Convergence characteristics of Monte Carlo–Metropolis computer simulations on liquid water

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Very long (~5000 K) Monte Carlo computer simulations are reported for liquid water described in terms of the analytical potential functions of Matsuoka, Clementi, and Yoshimine and Rahman and Stillinger's empirical ST2 potential. The convergence characteristics of both realizations are fully developed in terms of internal energy, heat capacity, molecular distribution functions, and structureal indices. A hierarchy in the calculated properties emerges with respect to the degree of computational effort required to obtain reproducible results. Mean energy and radial distribution functions are the most accessible quantities. Fluctuation properties such as heat capacity require roughly twice as many configurations to stabilize as simple orientational averaged quantities. The structural changes over the equilibrated segments of the realization were examined in terms of quasicomponent distribution functions and found to be small in chemical terms.

I. INTRODUCTION

Ab initio theoretical studies of molecular liquids require statistical mechanical calculations on systems involving relatively strong, orientation dependent interaction potentials. Integral equation methods and thermodynamic perturbation theories have been used effectively on systems with weak interaction potentials, but are not well suited for calculations where strong interactions are involved. Problems in this domain are treated by numerical solution of the corresponding many-body problem on a digital computer, a so-called "computer simulation" of the system. In classical statistical mechanics, this involves numerical integration of configurational integrals by Monte Carlo methods. The analogous problem in classical kinetic theory involves simultaneous solution of the Newton–Euler equations for the system, the method of molecular dynamics. The results of fully realized Monte Carlo calculations and molecular dynamics calculations should, according to the ergodic hypothesis, agree within numerical error bounds for a given temperature and density.[1]

The liquid water system, being of extraordinary importance in both basic and applied research in physical and in biological sciences, has understandably been the focus of a considerable amount of recent computer simulation research studies,[2–8] including several recent research papers contributed from this laboratory.[9–12] While broad agreement has been obtained by several groups working independently in Monte Carlo computer simulation,[5,6,9] several methodological aspects of the calculations require further detailed consideration. These problems involve the convergence characteristics of Monte Carlo calculations, the practical ergodicity of the results, and dependency on the number of particles explicitly considered in the simulation (N dependence). Also, the convergence characteristics of the standard Metropolis method must be well documented in order to critically evaluate the efficacy of the newly proposed methods[8,13,14] for accelerating the convergence of Monte Carlo calculations.

We describe herein a series of Monte Carlo–Metropolis computer simulations on liquid water designed to provide further detailed information on the convergence characteristics of the realizations and the implications thereof in computer simulation studies of molecular liquids and solutions. Some results on ergodicity and N dependence of the calculations are also obtained. Simulations are reported for both the empirical ST2 potential[4] and the analytical MCY–CI potential[15] representative of *ab initio* quantum mechanical calculations of the intermolecular interactions. The molecular potential for water is especially strong and anisotropic, giving rise to characteristic networks of intermolecular hydrogen bonds in condensed phases. This system is thus a sensitive test of computer simulation methodology as applied to associated liquids.

In the following section, the methodology is briefly reviewed and the problems under consideration are explicitly defined. In Sec. III, the calculations carried out are described and the results are presented. A discussion of results follows in Sec. IV, and the principal conclusions are collected in summary form in Sec. V.

II. BACKGROUND

Monte Carlo computer simulation as used herein involves the determination of average properties of an N-molecule system under canonical ensemble conditions, with temperature T, volume V, and number density N/V fixed and constant. An N-molecule configuration at the system is specified by configurational coordinates $\mathbf{X}^N$:

$$\mathbf{X}^N = \{\mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_N\} , \qquad (1)$$

where $\mathbf{X}_i$ represents the configurational coordinates of the ith particle, a product of positional coordinates $\mathbf{R}_i$, and orientational coordinates $\mathbf{\Omega}_i$. An average property of the system such as internal energy U, the "mean energy" of the system, is given by the configurational integral

$$U = \int \cdots \int E(\mathbf{X}^N) P(\mathbf{X}^N) \, d\mathbf{X}^N = \langle E(\mathbf{X}^N) \rangle , \qquad (2)$$

where $E(\mathbf{X}^N)$ is the configurational energy, and $P(\mathbf{X}^N)$ is the probability of finding the system in $\mathbf{X}^N$. The integration ranges over all possible configurations of the system. A condensed phase environment for the system is

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modeled using periodic boundary conditions.

The structure of the system follows from the spatial pair correlation function, an integral over the positional coordinates $\mathbf{R}^N$:

$$g(\mathbf{R}_1, \mathbf{R}_2) = \rho^{-2} \int \cdots \int P(\mathbf{R}^N) \times \sum_i \sum_{j \neq i} \delta[L_i(\mathbf{R}^N) - \mathbf{R}_1] \delta[L_j(\mathbf{R}^N) - \mathbf{R}_2] \, d\mathbf{R}^N, \quad (3)$$

where ρ is the number density, $L_i(\mathbf{R}^N)$ gives the position vector of particle i in configuration $\mathbf{R}^N$, and the bracketed quantities under the double summation are Dirac δ counting functions for the number of particles within $d\mathbf{R}_1$, jointly with particles within $d\mathbf{R}_2$ of $\mathbf{R}_2$. This quantity may be transformed directly into an interparticle $g(R)$, the radial distribution function. Further properties of the system such as heat capacity can be developed in terms of fluctuations in mean values

$$C_v = (1/kT^2)[\langle E(\mathbf{X}^N)^2 \rangle - \langle E(\mathbf{X}^N) \rangle^2] , \quad (4)$$

where the bracket notation is defined in Eq. (2).

A microscopic theoretical analysis of the structure of the system can be generated in terms of quasicomponent distribution functions (QCDF) for coordination number and binding energy.[16] The QCDF for coordination number can be displayed as the mole fraction

$$x_C(K) = \frac{1}{N} \left\langle \sum_i \delta[C_i(\mathbf{R}^N) - K] \right\rangle , \quad (5)$$

where the summation involves Dirac delta counting functions for the number of particles with coordination number K in configuration $\mathbf{R}^N$. The average coordination number $\bar{K}$ is given by the expression

$$\bar{K} = \sum_{k=0}^{\infty} \bar{K} x_C(K) = \rho \int_0^{R_M} g(R) 4\pi R^2 dR , \quad (6)$$

where $\mathbf{R}_M$ is the radius of the first coordination shell, customarily taken as the position of the first minimum in the radial distribution function.

The QCDF for binding energy B_i follows from the definition

$$B_i(X^N) = E(\mathbf{X}_1, \ldots, \mathbf{X}_{i-1}, \mathbf{X}_i, \mathbf{X}_{i+1}, \ldots, \mathbf{X}_N) - E(\mathbf{X}_1, \ldots, \mathbf{X}_{i-1}, \mathbf{X}_{i+1}, \ldots, \mathbf{X}_N) . \quad (7)$$

The mole fraction of particles with binding energy between ν and $\nu + d\nu$ is given by

$$x_B(\nu) = \frac{1}{N} \left\langle \sum_i \delta[B_i(\mathbf{X}^N) - \nu] \right\rangle . \quad (8)$$

This quantity is directly related to the mean energy

$$U = \frac{N}{2} \bar{\nu} = \frac{N}{2} \int_{-\infty}^{+\infty} \nu x_B(\nu) \, d\nu . \quad (9)$$

The individual characteristics of the particular system under consideration enter the calculation via the configurational potential energy $E(\mathbf{X}^N)$. The configurational energy can be expanded as

$$E(\mathbf{X}^N) = \sum_{i<j} E^{(2)}(\mathbf{X}_i, \mathbf{X}_j) + \sum_{i<j<k} E^{(3)}(\mathbf{X}_i, \mathbf{X}_j, \mathbf{X}_k) + \cdots , \quad (10)$$

where $E^{(2)}(\mathbf{X}_i, \mathbf{X}_j)$ is the pairwise interaction energy, $E^{(3)}(\mathbf{X}_i \mathbf{X}_j, \mathbf{X}_k)$ is a correction term for three-body interactions, etc. Most computer simulation work to date has been carried out under the assumption of pairwise additivity

$$E(X^N) \cong \sum_{i<j} V^{(2)}(\mathbf{X}_i, \mathbf{X}_j) . \quad (11)$$

Here, $V^{(2)}(\mathbf{X}_i, \mathbf{X}_j)$ may be an effective pairwise interaction energy containing the effects of the higher order terms in some average and empirical way or, as in the case of analytical potential function representative of quantum mechanical calculations, be identically equivalent to $E^{(2)}(\mathbf{X}_i, \mathbf{X}_j)$ with higher order energy terms neglected entirely. In any case, $V^{(2)}(\mathbf{X}_i, \mathbf{X}_j)$ is a relatively simple function of $\mathbf{X}_i$ and $\mathbf{X}_j$ and convenient for rapid evaluation of configurational energies on the computer. In the calculations described herein, we follow the customary practice[17] of using the functions $V^{(2)}(\mathbf{X}_i, \mathbf{X}_j)$ in truncated form in configurational energy calculations including all interactions within a radius of 7.75 Å for the MCY–CI potential and 8.46 Å for the ST2 potential.

Monte Carlo computer simulation is effectively the numerical integration of Eq. (2) on the computer by means of a stochastic walk through configuration space on points $\mathbf{X}^N$ which enter the integrals with a frequency proportional to $P(\mathbf{X}^N)$. The determination of average quantities then reduces to the simple summation

$$U = \frac{1}{M} \sum_{j=1}^{M} E(X_j^N), \quad j \in \text{Metropolis} , \quad (12)$$

where the points $\mathbf{X}^N$ are chosen by the Metropolis method[18] based on relative energy differences of successive randomly generated configurations. Other average properties of the system as $g(R)$, $x_C(K)$, $x_B(\nu)$, and fluctuation properties C_v are computed in parallel with the internal energy. In the computer simulation of a molecular liquid, calculations are typically carried out for up to several hundred molecules under periodic boundary conditions.

Once decisions on these basic characteristics of the calculation are finalized, the computer simulation proceeds as follows: An initial configuration is selected, and the Metropolis walk is initiated. During the initial phase of the calculation, the calculated internal energy is rapidly changing. After this initial phase of the realization, the internal energy should no longer be significiantly changing with further sampling, and the simulation is said to be equilibrated. The average properties of the system are calculated over the equilibrated section of the calculation.

Convergence characteristics of the calculation are further monitored using "control functions," i.e., mean energies U_j calculated over independent sections of length k of the stochastic walk. At the termination of the calculation, the total internal energy should be ideally constant and the values of the control functions should be fluctuating randomly about the internal energy. Statistical error bounds may be established based on control functions in terms of the standard deviation[19]

$$\sigma^2 = \frac{1}{n(n-1)} \sum_{j=1}^{n} [\langle E(X^N)^2\rangle_j - \langle E(X^N)\rangle_j^2] ,$$

where n is the number of "controls" or "groups." Here the control mean energies should be statistically independent. The convergence profile of a calculation is presented in terms of the behavior of U, the U_k, C_v, and other calculated properties as the calculation evolves.

The convergence of Monte Carlo–Metropolis calculations must also be viewed in the context of fundamental numerical ideas about ergodicity.[19,20] A system is said to be ergodic if all distinct low energy pockets of phase space are reached in a single-step Monte Carlo generated chain of finite length, such that independent full simulations on the system will produce identical average values of a mechanical variable for an ergodic system. When all basic characteristics of the calculations are equivalent, the Monte Carlo results for an average quantity (of an infinitely large system) should agree with those obtained from molecular dynamics within the statistical error bounds. When this is not the case, or when Monte Carlo calculations based on different initial configurations converge to statistically significant different values, the problem is said to be nonergodic. Nonergodic behavior is expected for a system in the region of a phase transition.

In recent studies related to these problems, Ladd[7] in Monte Carlo work using the ST2 potential on liquid water at 300 °K observed significant N dependence in the results, which could be due to boundary conditions or practical nonergodic behavior of the simulation. Pangali, Rao, and Berne[8] note possible convergence problems in Monte Carlo computer simulation on ST2 water at 283 °K, and also point out problems in serial correlations which lead to possible errors in fluctuation properties in associated liquids. Furthermore, recent Monte Carlo studies of the structure of molecular solutions by Owicki and Scheraga[6] and Swaminathan, Harrison, and Beveridge[11] both note the problem of large statistical errors in the calculation of differential internal energies, a consequence of the more limited statistical averaging possibilities for the calculated properties of a solute in solution. Owicki discusses this further in Ref. 21. The high sensitivity of the various dipole correlation functions, properties not involving an orientational average, to boundary conditions and system size was noted by Levesque *et al.*[22] for a model fluid and Pangali *et al.* find similar behavior in ST2 water.[23]

Overall, the Monte Carlo computer simulation procedures are a powerful means for accessing structural problems in molecular liquids, and are likely to be used extensively in future years for research on structure and process in solution. To develop this position, further detailed studies aimed at the clarification of the basic convergence characteristics and related numerical problems are in order. The calculations must be carried out an order of magnitude longer than those previously reported to produce significant results on these points, and be analyzed in the context of commonly accepted chemical tolerances for energetics and structure to place the results in proper perspective. Clearly, some properties of the classical fluid can be expected to be more accessible to calculation by computer simulation than others, and thus the capabilities and limitations of the methodology with respect to each individual molecular property needs to be studied. The study described herein is contributed as a step in this direction.

III. CALCULATIONS AND RESULTS

We report herein the results of two ~ 5000 K realizations on liquid water, very long compared to earlier works, and also a number of shorter runs on liquid water, generating full details of the convergence characteristics in each case. One long run is based on the pairwise additive MCY–CI potential representative of *ab initio* quantum mechanical calculations on the water dimer, and used in the Monte Carlo computer simulations on liquid water reported by Clementi and co-workers,[5] Owicki and Scheraga,[6] and Swaminathan and Beveridge.[9] The other long run is based on the pairwise additive ST2 potential determined from semiempirical considerations by Rahman and Stillinger[4] and used in the molecular dynamics computer simulation work and in the characterization of the force-bias Monte Carlo calculations by Pangali *et al.*[8,13] The MCY–CI calculations were carried out on 125 water molecules at $T = 25$ °C and a density of 0.997 g/cm^3. The ST2 calculations were done on 216 molecules at $T = 10$ °C and a density of 1 g/cm^3, chosen to correspond directly with the previous ST2 calculations. Simple cubic periodic boundary conditions were employed in both long simulations. A number of additional calculations based on the MCY–CI and ST2 potentials using both simple and face-centered cubic periodic boundary conditions[8,19] were carried out to study the effect of the starting configurations and boundary conditions on the realization and to obtain an indication of the extent of N dependence on the results.

The convergence information for a 4410K realization on 125 MCY–CI water molecules is shown in Fig. 1.

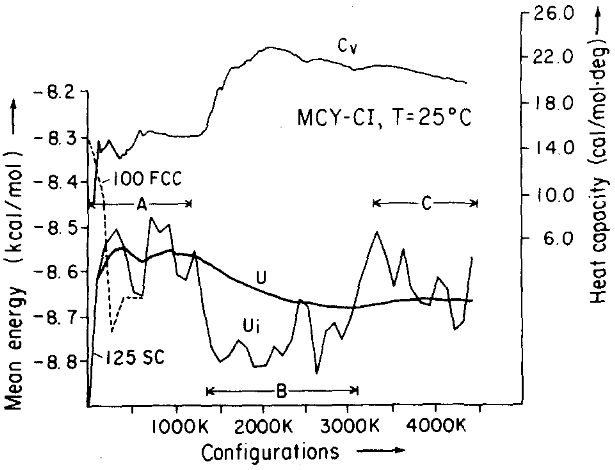

FIG. 1. Convergence curves for the Monte Carlo simulation on liquid water based on the MCY–CI potential. The heat capacity values only are corrected for internal modes.

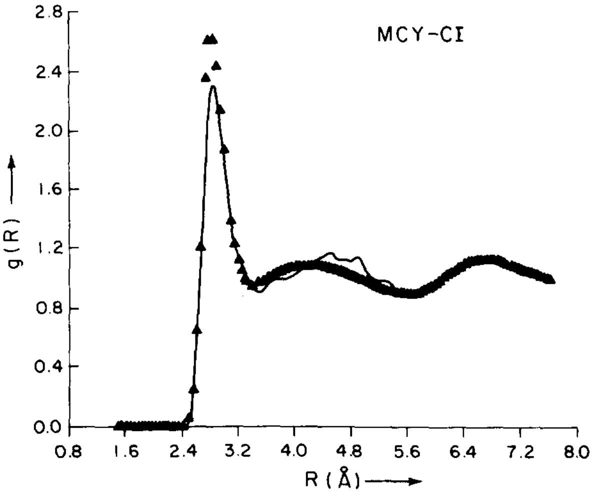

FIG. 2. Calculated points on the intermolecular radial distribution function $g(R)$ vs center-of-mass separation R. Experimental data (solid line) adapted from A. H. Narten and H. A. Levy, J. Chem. Phys. **55**, 2263 (1971).

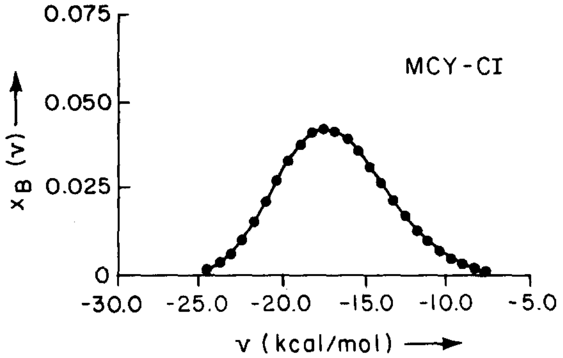

FIG. 4. Calculated quasicomponent distribution function $x_B(\nu)$ vs binding energy ν for the MCY–CI simulation on liquid water.

Note particularly the expanded scale chosen for the energy ordinate here and in subsequent analogous figures; the convergence characteristics must be discussed in tenths of kcal/mole. The calculation achieves a mean energy of -8.57 kcal/mole after $200K$ configurations. The mean energy oscillates within 0.1 kcal/mole of this value for the next $1000K$ configurations. The convergence profile indicates a mean energy value of -8.56 ± 0.03 kcal/mole for this section of the run. At $N = 1200K$ to $1400K$, the control function shows a sharp decline of 0.13 kcal/mole in energy to -8.78 kcal/mole at $N = 1400K$, and the onset of a region of $1600K$ configurations with a mean energy of -8.75 ± 0.02 kcal/mole. Concommitent with this decline is a sharp increase in heat capacity. At $N = 3000K$, the control function rises again, and at termination is oscillating about -8.64 ± 0.03 kcal/mole. The heat capacity is relatively constant from $N = 2000K$ on. The general appearance of the control function suggests that the high frequency oscillations in the control function are superimposed on a grand oscillatory cycle with an amplitude of 0.2 kcal in the realization, of which our calculation covers roughly one and one half cycles. The cumulative mean energy is -8.65 kcal/mole, with a heat capacity of 14.1 cal/mole deg, which after the kinetic energy correction results in -6.87 kcal/mole and 20.1 cal/mole deg for mean energy and heat capacity, respectively. The MCY–CI results reported previously on a $500K$ realization from this laboratory were $U = -6.9 \pm 0.03$ kcal/mole and $C_v = 18$ cal/mole deg.

The analyses of the MCY–CI results on liquid water in terms of $g(R)$, $x_C(K)$, and $x_B(\nu)$ updated on the basis of this more extensive calculation are shown in Figs. 2, 3, and 4, respectively. The basic interpretation of the results in terms of the energetic continuum model is the same as that described previously and does not require repeating here. The only significant change is in the 3.5 Å region of $g(R)$, where a shoulder in the second hydration shell is not in evidence in the results from the longer realization.

Analogous results for 216 ST2 water molecules are shown in Fig. 5. The ST2 potential is generally deeper than the MCY–CI potential (-6.8 kcal/mole vs -5.5 kcal/mole for the linear water dimer), and the convergence is generally more sluggish even considering the larger system size. One achieves a mean energy of ~ -10.4 kcal/mole after $750K$ configurations and ob-

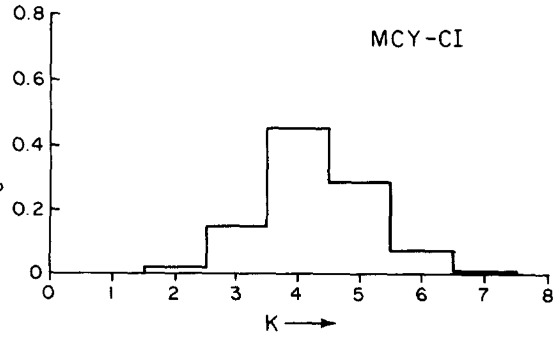

FIG. 3. Calculated quasicomponent distribution function $x_C(K)$ vs coordination number K for the MCY–CI simulation on liquid water.

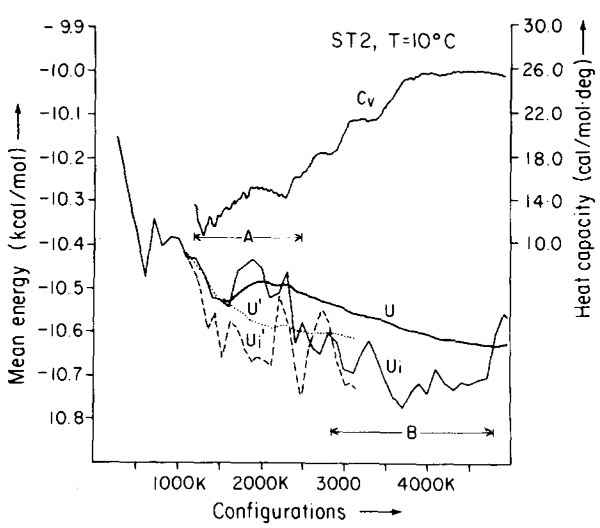

FIG. 5. Convergence curves for the Monte Carlo simulation on liquid water based on the ST2 potential. The heat capacity values only are corrected for internal modes.

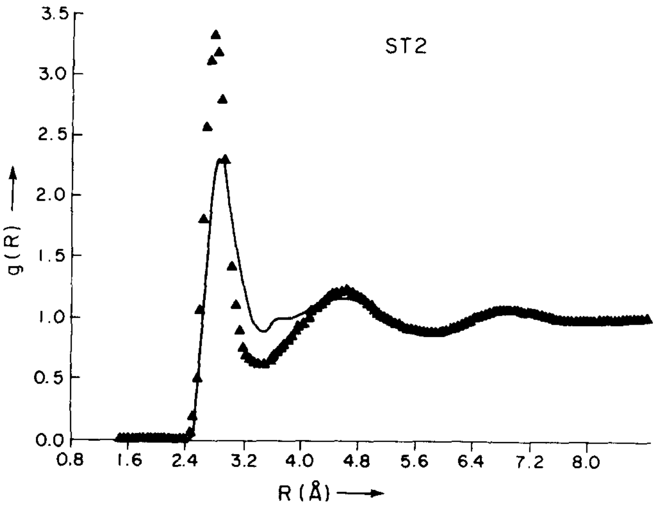

FIG. 6. Calculated points on the intermolecular radial distribution function $g(R)$ vs center-of-mass separation R from the ST2 simulation on liquid water. Experimental data (solid line) are from the same source as in Fig. 2.

serves a region of relative stability from $N = 1375K$ to $N = 2300K$ corresponding to a mean energy of -10.49 ± 0.03 kcal/mole. At this point, there is a gradual decline of 0.2 kcal/mole and a long, relatively stable region of $2000K$ configurations with a mean energy of -10.70 ± 0.02 kcal/mole. The cumulative mean energy from $N = 1375$ to termination is $-10.62 + 10.62 + 0.06$ kcal/mole, with $C_v = 20.6$ cal/mole deg. For comparison purposes, Fig. 5 also includes convergence data from the ST2 realization on liquid water using the force bias modification of the Metropolis method.[13] The analysis of our results of the ST2 water simulation is shown in Figs. 6–8. The structural interpretation of the results on ST2 water is qualitatively similar to that for MCY–CI water, and differs quantitatively in the direction of the higher structuration induced by the deeper ST2 potential.

The convergence profiles of a number of shorter realizations on ST2 water are shown in Fig. 9. Calculations for several different N values, different options for figuring the periodic boundary conditions, and different initial configurations are represented here.

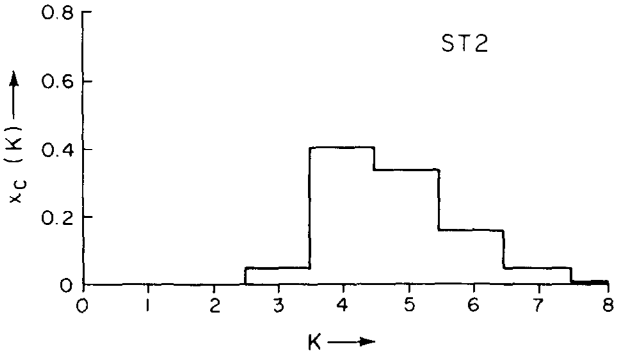

FIG. 7. Calculated quasicomponent distribution function $x_C(K)$ vs coordination number K from the ST2 simulation on liquid water.

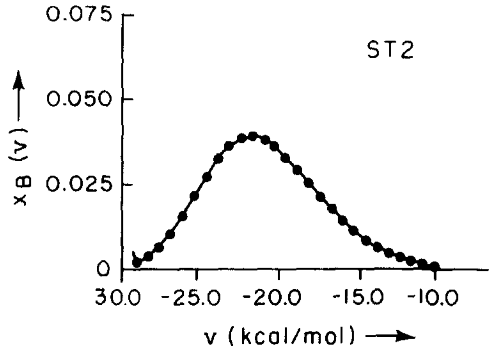

FIG. 8. Calculated quasicomponent distribution function $x_B(\nu)$ vs binding energy ν from the ST2 simulation on liquid water.

Three realizations based on face-centered cubic periodic boundary conditions were carried out, for $N = 54$, 100, and 155 molecules. The $N = 54$ and 155 were initiated at a high energy value. Both of these calculations appear to equilibrate in the region of -10.5 to -10.6 kcal/mole. The fluctuations in the control function are larger when the number of particles is smaller, as expected. The fcc realization for $N = 100$ was initiated at a configuration very near the energy minimum for the molecular assembly. The mean energy for the initial control function is however relatively high, and achieves a value ~ -10.5 kcal at termination. The fluctuations in the control function for this calculation are high, and do not indicate that the realization has reached equilibration at termination.

IV. DISCUSSION

The general behavior of the mean energy and control functions in Figs. 1–3 indicates that the number of configurations to be discarded to rid calculations of this size [O(100) molecules] of the memory of the arbitrarily chosen starting configuration is around $500K$. The mean energy and other properties of the system are determined over the remaining part of the run.

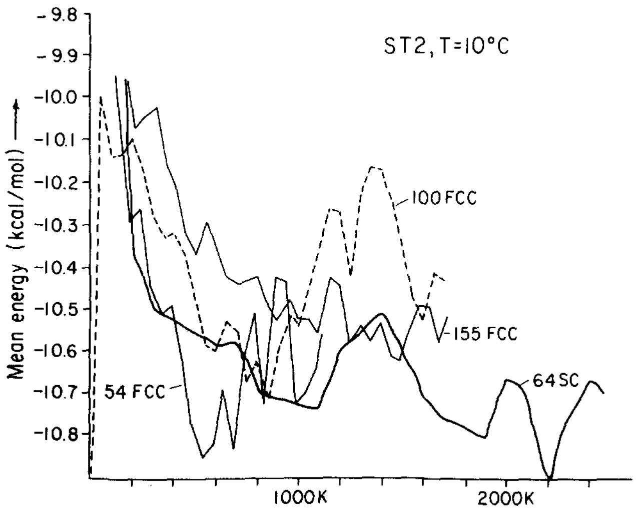

FIG. 9. Convergence curves for assorted smaller ST2 simulations on liquid water.

The mean energy at termination of both the MCY–CI and ST2 long runs has been stable over an extensive (2000K) segment of the realization and appear for all practical purposes to be well converged. The value of -8.65 kcal/mole for mean energy in the MCY–CI run agrees well with those of -8.68 kcal/mole obtained in comparable previous Monte Carlo studies, starting from distinctly different assumed starting configurations. The mean energy of -10.6 kcal/mole determined for the ST2 calculation agrees well with the corresponding results of -10.6 kcal/mole from force bias studies and -10.4 kcal/mole from molecular dynamics work of Rahman and Stillinger. A natural difference between the numerical results of the Monte Carlo and molecular dynamics results is expected due to the difference in the way truncation of the potential function affects the simulation. A numerical estimate of the difference in mean energy ($U_{MC}-U_{MD}$) is 0.1 kcal/mole.[24] Considering this correction factor, the Monte Carlo and molecular dynamics results are still in reasonable accord (see also Ref. 24).

The behavior of the control functions over the latter segment of the MCY and ST2 realizations on liquid water in Figs. 1 and 5 are not consistent with a simple, ideal convergence profile, and further analyses of the calculations were initiated in order to develop a better understanding of these results. In the MCY–CI calculation, the energy of the control groups fluctuates first about -8.56 kcal/mole, then about -8.75 kcal/mole, and at termination about -8.64 kcal/mole. Cumulatively, these results lead to a mean energy of -8.65 kcal/mole for the long MCY–CI calculation. This behavior in control function for MCY–CI water is similar in appearance to certain control functions determined in calculations on model potentials by Wood,[19] where fluctuations between two mean energies were noted. In assessing the viability of Monte Carlo calculations on associated liquids, it is necessary to understand the physical significance of the fluctuations, and whether or not there are significant structural changes in the system involved.

To develop a quantitative analysis of the fluctuations, we separated segments A, B, and C as defined on Fig. 1 and carried out separate structural analyses on each segment. Calculations of oxygen–oxygen radial distribution functions $g(R)$ and quasicomponent distribution functions for binding energy and coordination number were carried out in each case. The results are collected in Table I for MCY–CI water. The $g(R)$ results are given in terms of the magnitude of $g(R)$ at the position of the first maximum, first minimum, and second maximum in the function with respect to increasing R, where R is the interoxygen separation. The variation in the first peak over the three segments is 0.06 units in $g(R)$ and 0.5 Å in R. For the second maximum, the variation is 0.04 in $g(R)$ and again 0.05 Å in R. The corresponding variation in mean energy over the segments is 0.197 kcal.

The significance of these variations with respect to structure can be better understood by examining the quasicomponent distribution functions for coordination number and binding energy for each segment. The results for coordination are given in Table I in terms of the principal contributions $x_C(3)$, $x_C(4)$, and $x_C(5)$. The variation in $x_C(4)$ is 0.031, and the range of variation in $x_C(3)$ and $x_C(5)$ are both 0.01. The binding energy distribution functions are similar in appearance for all three segments, continuous and unimodal in each case. For the basic characteristics of the binding energy distribution, mean value, and amplitude, the variation in the former is reflected in the mean energy and the variation in the latter is 0.002. The trend in all the indices is consistent with increased "structure" in the lower energy segment of the realization. However, the magnitude of these variations in mean energy, radial distribution function, and quasicomponent distribution functions in passing from segment to segment of the realization is relatively small and no basic changes in the qualitative interpretation of structure are anywhere indicated. The change in heat capacity in passing from segment A to segment B is significant, and demonstrates the extremely high sensitivity of a fluctuation property to small structural reorganizations in the system.

We note one systematic observation in the variation in energy and structure: segments A and C, closer in energy than to region B, also have similar structural parameters. This could indicate the oscillations in the grand convergence cycle are between two classes of substructures, which however differ very little in units of structural chemical significance. A corresponding analysis of the results on the long run of ST2 water is shown in Table II. The control function profile for ST2 water in Fig. 5 does not lend itself to a very obvious definition of segments, and we have arbitrarily chosen the two defined as A and B. For the radial distribution function, the variation in the first peak is 0.10 units in $g(R)$, 0.05 Å for the first minimum, and 0.04 Å units also for the second maximum. The positions of the two peaks do not change significantly over the two segments of the run. The corresponding variation in mean energy is 0.23 kcal. The variation in $x_C(4)$ is 0.05 units or 0.1%, and the variation in $x_C(3)$ and $x_C(5)$ are of a similar order of magnitude.

Since a number of computer simulation results have been reported for liquid water based on considerably shorter Monte Carlo realizations than those described

TABLE I. Analysis of Monte Carlo simulation results on liquid based on the MCY–CI potential.

Segment	A	B	C
Interval	0K–1200K	1400K–3000K	3500K–4400K
U(kcal/mole)	-8.56 ± 0.03	-8.75 ± 0.02	-8.64 ± 0.03
r_{max1} (Å)	2.85	2.80	2.85
$g(r_{max1})$	2.59 ± 0.03	2.67 ± 0.03	2.60 ± 0.02
r_{min1} (Å)	3.45	3.40	3.45
$g(r_{min1})$	0.98 ± 0.02	0.92 ± 0.03	0.99 ± 0.02
r_{max2} (Å)	4.20	4.25	4.20
$g(r_{max2})$	1.09 ± 0.01	1.12 ± 0.02	1.08 ± 0.02
$x_C(3)$	0.156 ± 0.008	0.146 ± 0.005	0.155 ± 0.007
$x_C(4)$	0.449 ± 0.008	0.474 ± 0.008	0.443 ± 0.009
$x_C(5)$	0.288 ± 0.007	0.287 ± 0.007	0.298 ± 0.010

TABLE II. Analysis of Monte Carlo simulation results based on the ST2 potential.

Segment	*A*	*B*
Interval	1375*K*–2300*K*	2700*K*–4700*K*
U(kcal/mole)	−10.49 ± 0.03	−10.70 ± 0.02
$r_{\max 1}$	2.80	2.80
$g(r_{\max 1})$	3.26 ± 0.04	3.36 ± 0.02
$r_{\min 1}$	3.45	3.40
$g(r_{\min 1})$	0.66 ± 0.02	0.62 ± 0.01
$g(r_{\max 2})$	1.20 ± 0.02	1.24 ± 0.01
$r_{\max 2}$	4.60	4.60
$x_C(3)$	0.052 ± 0.003	0.046 ± 0.003
$x_C(4)$	0.378 ± 0.009	0.419 ± 0.010
$x_C(5)$	0.346 ± 0.010	0.332 ± 0.010

herein, it is of interest to estimate from the present results the convergence errors in the earlier work. Comparing the present MCY–CI results with those obtained previously (from a different initial configuration), the difference in internal energy is < 1% and the difference in calculated heat capacity is 10%.[9] Considering the MCY–CI results in Fig. 1, calculating the properties over an initial shorter segment of the realization (say the 500*K* to 1000*K* segment of *A*) would have led to a 1% error in internal energy and a 20% error in C_v. In the ST2 simulation, calculation of properties based on segment *A* would have resulted in errors of 1.2% in mean energy and 46% in heat capacity.

Based on these results, a hierarchy of calculated properties of the system with respect to computational effort is provisionally established as follows: Mean energy and orientationally averaged radial distribution functions are the quantities most accessible to calculation by computer simulation. Fluctuation properties such as heat capacity require at least twice as many configurations to calculate properly. The calculations of dipole correlation functions and other quantities not based on full orientational averaging can be expected to remain problematic at this time.[22,23]

The convergence profiles for several shorter realizations of diverse setup characteristics collected in Fig. 9 present some leading information on the influence of the starting configuration, N dependence, and boundary conditions on ST2 water. Comparing the results for $N = 100$, beginning at an initial configuration with low energy, with the other calculations in Fig. 5, which begin with a starting configuration with relatively high energy, we see the mean energy after equilibration trends to the same region of mean energy. The higher fluctuations here are a natural consequence of the smaller sizes. The variation in mean energy indicated as a consequence of N dependence and boundary conditions appears here to be ~ 0.4 kcal/mole. The sensitivity of computer simulation results on ST2 water to boundary conditions and sample size is dealt with more extensively in Ref. 23.

The present availability of results on 216 ST2 from both standard Monte Carlo and force-bias Monte Carlo simulations permits only a preliminary comparison of rates of convergence. The convergence profiles for internal energy and control functions based on data supplied by Rao, Pangali, and Berne are included as U' and U'_i, respectively, in Fig. 5. The force-bias method finds the converged mean energy region more directly and ~ 50% sooner than the standard Monte Carlo. Even recognizing that the force-bias method requires extra computational labor, these are encouraging results for the development of improved methodology from the force-bias point of view.

V. SUMMARY AND CONCLUSIONS

The convergence characteristics of Monte Carlo computer simulation on liquid water have been determined for two popular intermolecular potential functions for the system. Mean energies, heat capacities, and structural indices were determined for each potential. A hierarchy in the calculated properties emerges with respect to the degree of computational effort required to obtain reproducible results. The mean energy and radial distribution functions are the most accessible quantities. Fluctuation properties such as heat capacity require roughly twice as many configurations to stabilize as simple orientationally averaged quantities. The structural changes over the equilibrated segments of the realization were examined in terms of quasicomponent distribution functions and found to be small in chemical terms.

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