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On new efficient algorithms for PIMC and PIMD

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Abstract

The properties of various algorithms, estimators, and high-temperature density matrix (HTDM) decompositions relevant for path integral simulations are discussed. It is shown that Fourier accelerated path integral molecular dynamics (PIMD) completely eliminates slowing down with increasing Trotter number P . A new primitive estimator of the kinetic energy for use in PIMD simulations is found to behave less pathologically than the original virial estimator. In particular, its variance does not increase significantly with P . Two non-primitive HTDM decompositions are compared as well: one decomposition used in the Takahashi Imada algorithm and another one based on an effective propagator. In the latter case, effective potentials are constructed between two particles such that two-particle propagators are reflected exactly—even at finite P . © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Path integral (PI) techniques are widely used to simulate condensed matter systems at low temperatures where the quantum mechanical nature of ionic motion becomes relevant. Monte Carlo used to be the method of choice to treat such systems [1], but recently new ideas made path integral molecular dynamics (PIMD) [2] an attractive alternative. In order to render PI simulation into a powerful tool several requirements need to be satisfied.

- (i) **Good sampling:** The correlation time of observables should scale linearly with Trotter number P (as measured in CPU time).
- (ii) **Good estimators:** The variance of an estimator should not increase with P .

- (iii) **Good decompositions** of the high-temperature density matrix (HTDM) underlying the PI simulation: Convergence to the quantum limit should be fast and/or the amplitude of finite P corrections should be small.

These three issues will be discussed here. The focus will be on recent developments in PIMD although most results are relevant for PIMC as well.

2. Methods and results

An important step in making PI simulations accessible to molecular dynamics (MD) was the realization that the *dynamic* masses of the beads constituting the chain (which represents the quantum mechanical point particle) can be chosen arbitrarily [2]. This is because the physical mass m of the particle is already reflected in the harmonic spring connecting two adjacent beads

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of the chain and MD is merely used to generate the proper canonical distribution of the beads' positions. An efficient choice for quantum solids is to attribute dynamic masses m_q to the eigenmodes q instead of attributing them to individual beads. By doing so, it is possible to collapse all time scales (except for long wavelength vibrations and diffusion) in simple solids with the choice

$$m_q = (k_q + k_E)m/k_E, \quad (1)$$

where k_E reflects the harmonic coupling of an atom to its lattice site within the Einstein picture of solids and k_q is the stiffness associated with the eigenmode in a free chain. Similar m_q s will also be useful for quantum fluids. Here I want to show that such a treatment satisfies the requirement (i) from the introduction if a Langevin thermostat (LT) is applied. The treatment is similar to the pioneering work by Singer and Smith [3] except for the crucial choice of dynamic masses. Their paper can yet serve as an introduction to the present rather condensed presentation.

The reason why the LT (Singer and Smith call the resulting dynamics “Brownian”) is a good thermostat in the given context is due to the fact that most eigenfrequencies ω of the model collapse and hence the quality $Q = \gamma/\omega$ of each oscillator is the same where γ denotes the friction term in the LT. Hence the time after which modes have “forgotten” their original state is similar for the chain's internal modes and its center of mass mode. It is not clear whether different thermostating, e.g., in terms of Nosé–Hoover chains attached to each bead [4], also produces a similarly narrow distribution of Q s. I want to note in passing that even the time scale of the strain tensor's motion can be adjusted to the “atomic” time scales by using appropriate inertia associated with the box geometry. This makes the use of the Parrinello–Rahman method very efficient for the evaluation of elastic properties of quantum solids like ^3He [5].

In Fig. 1 the time autocorrelation function $C_{VV}(t)$ of the potential energy per particle V , namely

$$C_{VV}(t) = \langle V(t)V(0) \rangle, \quad (2)$$

is shown for various Trotter numbers. The test model is liquid neon. Since I am not interested in precise thermodynamic values at this point, a simple Lennard–Jones potential with standard parameters $\epsilon = 36.68 k_B K$ and $\sigma = 2.787 \text{ \AA}$ is chosen. The interactions are cut off at $r_c = 5 \text{ \AA}$ and $N = 256$ atoms

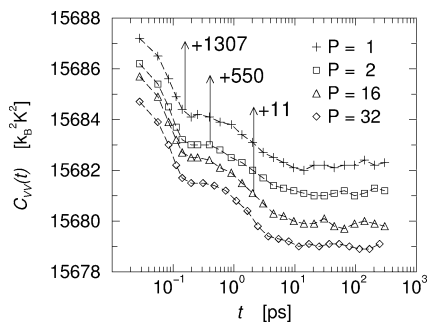


Fig. 1. Autocorrelation function $C_{VV}(t)$ of the potential energy V of liquid neon as a function of time t for various Trotter numbers P . The arrows indicate by how much the $P = 1$ and $P = 2$ curve have to be shifted upwards.

were used. Simulations are carried out at a temperature $T = 26.8 \text{ K}$ and with a fixed atomic volume of 27.556 \AA^3 . It can be seen that $\langle V \rangle^2$ (the plateau value of $C_{VV}(t)$ at large times t) differs between small P and large P reflecting the role of quantum effects. However, the shape of $C_{VV}(t)$ is relatively independent of P indicating the optimum elimination of slowing down with increasing P : eigenfrequencies and required time step Δt independent of P , generation of neighbor lists basically independent of P , evaluation of forces and propagation of coordinates linear in P (large prefactor, simultaneous/parallel update of Fourier modes), and Fourier transforms of forces into reciprocal space $P \log P$ (small prefactor).

Fig. 1 also shows that requirement (ii) is satisfied for the potential energy. This behavior cannot be guaranteed for observables that are not orthogonal in coordinate space like the kinetic energy. This discussion goes back to Herman et al. [6] who pointed out the failure of the so-called primitive estimator $T_{\text{kin, prim}}$ for the kinetic energy

$$T_{\text{kin, prim}} = 1.5 k_B T^2 P^2 - \langle V_{\text{chain}} \rangle / N, \quad (3)$$

where $\langle V_{\text{chain}} \rangle$ denotes the expectation value of the potential energy in the springs connecting adjacent beads. The variance of the primitive estimator increases with P . At the time, efficient sampling algorithms had not yet been devised, which made the situation even worse.

Recently it was claimed that the primitive estimator can be significantly improved if the term $1.5 k_B T^2 P^2$ is replaced with the actual dynamic kinetic energy of the PIMD simulation. This modified estimator will

be denoted by K . The variance of K is even larger than that of $T_{\text{kin, prim}}$. However, the final statistical properties are quite favorable owing to the dynamic reshuffling of the dynamic kinetic energy and V_{chain} and the resulting fortuitous but systematic cancellation of statistical fluctuations. This behavior is discussed by analyzing the time-dependent (squared) variance

$$\sigma_K^2(t) = \left\langle \left\{ \frac{1}{t} \int_0^t dt' K(t') - \langle K \rangle \right\}^2 \right\rangle, \quad (4)$$

which gives the expected deviation of a finite time average of K with respect to an ideal, infinitely long average. The fast relaxation of σ_K^2 is illustrated for two different P s in Fig. 2. It can be seen that $\sigma_K^2(t)$ decreases significantly after a typical inverse vibrational frequency. The standard deviation in the important limit $t \rightarrow \infty$ falls off as usual proportionally to $1/\sqrt{t}$ at times larger than the largest inverse frequency of a long wavelength vibration. For the modified estimator the prefactor is rather insensitive to P while the prefactor for the original estimator increases linearly with P .

One may argue that the virial estimator, whose use for PI simulations was suggested by Herman et al. [6], has properties similar to the modified estimator K . However, an additional advantage of K is that the ideas invoked here can be extended to higher moments of V_{chain} . Thus a guideline is given how to evaluate more efficiently the specific heat. Furthermore, it seems to us that the virial estimator deviates from the primitive estimator if the number of unbound quantum states increases; the most extreme example being the

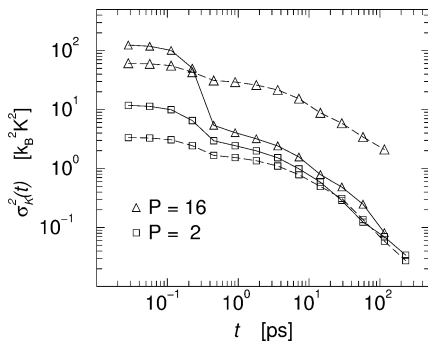


Fig. 2. Time-dependent variance of primitive estimator $T_{\text{kin, prim}}$ (data connected with broken lines) and modified estimator K (solid lines) for two different values of P .

Table 1

Kinetic energy as obtained with (modified) primitive estimator K and virial estimator T_{vir} for various atomic volumes v at $T = 26.8$ K. The thermal expectation value of V is inserted as well. Energies in $k_B K$ per atom. Errors ± 0.1

v [\AA^3]	20.617 (solid)	27.556 (fluid)	55.112 (gas)
$\langle K \rangle$	62.8	51.2	44.3
$\langle T_{\text{vir}} \rangle$	62.7	48.9	35.5
$\langle V \rangle$	-154.8	-125.2	-67.55

ideal gas for which the virial estimator always gives an average kinetic energy of zero while the primitive estimator gives the correct answer $1.5k_B T$. Some representative results are presented in Table 1 for neon. All simulations were run with the same code and same set of parameters. Merely the volume per atom v was varied. $\langle K \rangle$ for the fluid system agrees well with the experimental value of $52.8 k_B K$ that was obtained for a similar density and temperature [7].

I will now turn to the discussion of criterion (iii), namely the issue of good decompositions of the HTDM. It is well known that the regular decomposition of the HTDM leads to systematic errors of order $1/P^2$ for well-behaved potentials. Takahashi and Imada proposed the use of higher-order decompositions of the HTDM with resulting systematic deviations of order $1/P^4$. Another approach is to use effective potentials that are derived from an effective propagator (EPr). This propagator is constructed such that it produces correctly one and two-particle imaginary time correlation functions in the limit of small densities even for finite Trotter numbers P [1]. A detailed description of the procedure is given in Ref. [8]. It is yet worth pointing out that the Takahashi Imada (TI) and the EPr approach are conceptually different: In an EPr path integral simulation, one tries to generate radial distribution functions that are in the quantum limit (at least in a low-density approximation). Evaluating observables such as the thermal expectation value of the potential energy $\langle V_{\text{pot}} \rangle$ is done by simply evaluating the operator of the potential energy at the given distance. In a HOA path integral simulation, generalized estimators have to be defined even for those observables that are orthogonal in real space. This last comment is also relevant for the calculation of radial distribution functions, which is discussed in more detail in Ref. [8].

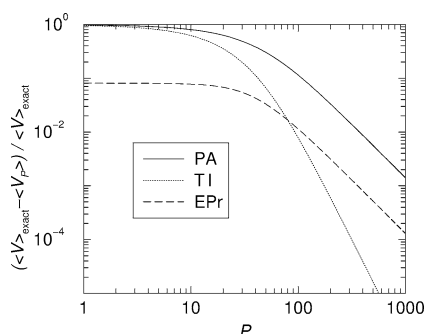


Fig. 3. Relative error of the potential energy for an $N = 5$ chain well below the Debye temperature as a function of the Trotter number P for the regular primitive decomposition (PA), the Takahashi Imada (TI) approach and the effective propagator (EPr) method.

The different approaches were applied to a linear chain of harmonically coupled atoms. Hence the resulting path integral representation consists of a $(1 + 1)$ -dimensional harmonic solid and convergence of thermal expectation values to the quantum limit $P \rightarrow \infty$ can be analyzed analytically. The main property to investigate is the deviation of the thermal expectation value from the quantum limit as a function of P . Such an analysis is shown in Fig. 3. It can be seen that the EPr approach gives very good estimates, in particular the prefactor of the $1/P^2$ corrections is small. However, at sufficiently large P , the TI approach (which is easier to implement than EPr) converges much faster. Similar results were obtained for less well-behaved potentials such as the Lennard–Jones potential in a separate study [8].

3. Conclusions

In this paper three requirements were formulated for an efficient path integral code:

- (i) no slowing down with P ,
- (ii) no increasing variance of estimators with P , and
- (iii) fast convergence with P to the quantum limit.

It was shown that a Fourier accelerated PIMD code in which appropriate masses are given to the eigenmodes satisfies criterion (i)—at least if thermostated in terms of Brownian/Langevin dynamics. The use of PIMD furthermore allows one to use a new primitive kinetic energy estimator whose variance does not increase with P . Moreover, the estimator can be used adequately in the gas or fluid phase, where we observed difficulties with the virial estimator. Generalizations of the invoked ideas are likely to make the calculation of specific heat from fluctuation relations much more feasible than at present. Criterion (iii) is satisfied best by employing the ideas of Takahashi and Imada. However, utmost care has to be taken when evaluating thermal expectation values. Corrections have to be applied to most observables including the radial distribution function.

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