

# Equilibrium properties of quantum water clusters by the variational Gaussian wavepacket method

Pavel A. Frantsuzov and Vladimir A. Mandelshtam<sup>a)</sup>

Chemistry Department, University of California at Irvine, Irvine, California 92697, USA

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The variational Gaussian wavepacket (VGW) method in combination with the replica-exchange Monte Carlo is applied to calculations of the heat capacities of quantum water clusters,  $(\text{H}_2\text{O})_8$  and  $(\text{H}_2\text{O})_{10}$ . The VGW method is most conveniently formulated in Cartesian coordinates. These in turn require the use of a flexible (i.e., unconstrained) water potential. When the latter is fitted as a linear combination of Gaussians, all the terms involved in the numerical solution of the VGW equations of motion are analytic. When a flexible water model is used, a large difference in the timescales of the inter- and intramolecular degrees of freedom generally makes the system very difficult to simulate numerically. Yet, given this difficulty, we demonstrate that our methodology is still practical. We compare the computed heat capacities to those for the corresponding classical systems. As expected, the quantum effects shift the melting temperatures toward the lower values. © 2008 American Institute of Physics. [DOI: 10.1063/1.2833004]

## I. INTRODUCTION

The first numerical simulations of bulk water started as early as in the late 1960s.<sup>1</sup> Examples of first water models include BNS,<sup>2</sup> ST2,<sup>3</sup> and MCY.<sup>4</sup> The next stage of simulations began in the 1980s when the simple point charge (SPC) model<sup>5</sup> and three-point (TIP3P) and four-point (TIP4P) transferable intermolecular potential models<sup>6</sup> were introduced. These force field models were optimized in order to reproduce several experimentally measured thermodynamic properties of liquid water by classical Monte Carlo (MC) or Molecular Dynamics (MD) simulations. More sophisticated classical force field models, such as rigid TIP5P,<sup>7</sup> polarizable SPC/E,<sup>8</sup> flexible SPC/F,<sup>9</sup> SPC/Fw,<sup>10</sup> etc., were introduced recently to fit a wider range of thermodynamic properties of liquid water. Some authors attempted to extract interaction potential from *ab initio* calculations of water dimers or trimers. By now the total number of suggested water models is about 50 (see Refs. 11 and 12, and references therein).

Modern classical MC and MD techniques allow one to routinely simulate the water-vapor phase transition<sup>13–18</sup> as well as the ice-water transition.<sup>19–22</sup> Monte Carlo simulations using *ab initio* electronic energy have also been performed.<sup>23–26</sup>

However, early classical simulations including quantum corrections<sup>27</sup> and later simulations by path integrals<sup>28,29</sup> demonstrated importance of the quantum effects in the structure and thermodynamics of liquid water.

Reference 30 introduced the SPC/F<sub>2</sub> model optimized to have better agreement between measured infrared spectrum of liquid water and the centroid Molecular Dynamics predictions. References 31–33 suggested TIP5P(PIMC) and q-SPC/Fw models fitted to the experimental thermodynamic data of liquid water using the path-integral Monte Carlo

(PIMC) and the centroid molecular dynamics calculations. Recently PIMC was used to compute some structural and spectroscopic properties of water<sup>34</sup> as well as its heat capacity<sup>35</sup> and properties of water-vapor phase equilibria.<sup>18</sup>

The ground state structure of small water clusters was addressed in multiple experiments and a great number of *ab initio* calculations (see, for example, Ref. 36, and references therein). However, relatively little is known about their thermodynamic properties at sufficiently low temperatures where the clusters are stable. Reference 37 provided an evidence of  $(\text{H}_2\text{O})_8$  cluster “melting” transition by classical MC simulations. Reference 38 reported the heat capacity curves for  $(\text{H}_2\text{O})_8$  and  $(\text{H}_2\text{O})_6$  using different interaction models, while utilizing the replica-exchange Monte Carlo (REMC) eventually allowed the authors of Ref. 39 to obtain converged heat capacity curves for classical  $(\text{H}_2\text{O})_8$  cluster using the MCY potential and for  $(\text{H}_2\text{O})_{n=6-9}$ , using the TIP4P model.<sup>40</sup> Larger water clusters appear to be much more difficult to be treated numerically, even using the REMC. A particular, but very instructive example is the  $(\text{H}_2\text{O})_{20}$  cluster that possesses multiple low-energy isomers that could be thermodynamically accessible at low temperatures.<sup>41</sup>

While the literature on classical water clusters is enormous, we are aware of only two examples of quantum path-integral simulations. Reference 42 reports mean energy calculations by the path-integral Molecular Dynamics using the (flexible) SPC/F<sub>2</sub> model, but these results seem to be not quite converged. Besides the numerical difficulties associated with the large differences between the inter- and intramolecular time scales, which are specific for simulations of water systems, the water clusters also exhibit very complex behavior that is generic for most clusters, even when the quantum effects are ignored completely. A particular difficulty that is generic in quantum simulations of various atomic and molecular clusters (including the water clusters) is the relatively low (compared to that of the bulk systems)

<sup>a)</sup>Electronic mail: mandelsh@uci.edu.

temperatures at which the interesting behavior occurs. This in turn requires large number of bids (or path variables) in the PIMC simulations. Furthermore, as noted in Ref. 43, quantum simulations of flexible water molecules by path integrals are hardly feasible because, again, the stiffness of the intramolecular modes relative to the intermolecular modes requires the use of too many path variables and also slows down the Monte Carlo convergence enormously. Consequently, the latter paper adapts the PIMC methodology to treating rigid water molecules and applies it to calculations of heat capacities of the  $(\text{H}_2\text{O})_n$  ( $n=2, \dots, 8$ ) clusters.

In the present work we further extend the variational Gaussian wavepacket (VGW) method<sup>44–48</sup> to calculations of equilibrium properties of water clusters. So far the method has been applied to some low-dimensional model systems<sup>44</sup> and to neon clusters assuming pair Lennard-Jones (LJ) interaction.<sup>45–47</sup> It has also been recently extended to computation of thermal time correlation functions in the initial value representation framework.<sup>49–51</sup> Albeit manifestly approximate, we believe that our method is practically accurate, at least for the problems considered so far. This has been demonstrated for the cases where our results could be compared to those obtained by numerically accurate methods.<sup>44,45</sup> In the preceding work the VGW method was formulated using Cartesian coordinates, which seems to be the most natural choice, at least for the (monoatomic) neon systems with pairwise interactions. In particular, the key component of the method was the ability to have all the terms (i.e., Gaussian integrals) involved in the “equations of motion” for propagating the “imaginary-time” VGWs in a compact analytic form, thus allowing for a fast numerical evaluation of these equations. The efficient analytic expressions for the Gaussian integrals were due to the representation of pairwise LJ interactions as a sum of a small number of Gaussians. For the present case of water molecules, the use of a flexible potential energy in combination with Cartesian coordinates still allows us to preserve this property of the method, but in order to have a compact Gaussian fit of the potential energy we modify its intramolecular part by including only pairwise atom-atom interactions. (The intermolecular part in most other flexible models is already given solely in terms of pairwise interactions.) The water model used here also leads to large differences in the timescales between the inter- and intramolecular degrees of freedom. This circumstance is a cause for certain numerical difficulties encountered in the numerical solution of the VGW equations of motion, namely, it makes them stiff (or ill-conditioned) and thus requires the use of a much smaller time step than what would be needed for solution of well-conditioned equations. In spite of this numerical difficulty, we are still able to make our method practical, which is demonstrated for  $(\text{H}_2\text{O})_8$  and  $(\text{H}_2\text{O})_{10}$  clusters.

The next section outlines the VGW method. The present flexible water model with its representation as a linear combination of Gaussians is then described. The following section presents the results of numerical calculations and the last section concludes.

## II. VGW: THE VARIATIONAL GAUSSIAN WAVEPACKET METHOD FOR QUANTUM STATISTICAL MECHANICS CALCULATIONS

The methodology outlined here has been described in detail in Refs. 44–47. Given an  $N_a$ -particle system, the quantum partition function is written as

$$Z = \text{Tr} \exp(-\beta \hat{H}),$$

with  $\beta = 1/k_B T$ . The equilibrium energy is computed by differentiating the partition function

$$E = -\frac{\partial \ln Z}{\partial \beta}, \quad (1)$$

whereas the heat capacity is obtained by differentiating the energy

$$C_V = \frac{\partial E}{\partial T}.$$

In Cartesian coordinates, the Hamiltonian is given by

$$\hat{H} = -\frac{\hbar^2}{2} \nabla^T M^{-1} \nabla + U(r), \quad (2)$$

with diagonal mass matrix  $M = \text{diag}(m_i)$ . By  $r = (r_1, \dots, r_{N_a})^T$ , we define a  $3N_a$  vector containing the particle coordinates.  $\nabla = (\nabla_1, \dots, \nabla_{N_a})^T$  represents the gradient.

The partition function can then be rewritten as the integral over the  $3N_a$ -dimensional configuration space,

$$Z = \int d^{3N_a} q_0 K(q_0; \beta), \quad (3)$$

where the integrand is

$$K(q_0; \beta) = \langle q_0; \beta/2 | q_0; \beta/2 \rangle. \quad (4)$$

This expression is exact if the states  $|q_0; \tau\rangle$  satisfy the Bloch equation. In the present framework, they are approximated by the variational Gaussian wavepackets defined by

$$\begin{aligned} \langle r | q_0; \tau \rangle &= (2\pi)^{-3N_a/2} \|G\|^{-1/2} \\ &\times \exp\left[-\frac{1}{2}(r-q)^T G^{-1}(r-q) + \gamma\right], \end{aligned} \quad (5)$$

with the time-dependent parameters  $G = G(\tau)$ ,  $q = q(\tau)$ , and  $\gamma = \gamma(\tau)$  corresponding, respectively, to the Gaussian width matrix (a  $3N_a \times 3N_a$  real symmetric and positive-definite matrix), the Gaussian center (a real  $3N_a$  vector), and a real scale factor. Given the Gaussian approximation, the integrand in Eq. (3) becomes

$$K(q_0; \beta) = (4\pi)^{-3N_a/2} \|G(\beta/2)\|^{-1/2} \exp[2\gamma(\beta/2)]. \quad (6)$$

The Gaussian parameters are computed by solving the system of ordinary differential equations

$$\dot{G} = -G\langle\nabla\nabla^T U\rangle G + \hbar^2 M^{-1}, \quad (7)$$

$$\dot{q} = -G\langle\nabla U\rangle,$$

$$\dot{\gamma} = -\frac{1}{4} \text{Tr}(\langle\nabla\nabla^T U\rangle G) - \langle U\rangle,$$

with the initial conditions

$$q(\tau_0) = q_0,$$

$$G(\tau_0) = \tau_0 \hbar^2 M^{-1}, \quad (8)$$

$$\gamma(\tau_0) = -\tau_0 U(q_0),$$

which are defined for a sufficiently small but otherwise arbitrary value of  $\tau_0$ . In Eq. (7),  $\langle U\rangle$  represents the averaged (over the Gaussian) potential,  $\langle\nabla U\rangle$  is the averaged force, and  $\langle\nabla\nabla^T U\rangle$  is the averaged Hessian

$$\begin{aligned} \langle U\rangle &:= \langle q_0; \tau | U | q_0; \tau \rangle K(q_0; 2\tau)^{-1}, \\ \langle \nabla U\rangle &:= \langle q_0; \tau | \nabla U | q_0; \tau \rangle K(q_0; 2\tau)^{-1}, \end{aligned} \quad (9)$$

$$\langle \nabla\nabla^T U\rangle := \langle q_0; \tau | \nabla\nabla^T U | q_0; \tau \rangle K(q_0; 2\tau)^{-1}.$$

The present methodology allows one to compute a number of different equilibrium properties,<sup>45,47</sup> however, here we only compute the heat capacity, which is a good characteristic for analyzing the structural transformations.

The success of the VGW method depends particularly on how both accurately and efficiently the integrals on the right-hand side (rhs) of Eq. (7) can be evaluated, which in turn requires both accurate and efficient representation of the potential energy in terms of Gaussians and polynomials. For a potential with isotropic two-atom interactions only, the Gaussian integrals in Eq. (9) are most conveniently evaluated by representing the pair potentials as sums of Gaussians (see the next section). In order to be able to apply the VGW method to systems with many-body interactions, the problem of both accurate and compact representation of the potential in an appropriate form has to be solved.

The most flexible variant of the VGW is a fully coupled Gaussian (full matrix  $G$ ). In this case, the numerical effort to solve the equations of motion (7) for the Gaussian parameters scales as  $\sim N_a^3$  (due to the need to evaluate the determinant of a full  $3N_a \times 3N_a$  matrix). A computationally less intensive, albeit less accurate, version that was implemented in Refs. 46 and 47 for neon clusters employed direct products of single-atom VGWs. In the latter case,  $G$  is block diagonal, each block being a  $3 \times 3$  real symmetric matrix representing a single atom. This version has numerical scaling  $\sim N_a^2$  (due to the  $\sim N_a^2$  terms in the potential energy). For the present case of water clusters, the single-atom VGW would result in a poor representation of the soft intermolecular modes. Therefore, here we use an intermediate approximation based on single-molecule VGWs. This also corresponds to a block-diagonal matrix  $G$ , each block being now a  $9 \times 9$  real symmetric matrix representing a single water molecule. This version of the VGW method still has an  $\sim N_a^2$  numerical scaling. Analytic expressions for all the Gaussian integrals involved on the rhs of Eq. (7) can be found in Ref. 45.

The integral in Eq. (3) is most efficiently computed by the Monte Carlo method. The sampling strategy employed in Refs. 45 and 46 for calculating the heat capacities of  $\text{Ne}_{13}$  and  $\text{Ne}_{38}$  was based on using a single Metropolis random walk at a sufficiently high temperature  $T_{\text{MC}}$  to produce  $Z=Z(T)$  for the entire temperature interval of interest ( $T < T_{\text{MC}}$ ). However, a later application of VGW to more complex systems<sup>47</sup> (such as  $\text{Ne}_{30}$ ), which do undergo low-temperature structural transformations, demonstrated that the REMC,<sup>52</sup> which generally provides much better sampling at low temperatures, may be preferable in such cases. The latter is therefore used in the present work.

### III. THE FLEXIBLE WATER POTENTIAL AND ITS GAUSSIAN FIT

Here we utilize a flexible variant of the SPC (Ref. 5) and SPC/F<sub>2</sub> (Ref. 30) models. In these models the interaction between all the atoms is given as a sum of the intermolecular and intramolecular parts

$$U = V_{\text{inter}} + \sum_i^N V_{\text{intra}}^i, \quad (10)$$

where  $N$  is the number of water molecules ( $N_a=3N$ ). The intermolecular part consists of oxygen-oxygen LJ interactions and Coulombic interactions between point charges located on oxygen and hydrogen atoms of different molecules

$$\begin{aligned} V_{\text{inter}} = \sum_i^N \sum_{j>i}^N \left\{ 4\epsilon \left[ \left( \frac{\sigma}{r_{O_i O_j}} \right)^{12} - \left( \frac{\sigma}{r_{O_i O_j}} \right)^6 \right] \right. \\ \left. + \sum_n \sum_m \frac{q_n q_m}{r_{ij}^{mn}} \right\}, \end{aligned} \quad (11)$$

where  $r_{O_i O_j}$  is the distance between oxygen atoms in  $i$ th and  $j$ th molecules and  $r_{ij}^{mn}$  is the distance between  $n$ th atom in  $i$ th molecule and  $m$ th atom in  $j$ th molecule. The parameters are  $\epsilon=78.22$  K,  $\sigma=3.165$  Å,  $q_H=0.41e$ , and  $q_O=-0.82e$ .

Compared to other existing flexible models, such as SPC/F,<sup>9</sup> SPC/F<sub>2</sub>,<sup>30</sup> or TIP4F,<sup>32</sup> we use the most simple form for the intramolecular energy, which is defined by three pair atom-atom harmonic interactions

$$\begin{aligned} V_{\text{intra}} = k_{\text{OH}}[(r_{\text{OH}_1} - R_{\text{OH}})^2 + (r_{\text{OH}_2} - R_{\text{OH}})^2] \\ + k_{\text{HH}}(r_{\text{H}_1\text{H}_2} - R_{\text{HH}})^2, \end{aligned} \quad (12)$$

where  $r_{\text{OH}_1}$ ,  $r_{\text{OH}_2}$ , and  $r_{\text{H}_1\text{H}_2}$  are the corresponding interatomic distances in the molecule. The equilibrium distances and force constants are:  $R_{\text{OH}}=1$  Å,  $k_{\text{OH}}=2.8598 \times 10^5$  k/Å<sup>2</sup>,  $R_{\text{HH}}=1.618$  Å, and  $k_{\text{HH}}=1.30646 \times 10^5$  k/Å<sup>2</sup>. This choice for the intramolecular term is made in order to keep the overall potential energy as a sum of two-body central potentials only

$$U(r) = \sum_{i>j} V_{ij}(r_{ij}), \quad (13)$$

$$r_{ij} := |r_i - r_j|.$$

Each two-body term can then be easily represented as a sum of Gaussians

$$V(r_{ij}) \approx V(r_{ij}, \{c_p, \alpha_p\}, p=1, P) = \sum_{p=1}^P c_p \exp(-\alpha_p r_{ij}^2), \quad (14)$$

with certain parameters  $c_p$  and  $\alpha_p$ . We have obtained compact Gaussian fits for all three types of pair potentials involved. More specifically, for the harmonic potential we used four Gaussians

$$(r_{ij} - 1)^2 \approx V_h(r_{ij}, \{c_p, \alpha_p\}, p=1, 4) + V_0, \quad (15)$$

with  $V_0 = -2.45956545836810$  and

$p$	$c_p$	$\alpha_p$
1	1.86600759316661	-0.15482960316719
2	0.86367781214929	1.14345548180140
3	0.27630128955453	3.86455703950881
4	0.15271012881172	9.18436481397555

Unlike the LJ potential for weakly bound van der Waals clusters,<sup>45</sup> which is adequately represented using as few as three Gaussians, for the water molecules the most important contribution coming from the LJ potential is the short-range repulsion, adequate representation of which requires six Gaussians

$$4[r_{ij}^{-12} - r_{ij}^{-6}] \approx V_{LJ}(r_{ij}, \{c_p, \alpha_p\}, p=1, 6), \quad (16)$$

with

$p$	$c_p$	$\alpha_p$
1	31279960.65933084	35.14249661727566
2	1668963.963961670	21.73050942017830
3	91092.34069670191	13.25329843520143
4	3354.805129558428	7.60982070333635
5	-8.46844309983970	1.67180258175699
6	-0.38418467585210	0.50261814095335

Finally, eight Gaussians provide a good fit for the Coulomb potential in the range  $r_{ij} \in [0.7; 7]$ ,

$$1/r_{ij} \approx V_c(r_{ij}, \{c_p, \alpha_p\}, p=1, 8), \quad (17)$$

with

$p$	$c_p$	$\alpha_p$
1	0.21760999804997	0.11760379828230
2	0.28105489315866	0.31461999139278
3	0.39181678649027	0.73117924865395
4	0.18586293062381	0.02747369882643
5	0.56465078834542	1.62205104093521
6	0.83006464665923	3.54449454583635
7	1.31592498751225	7.86683801844558
8	0.09597636825530	0.00046497796251

We note here that even seemingly small differences between two potentials can lead to noticeable differences in the thermodynamic properties of a sufficiently large system. In order to demonstrate the quality of the Gaussian fit that we produced, in Fig. 1 we compare the heat capacities of clas-

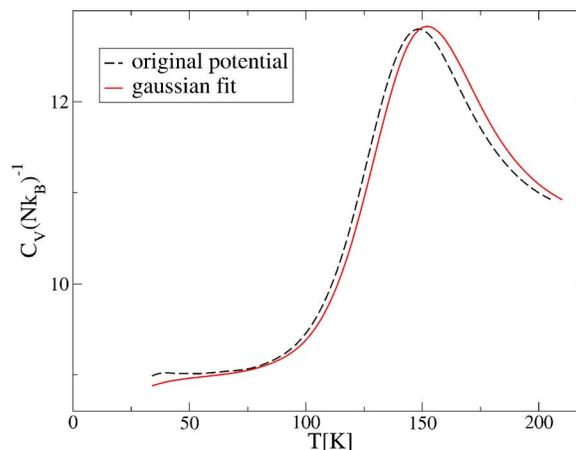


FIG. 1. (Color online) Heat capacities  $C_V(T)$  of the classical  $(\text{H}_2\text{O})_8$  cluster using the original potential [Eq. (10)] and that fitted by Gaussians [cf. Eq. (14)].

sical  $(\text{H}_2\text{O})_8$  cluster using the original potential (10) and that fitted by Gaussians. The results were obtained using the REMC. We made sure that the statistical errors are substantially smaller than the differences between the two curves. Clearly, the latter are insignificant and are in turn much smaller than the differences between any two different water potentials used in the literature (see, e.g., Ref. 38).

#### IV. RESULTS AND DISCUSSION

The quantum REMC simulations were performed for both clusters,  $(\text{H}_2\text{O})_8$  and  $(\text{H}_2\text{O})_{10}$ , using parallel calculations with a single processor dedicated to a single random walk. The temperatures  $T_k$  ( $k=1, \dots, K$ ) of the random walks were distributed in the interval between 35 and 500 K. The initial configurations for all the random walks were set to be the corresponding ground state configurations, which are shown in Fig. 2. We implemented three types of local Metropolis moves, namely, rotation of a single molecule, translation of the center-of-mass of a single molecule, and translation of a single atom in a molecule, which were alternated in a random fashion. Besides these moves, once in 100 MC steps (on average) an attempt of exchanging the configurations within each replica pair with adjacent temperatures was made.

For the  $(\text{H}_2\text{O})_8$  cluster, we used  $K=11$  replicas with  $\sim 3.3 \times 10^6$  MC steps performed for the lowest temperature and  $\sim 10^7$  MC steps, for the highest temperature, where one MC step corresponds to an accepted Metropolis move with  $\sim 50\%$  acceptance probability. The difference in the number of MC steps for random walks at different temperatures is due to the difference in the CPU time needed to propagate the VGWs [cf. Eq. (7)] with different final values of the inverse temperature  $\tau$ . A constraining sphere with radius  $R_c = 4.5 \text{ \AA}$  was used.

For the  $(\text{H}_2\text{O})_{10}$  cluster, we used  $K=15$  replicas with  $\sim 3.3 \times 10^6$  MC steps performed for the lowest replica and  $\sim 1.8 \times 10^7$  MC steps, for the highest. The constraining radius was  $R_c = 5 \text{ \AA}$ .

The corresponding classical REMC simulations were performed using  $\sim 2 \times 10^9$  MC steps per temperature.

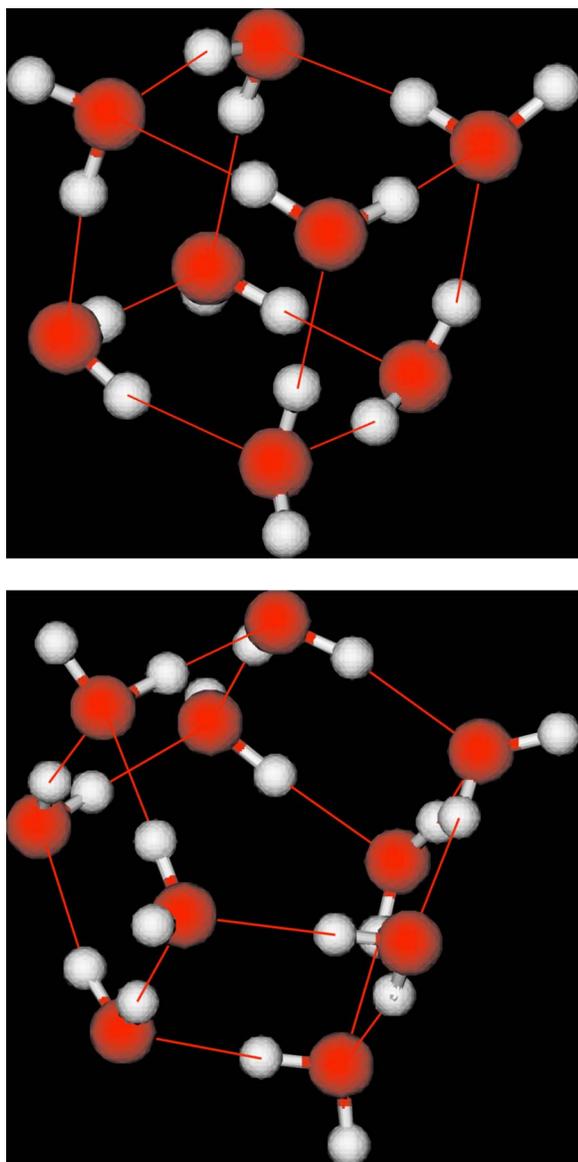


FIG. 2. (Color online) Ground state configurations of  $(\text{H}_2\text{O})_8$  and  $(\text{H}_2\text{O})_{10}$  clusters.

One can notice that there were much fewer MC steps implemented in the case of the quantum simulations compared to that for the classical case. The reason is that during a MC VGW calculation the configuration space is sampled by Gaussians. Apparently this helps in improving the local sampling and thus reduces the overall number of MC steps. In spite of this fact, the VGW calculations for water clusters turned out to be still quite expensive, so that the entire calculation took several months of computing for a computer cluster. The convergence of the heat capacities have been monitored during the calculations by comparing results obtained from independent runs. As an example, Fig. 3 presents two heat capacity curves for the  $(\text{H}_2\text{O})_8$  cluster, each averaged using half of the available data. Similar favorable agreement was obtained for the  $(\text{H}_2\text{O})_{10}$  cluster (not shown here). Such an agreement is a good indication of the convergence, although one must not disregard completely the possibility of the opposite (see an example in Ref. 53).

The reason for the present VGW calculations being very

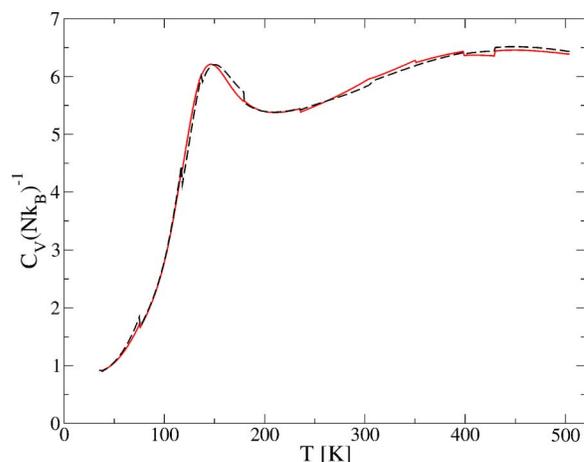


FIG. 3. (Color online) The heat capacity  $C_V(T)$  of quantum  $(\text{H}_2\text{O})_8$  cluster obtained by two independent replica-exchange calculations, both using half of the available data at each temperature. Each curve is piecewise continuous with discontinuities occurring at the replica temperatures. The differences between the two results and the magnitudes of the discontinuities give a rough estimate of the statistical errors.

expensive is the same as that for the pathological convergence of the PIMC calculations for flexible water molecules.<sup>43</sup> This is because of the large difference in time scales between the intermolecular and intramolecular degrees of freedom. In the present framework this large difference manifests itself in the stiffness of the equations of motion for the VGW (7), which in turn require long propagation times. For comparison, propagation of a single VGW for a water cluster needs by at least an order of magnitude more time steps than that needed in the case of neon clusters.

Finally, Fig. 4 compares the quantum and classical heat capacities  $C_V(T)$  for  $(\text{H}_2\text{O})_8$  and  $(\text{H}_2\text{O})_{10}$ . The peaks in the  $C_V(T)$  curves correspond to the melting transitions. Due to the quantum effects the positions of the peak maxima are shifted toward lower temperatures: by  $\sim 6$  K for  $(\text{H}_2\text{O})_8$ , and by  $\sim 18$  K for  $(\text{H}_2\text{O})_{10}$ .

The fact that the heat capacity peaks survive in the quan-

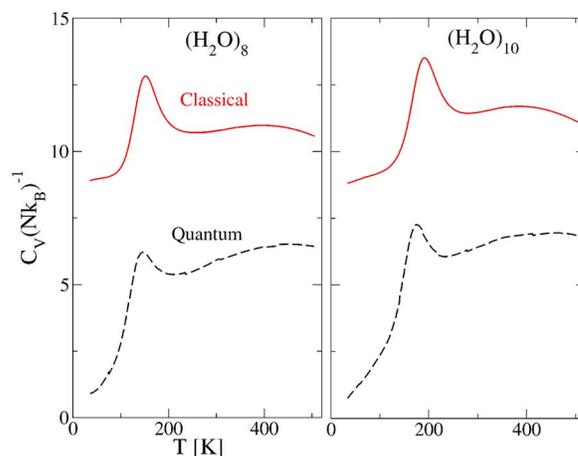


FIG. 4. (Color online) Heat capacities  $C_V(T)$  of quantum  $(\text{H}_2\text{O})_8$  and  $(\text{H}_2\text{O})_{10}$  clusters calculated by the VGW method (dashed lines) in comparison with those of the corresponding classical systems (solid lines). All the curves are normalized by the total number,  $N$ , of water molecules in the cluster.

tum regime is not consistent with the recent PIMC results reported in Ref. 43, where the authors did not observe the heat capacity peak at the temperatures corresponding to the melting transition of the quantum  $(\text{H}_2\text{O})_8$  cluster, while it was observed for the corresponding classical case. Unlike the flexible water model used here, a rigid model was used in the latter work, which is a likely reason for the disagreement between the two results, yet we have no good explanation of why the quantum effects lead to disappearance of the heat capacity peak in one model and do not in the other one. Although the fact that rigid water models have generally better convergence properties, the present results and the comparison with those of Ref. 43 suggest that excluding all of the intramolecular degrees of freedom may be inadequate.

## V. SUMMARY

In this paper we have further extended the VGW method to treat more complex (than previously considered) quantum systems, such as the water clusters. In spite of the well recognized difficulty associated with the presence of large difference between the inter- and intramolecular time scales, we were still able to make our approach practical. Our results for small water clusters,  $(\text{H}_2\text{O})_8$  and  $(\text{H}_2\text{O})_{10}$ , using a flexible water model, are reasonably well converged, and as such they can be used, together with the PIMC results of Ref. 43 to characterize and quantify the quantum effects in water clusters at equilibrium. These effects are noticeable, but not dramatic: both clusters undergo melting transitions in the quantum regime, albeit at lower temperatures compared to that for the corresponding classical clusters. However, at this point it is still unclear whether the present simplistic model (as well as that of Ref. 43) is adequate for water clusters as the corresponding experimental data is hardly available.

Simulations of substantially bigger water systems using the current setup seem too expensive. Extension of the VGW method to treat rigid (rather than flexible) water molecules may lead to a significant speed-up of a single VGW propagation, since a properly formulated rigid model should give well-conditioned equations of motion for the VGW. If such an extension is made, it would also open a possibility for comparison of our results with those using the PIMC, as the latter seems to be applicable only to rigid water models. However, one must be aware of the approximate character of rigid models that may not always provide an adequate representation of the true water, which is flexible.

## ACKNOWLEDGMENTS

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