Comment on "A comparison of the efficiency of Fourier- and discrete time-path integral Monte Carlo" [J. Chem. Phys. 109, 2123 (1998)]

J. D. Doll and David L. Freeman

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COMMENTS

Comment on ''A comparison of the efficiency of Fourier- and discrete time-path integral Monte Carlo'' [J. Chem. Phys. 109, 2123 (1998)]

J. D. Doll[a)]
Department of Chemistry, Brown University, Providence, Rhode Island 02912

David L. Freeman
Department of Chemistry, University of Rhode Island, Kingston, Rhode Island 02881

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In a paper entitled ''A comparison of the efficiency of Fourier- and discrete time path integral Monte Carlo,'' [1] Chakravarty, Gordillo, and Ceperley present a numerical study of the convergence characteristics and efficiencies of discrete and Fourier path integral Monte Carlo methods for a model of the $(H_2)_{22}$ cluster system. The central claim of the study is that while the Fourier method[2] has a comparable efficiency for observables diagonal in the coordinates, it is significantly worse than a pair-based discretized method for estimating the kinetic and total energies. Specifically, the authors report that at 6 K ''about 300 times as much computer time'' is required to reach a target value of 0.25 K/particle for the absolute and statistical errors in the kinetic energy using the Fourier as opposed to the discretized approach.

Assertions of such fundamental differences between the Fourier and discrete path integral Monte Carlo methods are, at face value, surprising in view of the established links[3] between the two approaches. On the basis of an integrated series of numerical and analytic investigations we make the following points.

(1) The title of Ref. 1 is inappropriate. It implies that the comparison is one between the Fourier and discretized path integral *methods*. In fact, the comparison presented is one that involves both different *methods* (Fourier versus discretized) *and* different energy *estimators* (thermodynamic versus virial).

(2) In agreement with analytic predictions, and contrary to the assumptions used in analyzing the data generated in Ref. 1, the errors in the partial averaged Fourier path integral method asymptotically approach zero as the inverse of the square of the number of path variables.

(3) The efficiency advantage cited in Ref. 1 for the pair-based discretized approach relative to the partial averaged Fourier method for molecular hydrogen clusters drops from 300:1 to approximately 1:1 when virial estimators are used in both calculations.

As discussed elsewhere,[4] it is possible to establish analytically the asymptotic convergence of the Fourier method with partial averaging. Specifically, errors in path averaged potential, kinetic, and total energies for this method all approach zero asymptotically as the inverse of the square of the number of path variables for systems with continuous, differentiable potentials. It is straightforward to confirm special cases of these general predictions for various one-dimensional model problems. For brevity, we restrict the present discussion to the many-body cluster application presented in Ref. 1.

We show in Fig. 1 partial averaged Fourier path integral calculations of the total energy of the $(H_2)_{22}$ cluster system at 6 K as functions of the number of path variables, $k_{\max}$. These results, obtained using the virial estimator, display $(1/k_{\max})^2$ asymptotic convergence. It is important to note that the virial and standard thermodynamic estimators are formally equivalent in the mean. As originally discussed by Herman, Bruskin, and Berne,[5] however, the virial result is preferable for highly quantum-mechanical systems. In particular, the virial formulation analytically cancels sets of free-particle terms that, if computed numerically, produce a variance that asymptotically diverges linearly in the number of path variables. By itself, this analytic variance reduction suggests a $k_{\max}$-fold asymptotic increase in the efficiency of the virial estimator relative to that of its thermodynamic counterpart.

In Table I we examine the ratio of the efficiencies (as defined in Ref. 1) of the virial and thermodynamic estimators. Values of this ratio are shown as a function of the number of path variables used in the partial averaged Fourier simulations of the $(H_2)_{22}$ cluster system. For small numbers of path variables, the thermodynamic and virial estimators are of roughly comparable efficiency. As the number of path variables increases, however, the advantage of the virial formulation becomes apparent. We note in Table I that the calculated efficiency ratio asymptotically exceeds the anticipated value of $k_{\max}$. This ''efficiency bonus'' is a

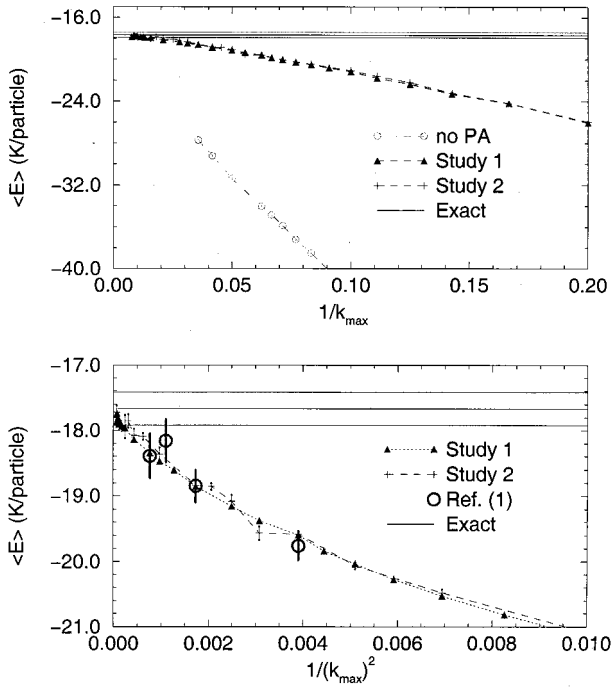

FIG. 1. Total energies for a Lennard-Jones model of the $(H_2)_{22}$ cluster system of Ref. 1 as a function of the number of path variables, k_{max}. Convergence is shown both as a function of $1/k_{max}$ (top panel) and $(1/k_{max})^2$ (bottom panel) for $T=6$ K. Present results, obtained using standard (FPI) and partial averaged (FPI-PA) Fourier/virial methods, are denoted by filled symbols. Studies labeled FPI-PA1 and FPI-PA2 utilize, respectively, the ran3 and ran2 random number generators of Press *et al.*—Ref. 7. The FPI-PA results of Ref. 1 obtained with the thermodynamic estimator are plotted with open symbols in the bottom panel. Chakravarty, Gordillo, and Ceperley's best estimate of the total energy, along with their target error window of ± 0.25 K/particle, are shown as solid lines.

consequence of the reduction in serial correlation (relative to that of the thermodynamic estimator) obtained when the virial estimator is used in conjunction with a normal mode (Fourier) path sampling strategy.[6]

Reference 1 finds that roughly 60 Fourier path variables are required to achieve its target value for the absolute error in the kinetic energy of 0.25 K/particle for the system in question. From Table I, we see that for 64 path variables, the virial kinetic energy estimator is approximately 300 times more efficient than the thermodynamic estimator. Thus, the 300-fold efficiency advantage cited in Ref. 1 for the discretized/effective-pair versus Fourier path integral method for the kinetic energy calculation of the molecular hydrogen cluster application falls to roughly 1:1 when virial estimators are used in both approaches. We conclude, therefore,

TABLE I. Listed is the ratio of the efficiency (as defined in Ref. 1) of the virial estimator for the kinetic energy (ζ_V) versus that for the thermodynamic estimator (ζ_T) for the $(H_2)_{22}$ cluster system. The results shown are for calculations at 6 K, for varying numbers of Fourier path variables (k_{max}). Partial averaging has been used in all cases.

k_{max}	ζ_V/ζ_T
4	2.1
8	1.2×10^1
16	3.7×10^1
32	1.1×10^2
64	3.0×10^2
128	4.1×10^2

that the efficiency differences discussed in Ref. 1 largely reflect differences in estimator performance as opposed to essential distinctions in path integral methodology. We also note from Fig. 1 that the partial averaged Fourier total energies *calculated* in the present work also converge to the target value of 0.25 K/particle absolute error by approximately 60 Fourier path variables, not the *extrapolated* value of 131 reported in Ref. 1.

Finally, it is important to note that while the convergence properties of the methods employed in Ref. 1 are desirable (errors asymptotically scale inversely as the cube of the number of path variables), their system-specific nature is a potential concern. For sufficiently demanding applications involving pair-decomposable systems, ''cubic'' approaches must ultimately enjoy an efficiency advantage relative to lower-order methods. When more general interactions are involved, however, or when the demands of the simulation are less severe (e.g., achieving the 0.25 K/particle energy convergence thresholds for the $(H_2)_{22}$ system at 6 K set forth in Ref. 1), their advantage is no longer certain.

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[a]Electronic mail: doll@ken.chem.brown.edu

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