

$$\begin{pmatrix} \tilde{p}_k \\ \tilde{q}_k \end{pmatrix} := \begin{pmatrix} \cos \omega_k \delta t & -m\omega_k \sin \omega_k \delta t \\ (1/m\omega_k) \sin \omega_k \delta t & \cos \omega_k \delta t \end{pmatrix} \begin{pmatrix} \tilde{p}_k \\ \tilde{q}_k \end{pmatrix}$$

$$p_j := \sum_{k=0}^{n-1} C_{jk} \tilde{p}_k \qquad q_j := \sum_{k=0}^{n-1} C_{jk} \tilde{q}_k$$

$$p_j := p_j - \frac{\delta t}{2} \frac{dV(q_j)}{dq_j}.$$

Non-ergodicity

These microcanonical ring polymer trajectories are all very well, but they are no good (on their own) for calculating thermal averages such as

$$\langle V \rangle = \frac{1}{(2\pi\hbar)^n Q} \int d\mathbf{p} \int d\mathbf{q}\, e^{-\beta_n H_n(\mathbf{p},\mathbf{q})} \mathcal{V}(\mathbf{q}),$$

for two reasons:

1. They conserve $H_n(\mathbf{p},\mathbf{q})$. So they do not explore all (Boltzmann-weighted) values of $H_n(\mathbf{p},\mathbf{q})$.

2. They are far from ergodic.[8] (E.g., for the SHO potential, $V(q) = \frac{1}{2}m\omega^2 q^2$, $H_n(\mathbf{p},\mathbf{q})$ is diagonal in the normal mode representation; there is no energy flow between the normal modes. And for a mildly anharmonic potential, one would have to run a microcanonical trajectory for an awfully long time to see any energy flow.)

The PILE thermostat

Both problems can be fixed by attaching a "path integral Langevin equation" (PILE) thermostat to the dynamics. I.e., by replacing

$$e^{-\mathcal{L}_V \delta t/2} e^{-\mathcal{L}_0 \delta t} e^{-\mathcal{L}_V \delta t/2}$$

with

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

in which the thermostatting ($e^{-\mathcal{L}_\gamma \delta t/2}$) steps are implemented as follows:[7]

$$\tilde{p}_k := \sum_{j=1}^{n} p_j C_{jk}$$

$$\tilde{p}_k := e^{-\gamma_k \delta t/2}\, \tilde{p}_k + \sqrt{m(1 - e^{-\gamma_k \delta t})/\beta_n}\, \xi_k$$

$$p_j = \sum_{k=0}^{n-1} C_{jk} \tilde{p}_k.$$

Here ξ_k is an independent Gaussian number (a normal deviate with zero mean and unit variance) that is different for each invocation of $e^{-\mathcal{L}_\gamma \delta t/2}$.

The PILE algorithm corresponds to attaching a separate Langevin thermostat to each internal mode of the free ring polymer,

$$\frac{d}{dt}\tilde{q}_k = \frac{\tilde{p}_k}{m}$$

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

where $\xi_k(t)$ represents an uncorrelated, Gaussian-distributed random force with unit variance and zero mean [$\langle\xi_k(t)\rangle = 0$ and $\langle\xi_k(0)\xi_k(t)\rangle = \delta(t)$].

The autocorrelation time

$$\tau_V = \frac{1}{\langle V^2 \rangle - \langle V \rangle^2} \int_0^\infty \langle (V(0) - \langle V \rangle)(V(t) - \langle V \rangle) \rangle \; dt$$

of the free ring polymer normal mode potential $V = m\omega_k^2 \tilde{q}_k^2/2$ can be worked out analytically for this Langevin dynamics and is[9]

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

for $k > 0$ $[\omega_k > 0]$. The optimum friction coefficient γ_k (which minimises τ_V) is therefore simply $\gamma_k = \omega_k$ for $k > 0$, leaving a single physical parameter τ_0 to be specified for thermostatting the centroid mode ($k = 0$):

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

4. Multidimensional generalisation

The above equations have been given for a simple one-dimensional problem with

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

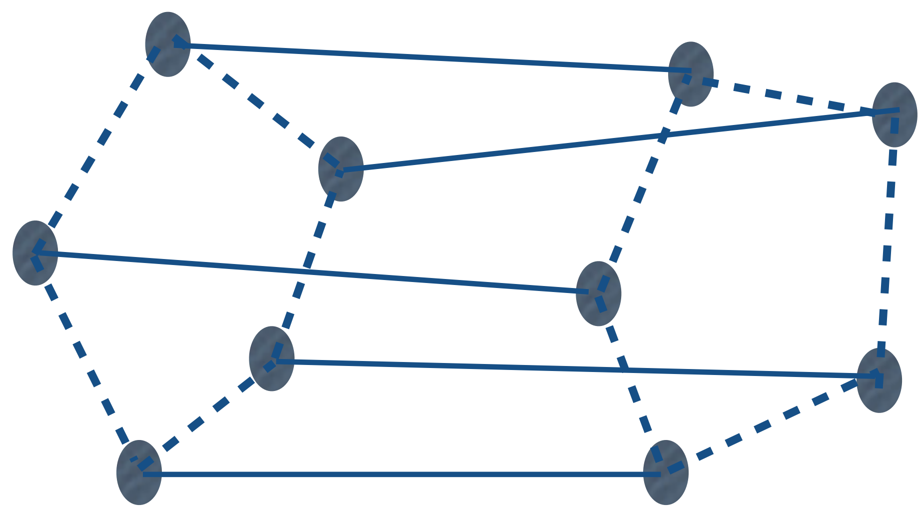
However, in the absence of identical particle (fermionic and bosonic) exchange effects, they are straightforward to generalise to a multidimensional Hamiltonian of the form

$$\hat{H} = \sum_{i=1}^{N} \frac{|\hat{\mathbf{p}}_i|^2}{2m_i} + V(\hat{\mathbf{r}}_1, \ldots, \hat{\mathbf{r}}_N).$$

For example, the ring polymer Hamiltonian becomes

$$H_n(\{\mathbf{p}\}, \{\mathbf{r}\}) = \sum_{i=1}^{N} \sum_{j=1}^{n} \left(\frac{|\mathbf{p}_{ij}|^2}{2m_i} + \frac{1}{2} m_i \omega_n^2 |\mathbf{r}_{ij} - \mathbf{r}_{ij+1}|^2 \right) + \sum_{j=1}^{n} V(\mathbf{r}_{1j}, \ldots, \mathbf{r}_{Nj}).$$

E.g., for N=2 particles and n=5 beads:



physical potential interactions

harmonic springs between beads

Identical particle exchange effects

Identical particle exchange effects become important when the de Broglie thermal wavelengths $\Lambda(T) = h/\sqrt{2\pi m_i kT}$ 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[2]).

However, it is hardly ever necessary for those of us who work in chemistry departments to have to worry about them, because (e.g.) they are negligible in liquid para-hydrogen even at its melting temperature (13.8 K).

5. References

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