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On the short-time limit of ring polymer molecular dynamics

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Abstract

We examine the short-time accuracy of a class of approximate quantum dynamical techniques that includes the centroid molecular dynamics (CMD) and ring polymer molecular dynamics (RPMD) methods. Both of these methods are based on the path integral molecular dynamics (PIMD) technique for calculating the exact static equilibrium properties of quantum mechanical systems. For Kubo-transformed real-time correlation functions involving operators that are linear functions of positions or momenta, the RPMD and (adiabatic) CMD approximations differ only in the choice of the artificial mass matrix of the system of ring polymer beads that is employed in PIMD. The obvious ansatz for a general method of this type is therefore to regard the elements of the PIMD (or Parrinello-Rahman) mass matrix as an adjustable set of parameters that can be chosen to improve the accuracy of the resulting approximation. We show here that this ansatz leads uniquely to the RPMD approximation when the criterion that is used to select the mass matrix is the short-time accuracy of the Kubo-transformed correlation function. In particular, we show that the leading error in the RPMD position autocorrelation function is $O(t^8)$ and the error in the velocity autocorrelation function is $O(t^6)$, for a general anharmonic potential. The corresponding errors in the CMD approximation are $O(t^6)$ and $O(t^4)$, respectively.

I. INTRODUCTION

There is considerable current interest in the inclusion of quantum mechanical zero-point energy and tunneling effects in condensed phase molecular dynamics simulations. At the most rigorous level, these effects can be included using a complex-time Feynman path integral,[1–3] and significant progress has now been made in this direction as exemplified by the recent short-time path integral study of sub-critical liquid *para*-hydrogen by Nakayama and Makri.[4] For more general problems involving the longer time dynamics of more complicated systems at higher densities, however, the approach of Nakayama and Makri becomes less practical, and it is clear that there will always be many interesting problems for which one will have to resort to the use of a less accurate quantum dynamical technique.

There are essentially three distinct classes of such technique that have been applied to condensed phase systems, each with its own strengths and weaknesses. The methods in the first class include the numerical analytic continuation (NAC) approach of Berne and co-workers,[5–8] and the quantum mode-coupling theory (QMCT) of Reichman and Rabani.[9–14] These methods make analytical use of numerically-computed imaginary-time information to construct an approximation to a real-time quantum correlation function. The nature of the approximation is such that the short-time behavior of the correlation function is captured very accurately; this and the ease with which the required imaginary-time information can be computed are the two main appeals of this class of technique. However, neither NAC nor QMCT is exact in the classical limit (where QMCT reduces to classical mode-coupling theory[15]), and the numerical inversion procedure used in NAC can run into difficulties if the spectrum of the correlation function has multiple maxima.[16] And although QMCT provides an appealing description of the dynamics of monatomic quantum fluids,[9–14] mode-coupling theory is extremely difficult to apply to molecular liquids.[17,18]

The second class of techniques includes the linearized semiclassical initial value representation (LSC-IVR) of Miller and co-workers,[19–22] the Feynman-Kleinert linearized path integral (FK-LPI) approach of Poulsen, Nyman and Rossky,[23–26] and the forward-backward semiclassical dynamics (FB-SD) approach of Makri and co-workers.[27–32] These methods combine what is in principle an exact treatment of the quantum Boltzmann operator with an approximate treatment of the real-time evolution based on classical dynamics. Their main strength is that they are exact in three important limits that often govern the behavior of condensed phase simulations: the short-time limit, the limit of a harmonic potential, and the classical (or high-temperature) limit. However, because classical trajectories do not in general conserve the quantum mechanical equilibrium distribution (in the form of the Wigner[33] or Husimi[34] functions of the quantum Boltzmann operator),[35] there are several important situations in which the methods in this class can lead to unphysical behavior, such as the flow of initially quantized zero-point energy from intramolecular to intermolecular modes in the simulation of a molecular liquid.[36]

The final class of approximate quantum dynamical techniques includes the centroid molecular dynamics (CMD) method developed by Voth and co-workers,[37–44] and the ring polymer molecular dynamics (RPMD) method developed within our research group.[45–50] These methods combine an exact treatment of the quantum Boltzmann operator with a *modified* form of classical mechanics that exactly conserves the quantum mechanical equilibrium distribution. In the case of CMD, the modification consists of replacing the classical potential energy function with an imaginary-time centroid potential of mean force,[39] and in the case of RPMD it consists of performing the classical molecular dynamics simulation in the extended phase space of the imaginary-time path integral.[45] For correlation functions involving linear functions of position and/or momentum operators, these methods are again exact in the limit as $t \to 0$, in the limit of a harmonic potential, and in the classical limit. However, both methods run into certain (as yet largely unresolved) difficulties for correlation functions involving strongly non-linear operators.[50–53]

Weighing up these various pros and cons, we believe that the CMD and RPMD methods probably provide two of the more promising ways to include quantum mechanical fluctuations in condensed phase molecular dynamics simulations (especially in the case of molecular liquids), and indeed both of these methods have now been shown to capture the dominant quantum mechanical effects in a wide variety of interesting situations.[46–50,54–59] This being the case, it is natural to ask whether one can do any better than either of these methods by exploring the entire class of related imaginary-time path integral techniques, which brings us to the point of the present paper.

In practical applications of the CMD method to complex systems, the centroid potential of mean force is typically calculated using an adiabatic CMD algorithm that bears a very close resemblance to RPMD.[41] In both methods, the dynamics is performed in an extended phase space of the type that arises in the exact path integral molecular dynamics (PIMD) method for calculating the static equilibrium properties of quantum mechanical systems.[60] As has been explained recently by Hone, Rossky and Voth,[61] the essential difference between the RPMD and (adiabatic) CMD algorithms is in the choice of the fictitious masses of the ring polymer beads that arise in PIMD.[60] These authors used this observation to develop a new method (termed partially-adiabatic CMD or PACMD) that essentially interpolates between the two approximations.[61] Here we shall use the same observation to address a different issue that is motivated by one of the many interesting questions raised by their work:[61] of all the possible imaginary-time path integral methods for real-time dynamics, which gives the most accurate result in the short-time limit?

The outline of the paper is as follows. Sec. II begins by introducing the Kubo-transformed[62,63] quantum correlation functions that are approximated in RPMD and CMD, and showing how their short-time behavior can be developed in a Taylor series. Sec. III then presents a general ansatz for an imaginary-time path integral-based dynamical method that includes the RPMD and CMD (and also PACMD) approximations as special cases. This ansatz involves an arbitrary mass matrix for the beads of the imaginary-time ring polymer of the type that was first introduced in diagonal form as an equilibrium sampling device by Parrinello and Rahman.[60] Sec. III ends by showing how this Parrinello-Rahman mass matrix can be determined by requiring that the resulting dynamical approximation reproduce the leading terms in the exact Taylor series expansion of the real-time correlation function.

In order to keep our notation as simple as possible, we have confined our attention in Secs. II and III to Kubo-transformed correlation functions involving configurational (or local) operators in a simple one-dimensional model system. However, our results are much more general than this may seem to suggest, as Sec. IV illustrates by outlining how the theory in the preceding two sections can be extended to treat the Kubo-transformed velocity autocorrelation function of a monatomic liquid. Other multi-dimensional generalizations follow along the same lines, and give results that are entirely consistent with the one-dimensional results obtained in Secs. II and III; the only reason we have chosen to focus on the velocity autocorrelation function is that there has been a lot of recent interest in the frequency-dependent diffusion coefficients of simple quantum liquids[8,12,25,30,47,57,61,64] (see also the discussion at the end of Sec. IV). Sec. V concludes with a few brief remarks about the implications of our results and mentions one of the remaining issues concerning the difference between CMD and RPMD that we still do not fully understand.

II. KUBO-TRANSFORMED CORRELATION FUNCTIONS

As we have already mentioned in the Introduction, we shall begin by considering a simple one-dimensional Hamiltonian of the form

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{q}), \tag{1}$$

in which the potential energy function $V(q)$ is assumed to be differentiable as many times as our argument requires and to lead to a well-defined quantum mechanical partition function

$$Z = \mathrm{tr}\left[e^{-\beta\hat{H}}\right] \tag{2}$$

with $\beta = 1/k_{\mathrm{B}}T$. We shall also begin by restricting our attention to the Kubo-transformed correlation functions involving local (position-dependent) Hermitian operators

$$\tilde{c}_{AB}(t) = \frac{1}{\beta Z}\int_0^\beta d\lambda\,\mathrm{tr}\left[e^{-(\beta-\lambda)\hat{H}}\hat{A}\,e^{-\lambda\hat{H}}e^{+i\hat{H}t/\hbar}\hat{B}\,e^{-i\hat{H}t/\hbar}\right], \tag{3}$$

where $\hat{A} = A(\hat{q})$ and $\hat{B} = B(\hat{q})$. This is actually less of a restriction than it may seem, because many physically interesting correlation functions involving more general operators can be calculated as time derivatives of correlation functions of this special form.[46–49]

Since we shall ultimately be interested in the accuracy of short-time approximations to $\tilde{c}_{AB}(t)$, it is natural to consider expanding this function in a Taylor series. For Hermitian operators $\hat{A}$ and $\hat{B}$, it is straightforward to show by working in the basis of energy eigenstates that $\tilde{c}_{AB}(t)$ will be a real and even function of t, and so provided the series converges we will have

$$\tilde{c}_{AB}(t) = \sum_{r=0}^{\infty}\frac{t^{2r}}{(2r)!}\tilde{c}_{AB}^{(2r)}(0), \tag{4}$$

where $\tilde{c}_{AB}^{(k)}(0)$ is the k-th derivative of $\tilde{c}_{AB}(t)$ at time $t = 0$. Any real and even approximation to $\tilde{c}_{AB}(t)$ can clearly be expanded in the same way, and so by comparing the first few coefficients in the approximate and exact expansions one can determine the short-time accuracy of the approximation. But in order to do this we first need to obtain explicit expressions for the exact expansion coefficients $\tilde{c}_{AB}^{(2r)}(0)$.

The first expansion coefficient $\tilde{c}_{AB}^{(0)}(0)$ can be computed directly from Eq. (3):

$$\tilde{c}_{AB}^{(0)}(0) = \frac{1}{\beta Z}\int_0^\beta d\lambda\,\mathrm{tr}\left[e^{-(\beta-\lambda)\hat{H}}\hat{A}\,e^{-\lambda\hat{H}}\hat{B}\right]. \tag{5}$$

However, this is something of a special case, because repeated differentiation of Eq. (3) does not lead to very useful expressions for the remaining coefficients $\tilde{c}_{AB}^{(2r)}(0)$. A more convenient way to compute the coefficients with $r > 0$ is provided by the relation[65]

$$\tilde{c}_{AB}^{(1)}(t) = -\frac{2}{\beta\hbar}\,\mathrm{Im}\; c_{AB}(t), \tag{6}$$

where $c_{AB}(t)$ is the standard real-time correlation function

$$c_{AB}(t) = \frac{1}{Z}\mathrm{tr}\left[e^{-\beta\hat{H}}\hat{A}\,e^{+i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar}\right]. \tag{7}$$

Since the Boltzmann and evolution operators in Eq. (7) commute, and since the last evolution operator $e^{-i\hat{H}t/\hbar}$ can be brought around to the beginning of the trace, we can obtain a variety of different expressions for the derivatives of $c_{AB}(t)$ with respect to t. The most convenient of these expressions is obtained by performing $r-1$ differentiations with $e^{-i\hat{H}t/\hbar}$ on the left of the trace and r with it on the right, which in conjunction with Eq. (6) gives

$$\tilde{c}_{AB}^{(2r)}(0) = \frac{2(-1)^r}{\beta\hbar Z}\,\mathrm{Im}\;\mathrm{tr}\left[e^{-\beta\hat{H}}\hat{A}^{(r-1)}\hat{B}^{(r)}\right], \tag{8}$$

where $\hat{A}^{(r-1)}$ and $\hat{B}^{(r)}$ are the $(r-1)$-st and r-th Heisenberg time derivatives of the operators $\hat{A}$ and $\hat{B}$. ($\hat{A}^{(r-1)}$ can be computed recursively from $\hat{A}^{(0)} \equiv \hat{A}$ using the relation

$$\hat{A}^{(k)} = \frac{i}{\hbar}\left[\hat{H}, \hat{A}^{(k-1)}\right] \tag{9}$$

for $k = 1, 2, \ldots, r-1$, and $\hat{B}^{(r)}$ can be computed in the same way.) Eq. (8) simplifies further when we write

$$\hat{A}^{(r-1)}\hat{B}^{(r)} = \frac{1}{2}\left\{\hat{A}^{(r-1)}, \hat{B}^{(r)}\right\} + \frac{1}{2}\left[\hat{A}^{(r-1)}, \hat{B}^{(r)}\right], \tag{10}$$

the first bracket in which is the Hermitian anti-commutator and the second the anti-Hermitian commutator of the two Hermitian operators $\hat{A}^{(r-1)}$ and $\hat{B}^{(r)}$; since the trace of a product of two Hermitian operators is purely real the first bracket does not make any contribution to Eq. (8) and we obtain

$$\tilde{c}_{AB}^{(2r)}(0) = \frac{(-1)^r}{\beta\hbar Z}\,\mathrm{Im}\;\mathrm{tr}\Big(e^{-\beta\hat{H}}\left[\hat{A}^{(r-1)}, \hat{B}^{(r)}\right]\Big). \tag{11}$$

Let us now illustrate this result by applying it to the Kubo-transformed position autocorrelation function $\tilde{c}_{qq}(t)$, for which $\hat{A} = \hat{B} = \hat{q}$ and the first few Heisenberg time derivatives of the correlated operators are given by

$$\hat{q}^{(0)} = \hat{q}, \tag{12}$$

$$\hat{q}^{(1)} = \frac{1}{m}\hat{p}, \tag{13}$$

$$\hat{q}^{(2)} = -\frac{1}{m}V'(\hat{q}), \tag{14}$$

$$\hat{q}^{(3)} = -\frac{1}{2m^2}\Big[\hat{p}\,V''(\hat{q}) + V''(\hat{q})\,\hat{p}\Big]. \tag{15}$$

For this correlation function, the first expansion coefficient $\tilde{c}_{qq}^{(0)}(0)$ in Eq. (4) is given by Eq. (5) as

$$\tilde{c}_{qq}^{(0)}(0) = \frac{1}{\beta Z}\int_0^\beta d\lambda\,\mathrm{tr}\left[e^{-(\beta-\lambda)\hat{H}}\hat{q}\,e^{-\lambda\hat{H}}\hat{q}\right], \tag{16}$$

and it is hard to see how to make any further progress with this without resorting to an explicit imaginary-time path integral evaluation of the trace (see Sec. III). However, the second expansion coefficient $\tilde{c}_{qq}^{(2)}(0)$ is given by Eq. (11) as

$$\tilde{c}_{qq}^{(2)}(0) = -\frac{1}{\beta\hbar Z}\,\mathrm{Im}\ \mathrm{tr}\left(e^{-\beta\hat{H}}\left[\hat{q}^{(0)},\hat{q}^{(1)}\right]\right), \tag{17}$$

and since

$$\left[\hat{q}^{(0)},\hat{q}^{(1)}\right] = \frac{1}{m}\Big[\hat{q},\hat{p}\Big] = \frac{i\hbar}{m}, \tag{18}$$

this immediately simplifies to

$$\tilde{c}_{qq}^{(2)}(0) = -\frac{1}{\beta m}. \tag{19}$$

A similar simplification is obtained for the third expansion coefficient $\tilde{c}_{qq}^{(4)}(0)$, which is given by Eq. (11) as

$$\tilde{c}_{qq}^{(4)}(0) = \frac{1}{\beta\hbar Z}\,\mathrm{Im}\ \mathrm{tr}\left(e^{-\beta\hat{H}}\left[\hat{q}^{(1)},\hat{q}^{(2)}\right]\right). \tag{20}$$

Since

$$\left[\hat{q}^{(1)},\hat{q}^{(2)}\right] = -\frac{1}{m^2}\Big[\hat{p},V'(\hat{q})\Big] = \frac{i\hbar}{m^2}V''(\hat{q}), \tag{21}$$

this gives

$$\tilde{c}_{qq}^{(4)}(0) = \frac{1}{\beta m^2}\left\langle V''(q)\right\rangle, \tag{22}$$

where the angular brackets denote a thermal expectation value

$$\langle\Omega\rangle \equiv \frac{1}{Z}\mathrm{tr}\left[e^{-\beta\hat{H}}\hat{\Omega}\right]. \tag{23}$$

The Heisenberg time derivatives in Eqs. (14) and (15) also allow us to obtain the fourth expansion coefficient $\tilde{c}_{qq}^{(6)}(0)$ in Eq. (4), which is given by Eq. (11) as

$$\tilde{c}_{qq}^{(6)}(0) = -\frac{1}{\beta\hbar Z}\,\mathrm{Im}\ \mathrm{tr}\left(e^{-\beta\hat{H}}\left[\hat{q}^{(2)},\hat{q}^{(3)}\right]\right). \tag{24}$$

In this case we have

$$\Big[\hat{q}^{(2)},\hat{q}^{(3)}\Big] = \frac{1}{2m^3}\Big[V'(\hat{q}),\hat{p}\,V''(\hat{q})+V''(\hat{q})\,\hat{p}\Big] = \frac{i\hbar}{m^3}V''(\hat{q})^2, \tag{25}$$

and so

$$\tilde{c}_{qq}^{(6)}(0) = -\frac{1}{\beta m^3}\left\langle V''(q)^2\right\rangle. \tag{26}$$

The same argument can in principle be extended to higher orders. However, the resulting expressions become increasingly unwieldy as r increases, and since it suffices to determine the optimum Parrinello-Rahman mass matrix (see below) we shall stop in the present study at $\tilde{c}_{AB}^{(6)}(0)$.

It is more difficult to calculate so many terms for a Kubo-transformed correlation function involving more general Hermitian operators $A(\hat{q})$ and $B(\hat{q})$, but a similar argument readily produces the first two terms in the Taylor series [Eq. (4)]. The first coefficient $\tilde{c}_{AB}^{(0)}(0)$ has already been given in Eq. (5), and the second coefficient $\tilde{c}_{AB}^{(2)}(0)$ is given by Eq. (11) as

$$\tilde{c}_{AB}^{(2)}(0) = -\frac{1}{\beta\hbar Z}\,\mathrm{Im}\,\mathrm{tr}\Big(e^{-\beta\hat{H}}\left[\hat{A}^{(0)},\hat{B}^{(1)}\right]\Big), \tag{27}$$

where $\hat{A}^{(0)}=A(\hat{q})$ and

$$\hat{B}^{(1)} = \frac{1}{2m}\Big[\hat{p}\,B'(\hat{q})+B'(\hat{q})\,\hat{p}\Big]. \tag{28}$$

Since

$$\Big[\hat{A}^{(0)},\hat{B}^{(1)}\Big] = \frac{1}{2m}\Big[A(\hat{q}),\hat{p}\,B'(\hat{q})+B'(\hat{q})\,\hat{p}\Big] = \frac{i\hbar}{m}A'(\hat{q})B'(\hat{q}), \tag{29}$$

this gives

$$\tilde{c}_{AB}^{(2)}(0) = -\frac{1}{\beta m}\left\langle A'(q)B'(q)\right\rangle, \tag{30}$$

which reduces correctly to $\tilde{c}_{AB}^{(2)}(0)=-1/\beta m$ when $A(\hat{q})=B(\hat{q})=\hat{q}$. For more general $A(\hat{q})$ and $B(\hat{q})$, Eq. (30) has a similar structure to Eq. (26), and it turns out that the evaluation of the higher order coefficients $\tilde{c}_{AB}^{(2r)}(0)$ with $r>1$ is just as forbidding in this case as the evaluation the coefficients $\tilde{c}_{qq}^{(2r)}(0)$ with $r>3$. We shall therefore stop in the present study at $\tilde{c}_{AB}^{(2)}(0)$.

III. RING POLYMER MOLECULAR DYNAMICS

A general ansatz for a quantum dynamical method based on PIMD, which includes the RPMD and (adiabatic) CMD approximations as special cases, is as follows. The Kubo-transformed correlation function $\tilde{c}_{AB}(t)$ in Eq. (3) is approximated by

$$\tilde{c}_{AB}(t) \simeq \frac{1}{N}\int d\mathbf{p}\int d\mathbf{q}\, e^{-\beta_n H_n(\mathbf{p},\mathbf{q})} A_n(\mathbf{q}) B_n(\mathbf{q}_t), \tag{31}$$

with

$$N = \int d\mathbf{p}\int d\mathbf{q}\, e^{-\beta_n H_n(\mathbf{p},\mathbf{q})}, \tag{32}$$

where $\beta_n = \beta/n$,

$$H_n(\mathbf{p},\mathbf{q}) = \frac{1}{2}\mathbf{p}^T\mathbf{M}^{-1}\mathbf{p} + \frac{1}{2}\mathbf{q}^T\mathbf{K}\mathbf{q} + \sum_{j=1}^{n} V(q_j), \tag{33}$$

and

$$A_n(\mathbf{q}) = \frac{1}{n}\sum_{j=1}^{n} A(q_j), \quad B_n(\mathbf{q}) = \frac{1}{n}\sum_{j=1}^{n} B(q_j). \tag{34}$$

Here $H_n(\mathbf{p},\mathbf{q})$ is the Hamitonian of an n-bead harmonic ring polymer with an external potential of $V(q)$ acting on each bead.[66] The ansatz is completed by assuming that the time-evolved ring polymer configuration $\mathbf{q}_t \equiv \mathbf{q}_t(\mathbf{p},\mathbf{q})$ in Eq. (31) is obtained from the classical dynamics generated by this Hamiltonian,[45]

$$\dot{\mathbf{p}} = -\partial H_n(\mathbf{p},\mathbf{q})/\partial\mathbf{q} = -\mathbf{K}\mathbf{q} - \mathbf{g}(\mathbf{q}), \tag{35}$$

$$\dot{\mathbf{q}} = +\partial H_n(\mathbf{p},\mathbf{q})/\partial\mathbf{p} = +\mathbf{M}^{-1}\mathbf{p}, \tag{36}$$

where $g_j(\mathbf{q}) = V'(q_j)$. The only flexibility that this leaves is in the choice of the ring polymer force constant matrix $\mathbf{K}$ and the mass matrix $\mathbf{M}$, which we shall now determine by requiring that the approximation in Eq. (31) give the exact result for as many of the Taylor series expansion coefficients $\tilde{c}_{AB}^{(2r)}(0)$ in Eq. (4) as possible.

Let us assume from the outset that the mass matrix $\mathbf{M}$ is real-symmetric and positive-definite, so that the momentum integrals in Eqs. (31) and (32) are well defined. These integrals will then cancel from the approximation to $\tilde{c}_{AB}(t)$ at time $t = 0$, and so the first Taylor series expansion coefficient $\tilde{c}_{AB}^{(0)}(0)$ in Eq. (5) will be given by Eq. (31) as

$$\tilde{c}_{AB}^{(0)}(0) = \frac{1}{N'}\int d\mathbf{q}\, e^{-\beta_n V_n(\mathbf{q})} A_n(\mathbf{q}) B_n(\mathbf{q}), \tag{37}$$

where

$$N' = \int d\mathbf{q}\, e^{-\beta_n V_n(\mathbf{q})}, \tag{38}$$

with

$$V_n(\mathbf{q}) = \frac{1}{2}\mathbf{q}^T\mathbf{K}\mathbf{q} + \sum_{j=1}^{n} V(q_j). \tag{39}$$

Equation (37) has the form of a primitive imaginary-time path integral (Trotter product[67]) discretization of Eq. (5) involving n path integral beads.[45] A constraint on the force constant matrix that gives the correct result in the limit as $n \to \infty$ is thus[3,66]

$$\frac{1}{2}\mathbf{q}^T\mathbf{K}\mathbf{q} = \sum_{j=1}^{n} \frac{1}{2} m\omega_n^2 (q_j - q_{j-1})^2, \tag{40}$$

where m is the physical particle mass, $\omega_n = n/(\beta\hbar)$, and $q_0 \equiv q_n$. The first expansion coefficient $\tilde{c}_{AB}^{(0)}(0)$ in Eq. (4) will therefore be given exactly by Eq. (31) in the large-n limit if the elements of the force constant matrix $\mathbf{K}$ are given by

$$K_{jj'} = m\omega_n^2 \left(2\delta_{j,j'} - \delta_{j,j'-1} - \delta_{j,j'+1} - \delta_{j,1}\delta_{j',n} - \delta_{j,n}\delta_{j',1}\right). \tag{41}$$

Note that the resulting matrix $\mathbf{K}$ is real-symmetric and positive semi-definite, which is sufficient to ensure that the integrals over $\mathbf{q}$ in Eqs. (31) and (32) will converge for any potential $V(q)$ that leads to a well-defined partition function. The eigenvalues of $\mathbf{K}$ are $k_l = 4m\omega_n^2 \sin^2(l\pi/n)$ for $l = 0, 1, 2, \ldots, n-1$, and the normalized eigenvector $\mathbf{c}$ corresponding to $l = 0$ (the centroid mode of the ring polymer) has elements $c_j = n^{-1/2}$ for $j = 1, 2, \ldots, n$; the main result that we shall need below is that

$$\mathbf{K}\mathbf{c} = \mathbf{0}. \tag{42}$$

So far, we have used the first Taylor expansion coefficient $\tilde{c}_{AB}^{(0)}(0)$ in Eq. (4) to constrain the ring polymer force constant matrix $\mathbf{K}$, but the mass matrix $\mathbf{M}$ is still pretty much arbitrary. This is not surprising: $\tilde{c}_{AB}^{(0)}(0)$ is a static equilibrium property that can be computed exactly by PIMD using any choice of the fictitious masses for the ring polymer beads that were first introduced by Parrinello and Rahman.[60] In the RPMD method,[45] the mass matrix is chosen to be $\mathbf{M} = m\mathbf{I}$, where m is the physical particle mass and $\mathbf{I}$ is the $(n \times n)$ identity matrix. In the adiabatic CMD method,[41] the mass matrix is chosen to be diagonal in the basis that diagonalises $\mathbf{K}$, the mass of the centroid mode is chosen to be the physical mass m, and the masses of the remaining modes are specified as $m_l = 4m\gamma^2 n \sin^2(l\pi/n)$, where γ is an adiabaticity parameter.[61] These choices give the frequencies of the normal modes of the free ring polymer as $\omega_0 = 0$ and $\omega_l = \sqrt{k_l/m_l} = \sqrt{n}/(\beta\hbar\gamma)$ for $l > 0$. For a sufficiently small adiabaticity parameter γ, the high-frequency modes will thus be well-separated from the centroid mode, and the effective force on the centroid will be rapidly averaged over the fluctuations of the remaining modes.[41,61] It is claimed in Ref. 61 that this adiabatic separation of the centroid from the remaining modes leads to a more accurate short-time dynamics of the centroid coordinate and hence to a more accurate short-time approximation to $\tilde{c}_{qq}(t)$. We shall now investigate this claim by using the remaining Taylor series expansion coefficients $\tilde{c}_{AB}^{(2r)}(0)$ determined in Sec. II to find the Parrinello-Rahman mass matrix $\mathbf{M}$ that gives the most accurate short-time approximation to the Kubo-transformed correlation function.

The central result we shall use to do this is the following approximation to the expansion coefficient $\tilde{c}_{AB}^{(2r)}(0)$, which results from a repeated differentiation of Eq. (31):

$$\tilde{c}_{AB}^{(2r)}(0) \simeq \frac{(-1)^s}{N} \int d\mathbf{p} \int d\mathbf{q}\, e^{-\beta_n H_n(\mathbf{p},\mathbf{q})} A_n^{(s)}(\mathbf{q}) B_n^{(2r-s)}(\mathbf{q}). \tag{43}$$

Here s can be any integer between 0 and $2r$, and $A_n^{(s)}(\mathbf{q})$ and $B_n^{(2r-s)}(\mathbf{q})$ are respectively the s-th and $(2r-s)$-th time derivatives of the functions $A_n(\mathbf{q})$ and $B_n(\mathbf{q})$ in Eq. (34) at time $t=0$ as obtained from the ring polymer dynamics in Eqs. (35) and (36). [The reason why one can use any s in Eq. (43) is that the ring polymer dynamics conserves both the ring polymer Hamiltonian and the ring polymer phase space volume, and so Eq. (31) can be written equivalently in the form

$$\tilde{c}_{AB}(t) \simeq \frac{1}{N} \int d\mathbf{p}_t \int d\mathbf{q}_t\, e^{-\beta_n H_n(\mathbf{p}_t,\mathbf{q}_t)} A_n(\mathbf{q}) B_n(\mathbf{q}_t). \tag{44}$$

Shifting the integration variables back from $(\mathbf{p}_t, \mathbf{q}_t)$ to $(\mathbf{p}, \mathbf{q})$ gives

$$\tilde{c}_{AB}(t) \simeq \frac{1}{N} \int d\mathbf{p} \int d\mathbf{q}\, e^{-\beta_n H_n(\mathbf{p},\mathbf{q})} A_n(\mathbf{q}_{-t}) B_n(\mathbf{q}), \tag{45}$$

and performing s of the $2r$ differentiations with the equation in this form and $2r-s$ with it in the form of Eq. (31) gives the result we have written in Eq. (43).]

We shall begin as we did in Sec. II by considering the special case of the position autocorrelation function, for which $A(\hat{q}) = B(\hat{q}) = \hat{q}$. In this case, the functions $A_n(\mathbf{q})$ and $B_n(\mathbf{q})$ in Eq. (34) are the same,

$$A_n(\mathbf{q}) = B_n(\mathbf{q}) = q_n(\mathbf{q}) = \frac{1}{n}\sum_{j=1}^{n} q_j, \tag{46}$$

and their first few time derivatives are given by the classical ring polymer dynamics in Eqs. (35) and (36) as

$$q_n^{(0)}(\mathbf{q}) = \mathbf{e}^T\mathbf{q}, \tag{47}$$

$$q_n^{(1)}(\mathbf{q}) = \mathbf{e}^T\mathbf{M}^{-1}\mathbf{p}, \tag{48}$$

$$q_n^{(2)}(\mathbf{q}) = -\mathbf{e}^T\mathbf{M}^{-1}\left[\mathbf{K}\mathbf{q}+\mathbf{g}(\mathbf{q})\right], \tag{49}$$

$$q_n^{(3)}(\mathbf{q}) = -\mathbf{e}^T\mathbf{M}^{-1}\left[\mathbf{K}+\mathbf{H}(\mathbf{q})\right]\mathbf{M}^{-1}\mathbf{p}, \tag{50}$$

where $\mathbf{e} = n^{-1/2}\mathbf{c}$ is a column vector with elements $e_j = 1/n$ for $j = 1, 2, \ldots, n$, and $\mathbf{H}(\mathbf{q})$ is a diagonal matrix with diagonal elements $H_{jj}(\mathbf{q}) = V''(q_j)$.

Choosing $s = 1$ for convenience, the second expansion coefficient $\tilde{c}_{qq}^{(2)}(0)$ is given by Eq. (43) as

$$\tilde{c}_{qq}^{(2)}(0) = -\frac{1}{N}\int d\mathbf{p}\int d\mathbf{q}\, e^{-\beta_n H_n(\mathbf{p},\mathbf{q})}\,\left[\mathbf{e}^T\mathbf{M}^{-1}\mathbf{p}\right]^2, \tag{51}$$

the momentum integral in which can readily be evaluated with the help of the following identity:

$$\int d\mathbf{p}\, e^{-\beta_n\mathbf{p}^T\mathbf{M}^{-1}\mathbf{p}/2}\,\mathbf{a}^T\mathbf{p}\,\mathbf{b}^T\mathbf{p} = \frac{1}{\beta_n}\mathbf{a}^T\mathbf{M}\mathbf{b}\int d\mathbf{p}\, e^{-\beta_n\mathbf{p}^T\mathbf{M}^{-1}\mathbf{p}/2}. \tag{52}$$

In view of the definition of N in Eq. (32), the result is simply

$$\tilde{c}_{qq}^{(2)}(0) = -\frac{1}{\beta_n}\mathbf{e}^T\mathbf{M}^{-1}\mathbf{e}, \tag{53}$$

or equivalently (since $\beta_n = \beta/n$ and $\mathbf{e} = n^{-1/2}\mathbf{c}$)

$$\tilde{c}_{qq}^{(2)}(0) = -\frac{1}{\beta}\mathbf{c}^T\mathbf{M}^{-1}\mathbf{c}, \tag{54}$$

where $\mathbf{c}$ is the normalised centroid eigenvector of the ring polymer force constant matrix in Eq. (42). In order for this to agree with the exact result in Eq. (19), the mass matrix $\mathbf{M}$ must satisfy

$$\mathbf{c}^T\mathbf{M}^{-1}\mathbf{c} = \frac{1}{m}, \tag{55}$$

which (since $\mathbf{c}$ is normalised and both methods involve a non-singular mass matrix $\mathbf{M}$ that satisfies $\mathbf{M}\mathbf{c} = m\mathbf{c}$) is the case in both CMD and RPMD.

For the third Taylor series expansion coefficient $\tilde{c}_{qq}^{(4)}(0)$ in Eq. (4), it is again convenient to choose $s = 1$ in Eq. (43), which gives

$$\tilde{c}_{qq}^{(4)}(0) = \frac{1}{N}\int d\mathbf{p}\int d\mathbf{q}\, e^{-\beta_n H_n(\mathbf{p},\mathbf{q})}\,\mathbf{e}^T\mathbf{M}^{-1}\mathbf{p}\,\mathbf{e}^T\mathbf{M}^{-1}\left[\mathbf{K}+\mathbf{H}(\mathbf{q})\right]\mathbf{M}^{-1}\mathbf{p}. \tag{56}$$

The momentum integral in this equation can again be evaluated with the help of Eq. (52), and the result can again be simplified using the fact that $\beta_n = \beta/n$ and $\mathbf{e} = n^{-1/2}\mathbf{c}$:

$$\tilde{c}_{qq}^{(4)}(0) = \frac{1}{\beta N}\int d\mathbf{p}\int d\mathbf{q}\, e^{-\beta_n H_n(\mathbf{p},\mathbf{q})}\,\mathbf{c}^T\mathbf{M}^{-1}\left[\mathbf{K}+\mathbf{H}(\mathbf{q})\right]\mathbf{M}^{-1}\mathbf{c}. \tag{57}$$

For comparison with this result, the exact expression for $\tilde{c}_{qq}^{(4)}(0)$ in Eq. (22) can be written in the present notation (after an n bead path integral discretization of the thermal expectation value) as

$$\tilde{c}_{qq}^{(4)}(0) = \frac{1}{\beta m^2 N} \int d\mathbf{p} \int d\mathbf{q}\, e^{-\beta_n H_n(\mathbf{p},\mathbf{q})}\, \mathbf{c}^T \mathbf{H}(\mathbf{q}) \mathbf{c}. \tag{58}$$

Thus Eq. (31) will only give the exact result for $\tilde{c}_{qq}^{(4)}(0)$ if

$$\mathbf{c}^T \mathbf{M}^{-1} \left[\mathbf{K} + \mathbf{H}(\mathbf{q})\right] \mathbf{M}^{-1} \mathbf{c} = \frac{1}{m^2} \mathbf{c}^T \mathbf{H}(\mathbf{q}) \mathbf{c}, \tag{59}$$

which since $\mathbf{K}\mathbf{c} = \mathbf{0}$ will be satisfied provided that

$$\mathbf{M}^{-1} \mathbf{c} = \frac{1}{m} \mathbf{c}. \tag{60}$$

Note that this is a more severe constraint than the one in Eq. (55), and that it includes Eq. (55) as a special case. (That is, any mass matrix $\mathbf{M}$ that satisfies Eq. (60) will also satisfy Eq. (55), but not conversely.) Note also that Eq. (60) is satisfied by the mass matrices that are employed in CMD and RPMD.

The fourth Taylor series expansion coefficient $\tilde{c}_{qq}^{(6)}(0)$ in Eq. (4) places an even more severe restriction on the mass matrix, and suffices to determine it uniquely. In this case it is most convenient to choose $s = 3$ in Eq. (43), which gives

$$\tilde{c}_{qq}^{(6)}(0) = -\frac{1}{N} \int d\mathbf{p} \int d\mathbf{q}\, e^{-\beta_n H_n(\mathbf{p},\mathbf{q})} \left\{\mathbf{e}^T \mathbf{M}^{-1} \left[\mathbf{K} + \mathbf{H}(\mathbf{q})\right] \mathbf{M}^{-1} \mathbf{p}\right\}^2. \tag{61}$$

The momentum integral in this equation can yet again be evaluated using Eq. (52), and the result yet again simplified using $\beta_n = \beta/n$ and $\mathbf{e} = n^{-1/2}\mathbf{c}$. Assuming that the mass matrix $\mathbf{M}$ satisfies Eq. (60), so that the expansion coefficients $\tilde{c}_{qq}^{(2)}(0)$ and $\tilde{c}_{qq}^{(4)}(0)$ are given correctly, and noting again that $\mathbf{K}\mathbf{c} = \mathbf{0}$, we obtain

$$\tilde{c}_{qq}^{(6)}(0) = -\frac{1}{\beta m^2 N} \int d\mathbf{p} \int d\mathbf{q}\, e^{-\beta_n H_n(\mathbf{p},\mathbf{q})}\, \mathbf{c}^T \mathbf{H}(\mathbf{q}) \mathbf{M}^{-1} \mathbf{H}(\mathbf{q}) \mathbf{c}. \tag{62}$$

For comparison, the exact result in Eq. (26) can be written in the present notation as

$$\tilde{c}_{qq}^{(6)}(0) = -\frac{1}{\beta m^3 N} \int d\mathbf{p} \int d\mathbf{q}\, e^{-\beta_n H_n(\mathbf{p},\mathbf{q})}\, \mathbf{c}^T \mathbf{H}(\mathbf{q})^2 \mathbf{c}. \tag{63}$$

When the potential energy function $V(q)$ is harmonic, so that the matrix $\mathbf{H}(\mathbf{q})$ is simply a constant times a unit matrix, Eq. (62) will give the same result as Eq. (63) for any mass matrix $\mathbf{M}$ that satisfies Eq. (60). However, in the more general case of an anharmonic potential energy function, Eq. (62) will only give the same result as Eq. (63) if the following equation is satisfied for an arbitrary diagonal matrix $\mathbf{H}(\mathbf{q})$:

$$\mathbf{c}^T\mathbf{H}(\mathbf{q})\mathbf{M}^{-1}\mathbf{H}(\mathbf{q})\mathbf{c} = \frac{1}{m}\mathbf{c}^T\mathbf{H}(\mathbf{q})^2\mathbf{c}. \tag{64}$$

This is a very severe constraint indeed, and it uniquely determines the Parrinello-Rahman mass matrix as the one that is employed in RPMD:

$$\mathbf{M} = m\mathbf{I}. \tag{65}$$

Finally, let us consider the short-time accuracy of Eq. (31) for more general Hermitian operators $A(\hat{q})$ and $B(\hat{q})$. We have already argued that the first Taylor series expansion coefficient $\tilde{c}^{(0)}_{AB}(0)$ in Eq. (4) will be obtained exactly by the PIMD ansatz provided the ring polymer force constant matrix $\mathbf{K}$ is as specified in Eq. (41). This leaves the second expansion coefficient $\tilde{c}^{(2)}_{AB}(0)$, which is given by Eq. (43) as

$$\tilde{c}^{(2)}_{AB}(0) = -\frac{1}{N}\int d\mathbf{p}\int d\mathbf{q}\, e^{-\beta_n H_n(\mathbf{p},\mathbf{q})}A^{(1)}_n(\mathbf{q})B^{(1)}_n(\mathbf{q}). \tag{66}$$

Here $A^{(1)}_n(\mathbf{q})$ and $B^{(1)}_n(\mathbf{q})$ are the first time derivatives of the functions $A_n(\mathbf{q})$ and $B_n(\mathbf{q})$ at time $t = 0$. In view of Eq. (36), these are given by

$$A^{(1)}_n(\mathbf{q}) = \mathbf{e}^T\mathbf{A}^{(1)}(\mathbf{q})\mathbf{M}^{-1}\mathbf{p}, \tag{67}$$

$$B^{(1)}_n(\mathbf{q}) = \mathbf{e}^T\mathbf{B}^{(1)}(\mathbf{q})\mathbf{M}^{-1}\mathbf{p}, \tag{68}$$

where $\mathbf{A}^{(1)}(\mathbf{q})$ and $\mathbf{B}^{(1)}(\mathbf{q})$ are diagonal matrices with diagonal elements $A^{(1)}_{jj}(\mathbf{q}) = A'(q_j)$ and $B^{(1)}_{jj}(\mathbf{q}) = B'(q_j)$. Substituting these results into Eq. (66), using Eq. (52) to evaluate the momentum integral, and noting again that $\beta_n = \beta/n$ and $\mathbf{e} = n^{-1/2}\mathbf{c}$, we obtain

$$\tilde{c}^{(2)}_{AB}(0) = -\frac{1}{\beta N}\int d\mathbf{p}\int d\mathbf{q}\, e^{-\beta_n H_n(\mathbf{p},\mathbf{q})}\mathbf{c}^T\mathbf{A}^{(1)}(\mathbf{q})\mathbf{M}^{-1}\mathbf{B}^{(1)}(\mathbf{q})\mathbf{c}. \tag{69}$$

For comparison with this, the exact result in Eq. (30) can be written in the same notation as

$$\tilde{c}^{(2)}_{AB}(0) = -\frac{1}{\beta m N}\int d\mathbf{p}\int d\mathbf{q}\, e^{-\beta_n H_n(\mathbf{p},\mathbf{q})}\mathbf{c}^T\mathbf{A}^{(1)}(\mathbf{q})\mathbf{B}^{(1)}(\mathbf{q})\mathbf{c}. \tag{70}$$

Equation (31) will therefore only give the exact result for $\tilde{c}^{(2)}_{AB}(0)$ in the case of general (non-linear) operators $A(\hat{q})$ and $B(\hat{q})$ if the mass matrix $\mathbf{M}$ is such that

$$\mathbf{c}^T\mathbf{A}^{(1)}(\mathbf{q})\mathbf{M}^{-1}\mathbf{B}^{(1)}(\mathbf{q})\mathbf{c} = \frac{1}{m}\mathbf{c}^T\mathbf{A}^{(1)}(\mathbf{q})\mathbf{B}^{(1)}(\mathbf{q})\mathbf{c} \tag{71}$$

for arbitrary diagonal matrices $\mathbf{A}^{(1)}(\mathbf{q})$ and $\mathbf{B}^{(1)}(\mathbf{q})$. This constraint is just as restrictive as that in Eq. (64), and it again leads uniquely to the RPMD mass matrix in Eq. (65).

IV. A MULTI-DIMENSIONAL GENERALIZATION

In the preceding two sections, we have shown that the PIMD ansatz in Eq. (31) leads uniquely to the RPMD approximation[45] when the criterion that is used to select the Parrinello-Rahman[60] mass matrix is the short-time accuracy of the Kubo-transformed correlation function. In the case of the position autocorrelation function $\tilde{c}_{qq}(t)$, the RPMD approximation is exact to $O(t^6)$, for the velocity autocorrelation function $\tilde{c}_{vv}(t) = -\tilde{c}_{qq}^{(2)}(t)$ it is exact to $O(t^4)$, and for a general Kubo-transformed correlation function $\tilde{c}_{AB}(t)$ involving non-linear local operators the approximation is exact to $O(t^2)$. Although our analysis has not gone far enough to determine them explicitly, the leading errors in the RPMD approximations to $\tilde{c}_{qq}(t)$, $\tilde{c}_{vv}(t)$, and $\tilde{c}_{AB}(t)$ are therefore $O(t^8)$, $O(t^6)$, and $O(t^4)$, respectively. And although we have confined our attention to a simple one-dimensional problem, it is straightforward to show that these results apply equally well to systems with more degrees of freedom.

In the absence of identical particle exchange effects, the Kubo-transformed velocity autocorrelation function of a monatomic liquid, for example, is given exactly by

$$\tilde{c}_{\mathbf{v}\cdot\mathbf{v}}(t) = \frac{1}{\beta m^2 n_a Z} \sum_{i=1}^{n_a} \int_0^\beta d\lambda \, \mathrm{tr} \left[e^{-(\beta-\lambda)\hat{H}} \hat{\mathbf{p}}_i e^{-\lambda \hat{H}} \cdot e^{+i\hat{H}t/\hbar} \hat{\mathbf{p}}_i e^{-i\hat{H}t/\hbar} \right], \tag{72}$$

where n_a is the number of atoms in the liquid, m is their atomic mass, $\hat{\mathbf{p}}_i$ is the momentum operator of atom i, and $\hat{H}$ is the Hamiltonian operator

$$\hat{H} = \sum_{i=1}^{n_a} \frac{\hat{\mathbf{p}}_i^2}{2m} + V(\hat{\mathbf{r}}_1, \ldots, \hat{\mathbf{r}}_{n_a}). \tag{73}$$

This autocorrelation function is a real and even function of t which can be expanded as in Eq. (4), and the first few expansion coefficients can be obtained using the methods developed in Sec. II:

$$\tilde{c}_{\mathbf{v}\cdot\mathbf{v}}^{(0)}(0) = \frac{3}{\beta m}, \tag{74}$$

$$\tilde{c}_{\mathbf{v}\cdot\mathbf{v}}^{(2)}(0) = -\frac{1}{\beta m^2 n_a} \sum_{i=1}^{n_a} \sum_{\eta=x,y,z} \left\langle \frac{\partial^2 V(\mathbf{r}_1, \ldots, \mathbf{r}_{n_a})}{\partial \eta_i^2} \right\rangle, \tag{75}$$

$$\tilde{c}_{\mathbf{v}\cdot\mathbf{v}}^{(4)}(0) = \frac{1}{\beta m^3 n_a} \sum_{i,i'=1}^{n_a} \sum_{\eta,\eta'=x,y,z} \left\langle \left(\frac{\partial^2 V(\mathbf{r}_1, \ldots, \mathbf{r}_{n_a})}{\partial \eta_i \partial {\eta'}_{i'}} \right)^2 \right\rangle. \tag{76}$$

Here the sums over η and η' are over the Cartesian components of the position vectors $\mathbf{r}_i$ and $\mathbf{r}_{i'}$, and the angular brackets denote a thermal expectation value as in Eq. (23). Note the similarities and differences between these expansion coefficients and those in Eqs. (19), (22) and (26): the similarities arise because the velocity autocorrelation function is minus the second time derivative of a position autocorrelation function, and the differences arise because we are now considering an n_a-particle system in three-dimensional space.

Turning to the RPMD approximation, the analogue of Eq. (43) in the present context is

$$\tilde{c}^{(2r)}_{\mathbf{v}\cdot\mathbf{v}}(0) \simeq \frac{(-1)^s}{N} \int\!\!\int \prod_{k=1}^{n_a}\prod_{j=1}^{n} d\mathbf{p}_{k,j} d\mathbf{r}_{k,j}\, e^{-\beta_n H_n(\{\mathbf{p}_{k,j}\},\{\mathbf{r}_{k,j}\})}\, \frac{1}{m^2 n_a}\sum_{i=1}^{n_a} \mathbf{p}_i^{(s)}\cdot\mathbf{p}_i^{(2r-s)}, \tag{78}$$

where

$$N = \int\!\!\int \prod_{k=1}^{n_a}\prod_{j=1}^{n} d\mathbf{p}_{k,j} d\mathbf{r}_{k,j}\, e^{-\beta_n H_n(\{\mathbf{p}_{k,j}\},\{\mathbf{r}_{k,j}\})}. \tag{79}$$

Here $H_n(\{\mathbf{p}_{k,j}\},\{\mathbf{r}_{k,j}\})$ is the classical Hamiltonian of n_a atomic ring polymers which interact through the interaction potential V; with the RPMD choice of the Parrinello-Rahman mass matrix for each atomic ring polymer this is simply[47]

$$H_n(\{\mathbf{p}_{k,j}\},\{\mathbf{r}_{k,j}\}) = \sum_{k=1}^{n_a}\sum_{j=1}^{n}\left[\frac{\mathbf{p}_{k,j}^2}{2m} + \frac{1}{2}m\omega_n^2(\mathbf{r}_{k,j}-\mathbf{r}_{k,j-1})^2\right] + \sum_{j=1}^{n} V(\mathbf{r}_{1,j},\ldots,\mathbf{r}_{n_a,j}), \tag{80}$$

subject to the cyclic boundary condition $\mathbf{r}_{i,0} \equiv \mathbf{r}_{i,n}$. The quantities $\mathbf{p}_i^{(s)}$ and $\mathbf{p}_i^{(2r-s)}$ in Eq. (78) are the s-th and $(2r-s)$-th time derivatives of the momentum centroid of the i-th ring polymer at time $t=0$, as obtained from the classical dynamics generated by this ring polymer Hamiltonian; the first few of these derivatives are found to be

$$\mathbf{p}_i^{(0)} = \frac{1}{n}\sum_{j=1}^{n}\mathbf{p}_{i,j}, \tag{81}$$

$$\mathbf{p}_i^{(1)} = -\frac{1}{n}\sum_{j=1}^{n}\frac{\partial V(\mathbf{r}_{1,j},\ldots,\mathbf{r}_{n_a,j})}{\partial \mathbf{r}_{i,j}}, \tag{82}$$

$$\mathbf{p}_i^{(2)} = -\frac{1}{nm}\sum_{i'=1}^{n_a}\sum_{j=1}^{n}\frac{\partial^2 V(\mathbf{r}_{1,j},\ldots,\mathbf{r}_{n_a,j})}{\partial \mathbf{r}_{i,j}\partial \mathbf{r}_{i',j}}\cdot\mathbf{p}_{i',j}. \tag{83}$$

Substituting Eq. (81) into Eq. (78) with $r = s = 0$, and evaluating the resulting momentum integrals as described in Sec. III, it is easy to show that the RPMD approximation produces the exact expansion coefficient $\tilde{c}^{(0)}_{\mathbf{v}\cdot\mathbf{v}}(0)$ in Eq. (74), for any number of ring polymer beads. The analysis of the coefficients $\tilde{c}^{(2)}_{\mathbf{v}\cdot\mathbf{v}}(0)$ and $\tilde{c}^{(4)}_{\mathbf{v}\cdot\mathbf{v}}(0)$ proceeds along the same lines, but it is a bit more complicated, and in this case the result does depend on the number of ring polymer beads. One finds that setting $r = 1$ and $s = 0$ in Eq. (78) ultimately leads to an expression for $\tilde{c}^{(2)}_{\mathbf{v}\cdot\mathbf{v}}(0)$ that can be written in the form of Eq. (75), with the angular bracket defined as

$$\left\langle \frac{\partial^2 V(\mathbf{r}_1,\ldots,\mathbf{r}_{n_a})}{\partial\eta_i^2} \right\rangle = \frac{1}{N}\int\int \prod_{k=1}^{n_a}\prod_{j=1}^{n} d\mathbf{p}_{k,j}d\mathbf{r}_{k,j}\, e^{-\beta_n H_n(\{\mathbf{p}_{k,j}\},\{\mathbf{r}_{k,j}\})} \times \frac{1}{n}\sum_{j'=1}^{n} \frac{\partial^2 V(\mathbf{r}_{1,j'},\ldots,\mathbf{r}_{n_a,j'})}{\partial\eta_{i,j'}^2}. \tag{84}$$

And setting $r = 2$ and $s = 2$ in Eq. (78) leads to an expression for $\tilde{c}^{(4)}_{\mathbf{v}\cdot\mathbf{v}}(0)$ of the form in Eq. (79), with

$$\left\langle \left(\frac{\partial^2 V(\mathbf{r}_1,\ldots,\mathbf{r}_{n_a})}{\partial\eta_i\partial\eta_{i'}} \right)^2 \right\rangle = \frac{1}{N}\int\int \prod_{k=1}^{n_a}\prod_{j=1}^{n} d\mathbf{p}_{k,j}d\mathbf{r}_{k,j}\, e^{-\beta_n H_n(\{\mathbf{p}_{k,j}\},\{\mathbf{r}_{k,j}\})} \times \frac{1}{n}\sum_{j'=1}^{n} \left(\frac{\partial^2 V(\mathbf{r}_{1,j'},\ldots,\mathbf{r}_{n_a,j'})}{\partial\eta_{i,j'}\partial\eta_{i',j'}} \right)^2. \tag{85}$$

Recognizing the right-hand sides of these equations as n-bead path integral approximations to the exact thermal expectation values of the local operators $\partial^2 V(\hat{\mathbf{r}}_1,\ldots,\hat{\mathbf{r}}_{n_a})/\partial\hat{\eta}_i^2$ and $(\partial^2 V(\hat{\mathbf{r}}_1,\ldots,\hat{\mathbf{r}}_{n_a})/\partial\hat{\eta}_i\partial\hat{\eta}_{i'})^2$, one sees that the expansion coefficients $\tilde{c}^{(2)}_{\mathbf{v}\cdot\mathbf{v}}(0)$ and $\tilde{c}^{(4)}_{\mathbf{v}\cdot\mathbf{v}}(0)$ will be given exactly by Eq. (78) in the limit as $n \to \infty$. As in the simple one-dimensional case considered above, the RPMD velocity autocorrelation function of a monatomic liquid therefore has a leading error of $O(t^6)$, and one can again show that any other choice of the Parrinello-Rahman mass matrix will give an error of at least $O(t^4)$.

This is just one of several examples that we could have chosen to illustrate how the results in Secs. II and III extend to multi-dimensional problems, but it is an important one. Rabani *et al.* have recently compared a number of different approximate quantum dynamical simulations of the velocity autocorrelation spectrum of normal liquid helium at 4 K, where identical particle exchange effects can be neglected.[64] They found that the NAC and QMCT methods gave very similar spectra, with a significant tail extending to high frequencies ($\omega > 50$ cm^{-1}) owing to the rapid initial decay of the corresponding velocity autocorrelation functions. However, the (adiabatic) CMD method was found to give a noticeably different spectrum, without any high-frequency tail.[64] Since the RPMD velocity autocorrelation function $\tilde{c}_{\mathbf{v}\cdot\mathbf{v}}(t)$ is more accurate than the CMD autocorrelation function at short times, one would expect this problem to be fixed in RPMD, and indeed Hone *et al.* have recently shown that the RPMD velocity autocorrelation spectrum of normal liquid helium has the same high-frequency tail as is seen in NAC and QMCT.[68] This numerical result is consistent with the present analysis, and it provides a clear example of a situation in which the RPMD choice of Parrinello-Rahman mass matrix is preferable to that used in adiabatic CMD.

V. CONCLUDING REMARKS

In this paper, we have shown that the RPMD approximation is more accurate at short times than any other quantum dynamical approximation based on path integral molecular dynamics, including the adiabatic implementation of CMD. This provides some theoretical justification for using RPMD in preference to CMD, and it also goes some way towards explaining the success of several earlier RPMD calculations.[46−50] However, it does not constitute a derivation of the RPMD method, because it is hard to see how to obtain the ansatz in Eq. (31) from first principles. As we have stressed from the outset,[45] the RPMD approximation simply provides a convenient *model* for the effect of quantum fluctuations on the dynamics of complex (dissipative) chemical systems, and we would not want to claim any more of it than this. The model is consistent with the exact quantum mechanical detailed balance condition, it gives the exact result in the classical (high temperature) limit and in the harmonic limit, and it becomes exact at all temperatures in the limit as $t \to 0$.[45] All we have done here is to explore how accurately this short-time limit is approached.

Another important thing to bear in mind is that high accuracy in the short-time limit will not always be the main concern. We have argued above that this limit is important for normal liquid helium at 4 K, where the rapid initial decay of the velocity autocorrelation function leads to a pronounced high-frequency tail in the corresponding spectrum.[64,68] However, there are other problems for which the short-time limit is less important, such as the position autocorrelation function of the one-dimensional quartic oscillator considered in Ref. 61. Here the exact quantum mechanical Kubo-transformed autocorrelation function oscillates sinusoidally at low temperatures, and the first few terms in a Taylor series expansion are not enough to influence this sinusoidal behavior. This simple non-dissipative model system has been studied several times using RPMD and CMD, and the CMD approximation is found to capture more of the amplitude of the oscillation at longer times.[44,45,61] Why this should be we do not fully understand, and the present short-time analysis sheds no light on it.

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