Research Note
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RPMD Hamiltonian as Langevinic System and Force Autocorrelation Function

The RPMD Hamiltonian in normal mode coordinate can be written as

$$H_{RPMD}(\{u_k\},\{\gamma_k\}) = \sum_{k=1}^{P}\left(\frac{{\gamma_k}^2}{2m} + \frac{m{\alpha_k}^2}{2}{u_k}^2\right) + V(u_1,\dots,u_P) \tag{1}$$

where

$$V(u_1,\dots,u_P) = \sum_{k=1}^{P} U\big(x_k(u_1,\dots,u_P)\big)$$

Noting that the first normal mode u_1 is the centroid of the ring polymer and $\alpha_1 = 0$, we can rewrite equation 1 to have

$$H_{RPMD} = \frac{{\gamma_1}^2}{2m} + V(u_1,\dots,u_P) + \sum_{k=2}^{P}\left(\frac{{\gamma_k}^2}{2m} + \frac{m{\alpha_k}^2}{2}{u_k}^2\right).$$

We see that there are three parts to the full Hamiltonian: the centroid Hamiltonian $\frac{{\gamma_1}^2}{2m}$, the external potential Hamiltonian $V(u_1,\dots,u_P)$, and the noncentroid Hamiltonian $\sum_{k=2}^{P}\left(\frac{{\gamma_k}^2}{2m} + \frac{m{\alpha_k}^2}{2}{u_k}^2\right)$. We see that the noncentroid part is a Hamiltonian for P-1 uncoupled harmonic oscillators. This suggests that it may be possible to use the formalism of Langevin equations to understand RPMD type systems.

To cast the RPMD Hamiltonian in the context of Langevin equation, we make an approximation on the external potential Hamiltonian

$$V(u_1,\dots,u_P) \cong V(u_1,0,\dots,0) + u_1\left.\frac{\partial V}{\partial u_1}\right|_{u_1=0}. \tag{2}$$

The approximation on equation 2 approximates the full potential energy into two aspects: centroid potential and the nonlinear force that is linearly coupled to the centroid position. This is analogous to Langevin type systems in which there is a PMF for the system DOF and linear coupling between system and bath DOF. It is also important to note that this approximation produces analytical result in case of harmonic external potential

To evaluate the second term in equation 2, we have

$$\left.\frac{\partial V}{\partial u_1}\right|_{u_1=0} = \sum_{k=1}^{P} \frac{\partial}{\partial u_1} U[x_k(u_1, \ldots, u_P)]\Big|_{u_1=0} = \sum_{k=1}^{P} \frac{\partial U[x_k]}{\partial x_k} \frac{\partial x_k}{\partial u_1}\Big|_{u_1=0} .$$

(3)

Using coordinate transform $x_k = \sum_{l=1}^{P} O_{kl}^T u_l$ and the fact that first row element of O is all 1,

$$\left.\frac{\partial V}{\partial u_1}\right|_{u_1=0} = \sum_{k=1}^{P} U'\left[\sum_{l=1}^{P} O_{kl}^T u_l\right]\Big|_{u_1=0} = \sum_{k=1}^{P} U'\left[\sum_{l=2}^{P} O_{kl}^T u_l\right]$$

(4)

where O is the orthogonal matrix that diagonalize the characteristic matrix A as described in previous notes.

Combining the results, the Hamiltonian can be written as

$$H_{RPMD} = \frac{{p_1}^2}{2m} + V_1(u_1) - u_1 f + \sum_{k=2}^{P} \left(\frac{{p_k}^2}{2m} + \frac{m{\alpha_k}^2}{2} {u_k}^2\right)$$

(5)

where V_1 is the effective centroid potential and f is the effective force on the centroid from other noncentroid modes. These terms are defined as

$$V_1(u_1) = V(u_1, 0, \ldots, 0)$$

$$f = -\left.\frac{\partial V}{\partial u_1}\right|_{u_1=0} = -\sum_{k=1}^{P} U'\left[\sum_{l=2}^{P} O_{kl}^T u_l\right].$$

(6)

To apply the Langevin analysis, the force autocorrelation function of form

$$C_F(t) = \langle \delta f(0) \delta f(t) \rangle_B$$

(7)

where $\langle \ldots \rangle_B$ denotes the canonical average with respect to the bath Hamiltonian, must be calculated.

Since the bath Hamiltonian $H_B = \sum_{k=2}^{P} \left(\frac{{p_k}^2}{2m} + \frac{m{\alpha_k}^2}{2} {u_k}^2\right)$ is that of uncoupled harmonic oscillators, the bath dynamics can be written as

$$u_k(t) = u_k(0) \cos(\alpha_k t) + \frac{\dot{u}_k(0)}{\alpha_k} \sin(\alpha_k t)$$

(8)

for k = 2,…,P.

To get a formula for the force ACF as shown in equation 7, have

$$C_F(t) = \langle f(0)f(t)\rangle_B - \langle f\rangle_B{}^2 \tag{9}$$

where

$$\langle f(0)f(t)\rangle_B = \sum_{k=1}^{P}\sum_{m=1}^{P}\langle U'\left[\sum_{l=2}^{P} O_{kl}^T u_l(0)\right] U'\left[\sum_{n=2}^{P} O_{mn}^T u_n(t)\right]\rangle_B$$

$$\langle f\rangle_B{}^2 = \sum_{k=1}^{P}\sum_{m=1}^{P}\langle U'\left[\sum_{l=2}^{P} O_{kl}^T u_l(0)\right]\rangle_B \langle U'\left[\sum_{n=2}^{P} O_{mn}^T u_n(t)\right]\rangle_B. \tag{10}$$

To simplify, the correlation function can be written as

$$C_F(t) = \sum_{k=1}^{P}\sum_{m=1}^{P}\langle \delta F_k(0)\delta F_m(t)\rangle_B \tag{11}$$

where

$$F_k(t) = U'\left[\sum_{l=2}^{P} O_{kl}^T u_l(t)\right]. \tag{12}$$

To numerically calculate $C_F(t)$, we sample N points from the phase space described by the bath Hamiltonian H_B:

$$\vec{X}_1, \dots, \vec{X}_N$$

where $\vec{X}_i$ describes the $2P-2$ dimensional phase space vector that was sampled from the canonical distribution of H_B and will be used as the initial condition for calculation of the correlation function.

For each initial condition $\vec{X}_i$, calculate correlation function becomes

$$C_{F,i}(t) = \sum_{k=1}^{P}\sum_{m=1}^{P}\left[F_{k,i}(0)F_{m,i}(t) - F_{k,i}(0)F_{m,i}(0)\right] \tag{13}$$

where $F_{k,i}(t)$ is the force described in equation 12 calculated with *i* th initial condition.

Finally, for total N number of sampling from the canonical distribution, the numerical force ACF can be expressed as an average

$$C_F(t) = \frac{1}{N}\sum_{i=1}^{N} C_{F,i}(t). \tag{14}$$